Analytical Studies On Precision And Accuracy In Micro determination Of Pb(II), Cd(II),Cr(III)And Hg(II) With Modified Reagent   EAB- CTAB

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Abstract: *Analytical studies have been carried out by forming ternary complex between Eriochrome Azurol B, a Triphenylmethane dye; cationic surfactant Cetyl Trimethyl Ammonium Bromide CTAB; and some heavy metal ions mainly Cd(II), Hg(II) Cr(III)and Pb(II). The absorption spectra of Eriochrome Azurol B ,EAB; a triphenylmethane dye , has been studied in the presence as well as in the absence of cationic surfactant, Cetyl Trimethyl Ammonium Bromide, CTAB . At different pH values ranging from pH 1.00 to 12.00, the spectra is studied. Hypsochromic shift is observed in the absorption spectra in the presence of surfactant. Decrease in the values of dissociation constant, pK values in the presence of surfactant is observed which indicated formation of water soluble, stable, dye-surfactant complex. Composition of stable dye-surfactant complex is determined which is found to be EAB:CTAB as 1:2, and effect of foreign ions such as Chlorides i.e NaCl, KCl, NH_4Cl; nitrates i.e KNO_3, $NaNO_3$, NH_4NO_3; and sulphates i.eK_2SO_4,Na_2SO_4 and $(NH_4)_2SO_4$ has been studied in detail. Bathochromic shift has been observed in the presence of CTAB with metal ions under study. CTAB have shown to increase sensitivity of the color reactions of these complexes with greater solubility and higher stability. The addition of some heavy metal ions such as Cd(II) Hg(II), Cr(III)and Pb(II) to these sensitized modified reagents resulted in the formation of intense, water soluble and stable colored complexes and there is increase in sensitivity in presence of surfactant . Various analytical parameters including rate of color formation, effect of temperature and stability of color formation, range of adherence to Beers Law, Molar Extinction constants, Sensitivity, were studied for all systems in absence as well as in presence of CTAB. Precision and Accuracy of the method suggested for microdetermination of metal ions was determined and found out that method is both precise as well as accurate.*

Keywords: *Triphenylmethane Dye, Surfactant, Hypsochromic Shift, Bathochromic Shift, Stability, Sensitivity, Precision and Accuracy.*

I.   Introduction

The property of formation of colored complexes has been successfully applied for the spectrophotometric estimation of metal ions since last few decades. The addition of quaternary salts to the deeply colored solution of dyes, causes a marked color change with the change in wavelength of maximum absorption. The hypsochromic shift is caused by short range electrostatic forces on the surface of the micelle double layer. The purpose of addition of surfactants to the dyes is thus to decolorize them. [1]It is followed by Sign Rule which is an empirical statement. The interesting property of the aggregates formed is their ability to form colored complexes with various cations. Another advantage is that the determination of microamounts of metal ions can be done with much higher sensitivity in the presence of these long chain quaternary salts. [2-8] Reaction of triphenylmethane dyes with 4f and 5f metal ions have been a subject matter of study by several workers.The systematic design of surfactants induced dye metal interactions leading to the [6-10] sensitized photometric metal ion determination could obviously be facilitated by an accurate model of detail chemistry involved. [11] Complexation of Cu(II), Fe (II) & Al (III) with Chrome Azurol S in the presence of non ionic surfactants was studied The present investigation undertaken involves a detail study of the interaction of surfactant Cetyl Trimethyl Aminonium Bromide with triphenylmethane dye Eriochrome Azurol B. Composition of dye-surfactant complex is determined by adding varying concentration of surfactants to the dye solutions. [12]Higher concentration of mineral salts prevents the micelle formation due to occurrence of inorganic anions which displace dye as counter ions. Hence effect of mineral salts has been studied. The dye surfactant complexes thus formed was used to study complexation reactions of Cd (II) Hg(II), Cr(III)and Pb(II). and are compared with the complexation reaction of these metal ions with Eriochome Azurol B in absence of detergents too.

II. Experimental

Instruments: The absorption measurements were done on a UV Shimadzu spectrophotometer UV-240. Glass cuvettes of 1cm thickness supplied with the instrument were used; distilled water blanks were used. For pH measurements, Elico pH meter LI-10 operated on 220volts stabilized AC mains were used, with a glass calomel electrode system.

