RASĀYAN *J. Chem.*
Vol. 11 | No. 3 |1159 - 1165 | July - September | 2018
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

ANALYTICAL STUDIES ON PRECISION AND ACCURACY IN MICRODETERMINATION OF Pb , Cr, Cd AND Hg WITH EAB-CTAB AND EAB-TX COMPLEXES

Suparna Deshmukh
S. K. Gandhi College, Kada, Ashti, Dist. Beed
E-mail: suparna.deshmukh@gmail.com

ABSTRACT

Precision and Accuracy studies have been carried out by forming a ternary complex between Eriochrome Azurol B, a Triphenylmethane dye; a cationic surfactant Cetyl Trimethyl Ammonium Bromide CTAB; a Non Ionic Surfactant Triton X-100 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 by interaction with surfactants, Cetyl Trimethyl Ammonium Bromide, CTAB and Triton X-100 at different pH from ranging from pH 1.00 to 12.00. Absorption spectra showed a Hypsochromic shift in the presence of a surfactant. The decrease in the values of dissociation constants (pK), in the presence of surfactant, is observed which indicated the formation of water-soluble, stable, dye-surfactant complex. The composition of the stable dye-surfactant complex is determined which is found to be EAB:CTAB as 1:2 while the composition of chelates of Cd(II), and Hg(II) was found to be 1:2 in the absence of surfactant which changes to 1:1 in the presence of surfactant TritonX-100. Effect of foreign ions such as Chlorides; Nitrates and Sulphates of Sodium, Potassium, and Ammonium salts has been studied in detail. Bathochromic shift has been observed in the presence of CTAB and TX-100 with metal chelates under study. Surfactants have shown to increase the sensitivity of the color reactions of these complexes with greater solubility and higher stability. Various analytical parameters including the rate of color formation, effect of temperature and stability of color formation, the range of adherence to Beers Law, Molar Extinction constants, Sensitivity, were studied for all systems. Precision and Accuracy of the method suggested for micro determination 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.

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 the 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 the addition of surfactants to the dyes is thus to decolorize them. It is followed by Sign Rule which is an empirical statement[1]. The interesting property of the aggregates formed is their ability to form colored complexes with various cations. Another advantage is that the determination of micro amounts of metal ions can be done with much higher sensitivity in the presence of these long-chain quaternary salts. The reaction of triphenylmethane dyes with 4f and 5f metal ions have been a subject matter of study by several workers[2-8].The systematic design of surfactants induced dye metal interactions leading to the sensitized photometric metal ion determination could obviously be facilitated by an accurate model of detail chemistry involved[6-10]. Complexation of Cu(II), Fe(II) & Al(III) with Chrome Azurol S in the presence of nonionic surfactants was studied.[11] The present investigation undertaken involves a detailed study of the interaction of surfactant Cetyl Trimethyl Ammonium Bromide and Triton X-100, with triphenylmethane dye Eriochrome Azurol B.

Rasayan J. Chem., 11(3), 1159-1165(2018)
http://dx.doi.org/10.31788/RJC.2018.1134007

Composition of the dye-surfactant complex is determined by adding a varying concentration of surfactants to the dye solutions. Higher concentration of mineral salts prevents the micelle formation due to occurrence of inorganic anions which displace dye as counter ions[12]. 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.

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) , and Triton X-100 are prepared 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 and TX-100 solution was added to the reagent solutions which was kept for minimum 20min for decolorization. The absorbance readings were recorded only after 30 minutes of the addition of the reactants, a time necessary for equilibration.

RESULTS AND DISCUSSION

Absorption Spectra

Absorption spectra of EAB solution were recorded from pH1.0 to 12.0. The spectral studies in the presence of ten times excess of CTAB and TX were also recorded from pH1.0 to 12.0. The λmax values are summarized below in Table-1. Hypsochromic shift is observed at pH 5.0. Hence pH of study for using EAB and Surfactants is 5.0.

Table-1: λmax of EAB at Different pH Values

pH	λmax nm of EAB	λmax nm Of EAB-CTAB	λmax OF EAB-TX
1.0 – 2.0	470	480	470
3.0	460	510	480
4.0	460	450	520
5.0	450	420	415
6.0 -9.0	420	425	460
10.0- 11.0	425	610	430
12.0	595	610	595

Dissociation Constant (pK Values) of EAB

The EAB contains three replaceable protons in its molecule. Two of it correspond to 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:

$$H_3EAB \overset{pK_1}{\rightleftarrows} H_2EAB^- \overset{pK_2}{\rightleftarrows} HEAB^{2-} \overset{pK_3}{\rightleftarrows} EAB^{3-}$$

The above equilibrium reaction shows there exist three pK values for EAB. Experiments were carried out for the determination of pK values of EAB in the presence and absence of surfactant CTAB and TX. 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 spectra pK values were determined both in absence as well as in the presence of CTAB and TX-100. The lowering of pK values in presence of CTAB and TX indicates their action on EAB.

Table-2: Dissociation Constants of EAB

pK values	In absence of surfactant	In presence of CTAB	In presence of TX-100
pK_1	3.20	2.70	2.90
pK_2	5.69	5.04	5.60
pK_3	11.13	10.84	11.00

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

The composition of EAB-CTAB and EAB-TX Complex

The effect of varying concentration of CTAB on EAB absorbance was studied at pH 5.0 and at 420nm. The absorbance of EAB decreases linearly up to a definite ratio of EAB:CTAB, as 1:1, is reached. After this point, the addition of a 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)].The effect of varying concentration of TX on EAB absorbance was also studied at pH 5.0 and at 530nm. The absorbance of EAB decreases linearly up to a definite ratio of EAB:TX, as 1:1, is reached. After this point, the addition of a surfactant , even in excess amount did not alter the absorbance of EAB to any significant extent. Thus this complex formed can be represented as [EAB(TX)].

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 complex formation between TPM dyes and surfactants**.** The cations K^+, Na^+, NH_4^+ did not show any effect on the absorbance of the dye-detergent solution. Nitrates have shown some effect at pH 5.0, as the absorbance goes on increasing up to certain extent after which it remains unaltered. The mineral salts selected were the chlorides (KCl, NaCl, and NH_4Cl), the nitrates (KNO_3, $NaNO_3$,$(NH_4)NO_3$), and sulfates K_2SO_4, Na_2SO_4, $(NH_4)_2SO_4$.To study this in detail, different concentration of salt solutions were added to $1.0\text{x}10^{-3}$ M EAB solution containing $1.0\text{x}10^{-2}$ M CTAB and TX-100 into it.