Materials: All the reagents used were of BDH, Anal R grade purity. The surfactant, Cetyl Trimethyl Ammonium Bromide (CTAB), in 20% aq. methanol. The Dye solution was prepared in double distilled water by dissolving their purified samples and the standard solutions of metal solutions were prepared from different salts of Cd (II) Hg(II),and Pb(II) ,Cr(III) ions.

Procedure: Preparation of mixtures, measurements of absorbance, adjustment of pH etc. were carried out at room temperature. In all the experiments, CTAB solution was added to the reagent solutions which was for at least 20min for maximum decolorizing effect. The absorbance readings were recorded only after 30 minutes of the addition of the reactants, a time necessary for equilibration.

III. Results and Discussion

Absorption Spectra

Absorption spectra of EAB solution was recorded from pH1.0 to 12.0. The spectral studies in the presence of ten times excess of CTAB were also recorded from pH1.0 to 12.0. The λmax values in the absence as well as in the presence of CTAB are summarized below.

TABLE-1 λmax OF EAB AT DIFFERENT pH VALUES

pH	λmax nm in absence of CTAB	λmax nm in presence of CTAB
1.0 – 2.0	470	480
3.0	460	510
4.0	460	450
5.0	450	420
6.0 -9.0	420	425
10.0- 11.0	425	610
12.0	595	610

Hypsochromic shift is observed at pH 5.0. Hence pH of study for using EAB and CTAB is 5.0.

Dissociation Constant (pK values) of EAB

The EAB contains three replaceable protons in its molecule. Two of it correspond to-COOH groups while the third corresponds to-OH group. The equilibrium reaction which occurs in the stepwise dissociation of EAB can be written as follows.

$$H_3EAB \xrightleftharpoons{pK_1} H_2EAB^- \xrightleftharpoons{pK_2} HEAB \xrightleftharpoons{pK_3} EAB^{3-}$$
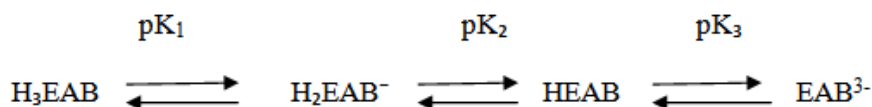
The above equilibrium reaction shows three pK values of EAB. Experiments were carried out for the determination of pK values of EAB in the presence and absence of surfactant CTAB. From the results, pK values obtained are recorded in Table 2. Several sets of solutions of suitable concentrations of dyes were prepared & pH was adjusted from 1.0 to 12.0. Spectra of these solutions were recorded from 380nm to 700nm. From the spectra,a graph was then plotted between absorbance and pH values at different λ max obtained from spectra. The S- shaped curves are obtained where the lower part of it represents the molecular species and the upper portion represents the ionic species. From these pK values were determined both in absence as well as in the presence of CTAB using equation given below. The color changes corresponding to a shift of pH values towards acidic and alkaline ranges was studied. This has been related to an early dissociation of protons of triphenylmethane dyes in the presence of surfactants showing a decrease in the value of their constants. The lowering of pK values in presence of CTAB indicates their action on EAB.

TABLE – 2 Dissociation Constants of EAB

pK values	In absence of surfactant	In presence of CTAB
pK1	3.00	2.70
pK2	5.69	5.04
pK3	11.13	10.84

Lowering of pK values indicates the action of surfactants on EAB.

Composition Of EAB-CTAB Complex :

The effect of varying concentration of CTAB on EAB absorbance was also studied at pH 5.0 and at 420nm. The absorbance of EAB decreases linearly upto a definite ratio of EAB:CTAB, as 1:1, is reached. After this point the addition of surfactant, even in excess amount did not alter the absorbance of EAB to any significant extent. Thus the complex formed can be represented as [EAB(CTAB)].It is represented in fig.The descending section of the curve represents the successive effect of CTAB on Eriochrome Azurol B upto the point at which the additional increase of CTAB, concentration does not further diminish the absorbance of EAB. Thus, it may be concluded from the curves that this point and hence the maximum decolorizing effect is reached at the minimal ratio of EAB to CTAB as 1:2. After this point the further addition of increased concentration of CTAB to EAB, does not alter the absorbance of EAB. Thus, at this point it was concluded that, the modified reagent species of EAB complex can be represented as [EAB (CTAB)$_2$] .

Effect Of Mineral Salts:

Caiwen and Quingyue(**13**) studied the effects of inorganic salts on the color reactions of triphenylmethane dyes in the presence of surfactants, which found to exert some sensitizing effect on the color complex formation between TPM dyes and surfactants**.** The cations K^+, Na^+, NH_4^+ did not show any effect on the absorbance of dye-detergent solution. Nitrates has shown some effect at pH 5.0, as the absorbance goes on increasing upto certain extent after which it remains unaltered. The mineral salts selected were the chlorides (KCl, NaCl, and NH$_4$Cl), the nitrates (KNO$_3$, NaNO$_3$, (NH$_4$)NO$_3$), and sulphates K$_2$SO$_4$, Na$_2$SO$_4$, (NH$_4$)$_2$SO$_4$.To study this in detail, different concentration of salt solutions were added to 1.0×10^{-3} M EAB solution containing 1.0×10^{-2} M CTAB into it.

Absorption spectra of the complexes:-

Absorption spectra of EAB, EAB- metal ion, EAB - CTAB and EAB - metal ion - CTAB were recorded at the pH of study. The nature of complexes found between EAB and Cd(II) Hg(II), Cr(III)and Pb(II) has been studied in detail. A representative absorption spectrum is shown in the fig. to indicate the methodology used. The metal ions selected for the present study are susceptible to hydrolysis in alkaline range. It was thus necessary to study the complex formation in the acidic range of pH 3.0 to 6.0. The absorption spectra of metal complexes of EAB was studied in the absence as well as in the presence of CTAB. The bathochromic shift and increase in the absorbance of complexes are attributed due to the early dissociation of phenolic protons of the dye in presence of surfactant.
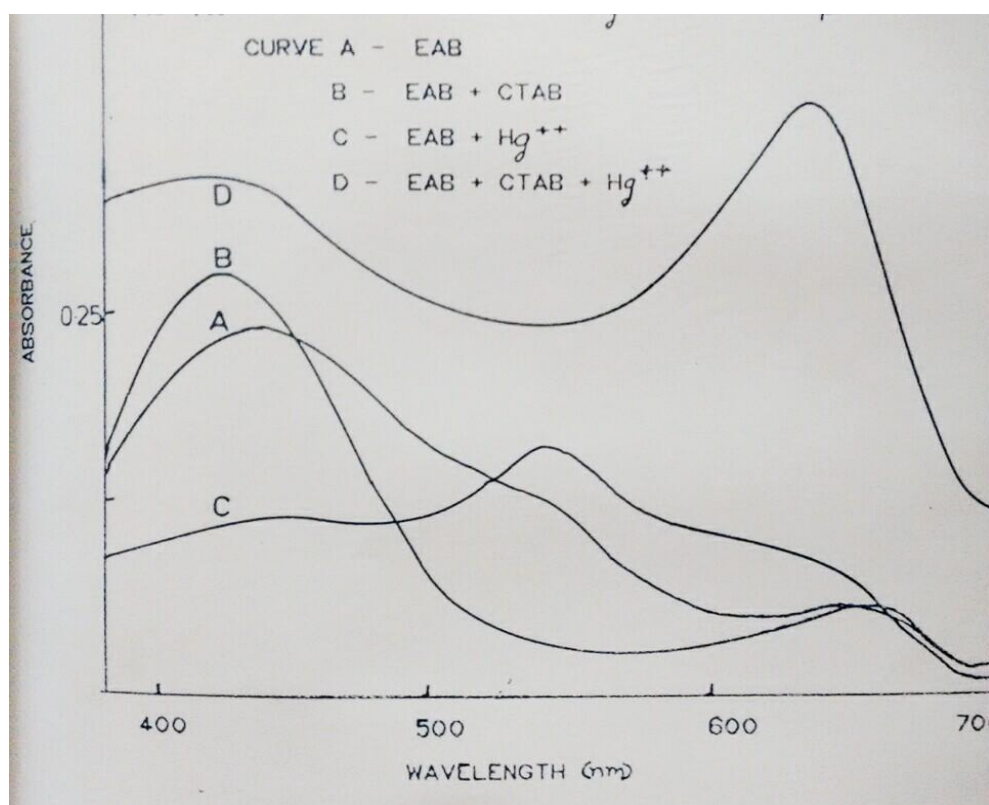
Fig. **Absorption Spectra Of Cd(II) in Absence and Presence of CTAB**

Table 3 λmax Of EAB And Its Chelates In Absence and Presence Of CTAB, at pH5.0, and M:L as 1:2

System	λmax (nm)
EAB	450
EAB+ CTAB	420
EAB + Hg(II)	540
EAB+ CTAB + Hg(II)	630
EAB + Pb(II)	540
EAB+ CTAB + Pb(II)	630
EAB + Pb(II)	540
EAB + CTAB + Pb(II)	640
EAB + Cr(III)	540
EAB + CTAB +Cr(III)	640

Composition of the Chelates:

The stoichiometry of complexes is ascertained by Job's method of continuous variation at the pH & wavelength of study. The composition of the complexes at metal ions under study with EAB remains same in the presence and in the absence of surfactants. The reason may lie in the pH selected for study where the dissociation of phenolic hydrogen may not be much accelerated in the presence of surfactants. From spectral studies, it was found that EAB forms complexes M:L ratios at 1:2 stoichiometric ratio in presence as well as in absence of CTAB.

Stability Constant :-The values of log K of chelates of metal ions under study in absence as well as in presence of CTAB are reported in Table 4

Table 4 Composition and Stability Constants Of Chelates

Chelates	Λmax(nm)	Composition M: EAB:CTAB	Log K Values By Job's Method
EAB + Hg(II)	540	1:2	10
EAB+ CTAB + Hg(II)	630	1:2:2	10.8
EAB + Pb(II)	540	1:2	9.9
EAB+ CTAB + Pb(II)	630	1:2:2	10.7
EAB + Pb(II)	540	1:2	9.7
EAB + CTAB + Pb(II)	640	1:2:2	10.1
EAB + Cr(III)	540	1:2	9.5
EAB + CTAB + Cr(III)	640	1:2:2	10.8

The results showed that the values of log K in the presence of CTAB are greater than that in the absence. This may be due to CTAB reacting earlier with EAB to allow an early dissociation of protons from the phenolic group of EAB which participates in the complex formation, thus allowing the attachment of the metal ion more easily at the pH of study and therefore increasing the value of stability constant. Thus this is due to the tendency of decrease in pK values of dye EAB (ligand) in the presence of surfactants.

Analytical applications:

In all the experiments, CTAB solution was added to EAB solution; which was then kept for at least 0.5hr for complete formation of dye - detergent complex, to which then metal ion solution was added. This sequence was fixed by carrying out experiment by varying sequences of additions, but the above one sequence showed to give constant absorbance readings. The temperature was found to have little effect on colour intensity from 25^0C to 60^0C in absence or presence of surfactants in all the systems reported here. The colour was stable up to 3 to 4 has after which is changes.

pH Range Of Stability:

For studying effect of pH on absorbance of metal chelates in absence as well as in presence of surfactants, the ratio of the dye: surfactant : metal was kept as 3:15:1 i.e. 1:5:0.33 & pH was adjusted from 3 to 6.5. Total volume was kept as 25ml. The pH range within which absorbance values do not change is taken as pH range of stability of colored complexes.

Beer's Law and Photometric Ranges:

The linearity between the absorbance of the chelates in the absence as well as in the present of CTAB Vs concentration of metal ions was tested by varying the metal ions concentration and keeping the reagent concentration constant at the pH and wavelength of study selected for various chelate systems. The effective photometric range was evaluated by Ringbom plots a plot of log of metal ion concentration Vs. % transmittance.

Sandell's Sensitivity and Molar Absorptivity of the System
Sensitivity of colour reaction of metal ion with EAB for log Io/It =0.0001, as defined by Sandell are listed below.

Table - 5 pH range of stability, Concentration Range for to Beer's Law & effective Photometric Range,
Sensitivity, and Molar Absorptivity at **pH of study = 5.0**

System	pH range of stability	Range of Beer's law In ppm	Photometric Range	Sandell Sensitivity SX10-2	Molar absorptivity EmX10-3	λmax (nm
EAB + Hg(II)	3.2-4.4	0.25-0.37	0.22-0.64	2.7	9.5	540
EAB+CTAB+Hg	4.5-5.5	1.88-4.28	1.99-4.26	5.0	40.0	630
EAB + Pb(II)	3.8-4.2	1.1-1.5	1.24-2.24	2.8	10.6	540
EAB+CTAB+ Pb	4.5-5.5	2.76-9.66	2.76-9.66	15.2	9.4	630
EAB + Cd (II)	4.2-4.8	0.77-4.32	1.65-2.36	10.2	3.5	540
EAB+CTAB+Cd	5.0-6.0	0.75-3.99	2.82-4.46	17.9	5.83	640
EAB + Cr(III	4.0-4.8	0.52-1.22	0.95-1.22	3.2	5.3	540
EAB+CTAB+Cr	4.5-5.5	0.69-2.77	1.15-1.95	6.9	7.1	640

Procedure for the Microspectrophotometric Determinations of Cu (II), Ni(II), and Cd (II), with EAB in the presence of surfactant CTAB

pH of EAB solution is adjusted containing that concentration of metal ion as mentioned under the effective photometric determination is also adjusted to pH 5.0 and added to the EAB solution or modified EAB solution (the modified Dyes is prepared by adding five fold excess of CTAB solution to EAB solution and keeping it for half an hour for the complete formation of dye surfactant complex). Total volume was made upto 25 ml with distilled water having pH adjusted to 5.0 and the absorbance of the solution is measured at its wavelength of study against the modified reagent solution as blank. The amount of metal ion present in unknown solution can then be obtained by comparing its absorbance from the calibration curve obtained under similar conditions. The mean absorbance, mean deviation and relative mean deviation are also found out. The value of most probable analytical errors is determined with root mean square deviation; for ten replicate determinations ranges between 0.0008 to 0.0037 at the confidence limit of t=99.5%. If the number of determinations are further increased that would subsequently decrease the value of tα. Consequently, a point would be reached when increase in precision will be too small to justify the expenditure of labour, time and reagents involved in increased number of determinations. On the basis of root mean square deviation(σ); the most probable error(ϵ), the difference between arithmetic mean ($\dot{X}$); and the true or most expected value (X_t) of absorbance for the systems under study, conclusions are drawn. Precision and accuracy data calculated are given in following table. The expected diminish in the probable errors would also decrease the level of confidence limit, hence ten replicate determinations have been done in present studies.

Table 5 Precision Data For Absorbance Measurement

System	$\dot{X}$	σ	ϵ	$\dot{X}$ - ϵ	$\dot{X}$ + ϵ
EAB + Hg(II)	0793	0.008	0.0093	0.783	0.802
EAB+CTAB+Hg	0.124	0.003	0.0035	0.119	0.126
EAB + Pb(II)	0.566	0.005	0.0058	0.560	0.572
EAB+CTAB+Pb	0.076	0.002	0.0023	0.074	0.078
EAB + Cd (II)	0.537	0.006	0.0070	0.530	0.544
EAB+CTAB+Cd	0.064	0.003	0.0035	0.0605	0.068
EAB + Cr(III	0.469	0.005	0.0058	0.463	0.475
EAB+CTAB+Cr	0.046	0.004	0.0046	0.041	0.050

Table 6 Accuracy Data For Absorbance Measurement Expressed as ($\Delta < \epsilon$)

System	$\dot{X}$	X_t	$\Delta = X_t - \dot{X}$	ϵ
EAB + Hg(II)	0.793	0.791	-0.002	0.0093
EAB+CTAB+Hg	0.124	0.122	-0.002	0.0035
EAB + Pb(II)	0.566	0.561	-0.005	0.0058
EAB+CTAB+Pb	0.076	0.075	-0.001	0.0023

EAB + Cd (II)	**0.537**	0.532	-0.005	**0.0070**
EAB+CTAB+Cd	**0.064**	0.065	0.001	**0.0035**
EAB + Cr(III	**0.469**	0.470	0.001	**0.0058**
EAB+CTAB+Cr	**0.046**	0.045	-0.001	**0.0046**

IV. Conclusions

It is observed that the stabilities of the complexes have increased in the presence of surfactants. One of the most important application of the coloured complexes is its use in the spectrophotometric determination of the metal ions with organic dyes. A good reagent has to possess properties like stability of the species, rate of colour formation, specificity of colour reactions and the sensitivity of colour reaction. The use of TPM dyes has its origin only because of these desired properties. The use of micelle forming surfactants in increasing the sensitivity of the colour reactions is one of the important aim of study. The increased sensitivity of the system in the presence of surfactants is the net advantage for microspectrophotometric determination of metal ions using triphenyl methane dyes as reagents. These metal ions when present in water at ppm level as a pollutant thus may be detected by using this method. The precision and accuracy data recorded reveal that the methods proposed are both precise as well as accurate

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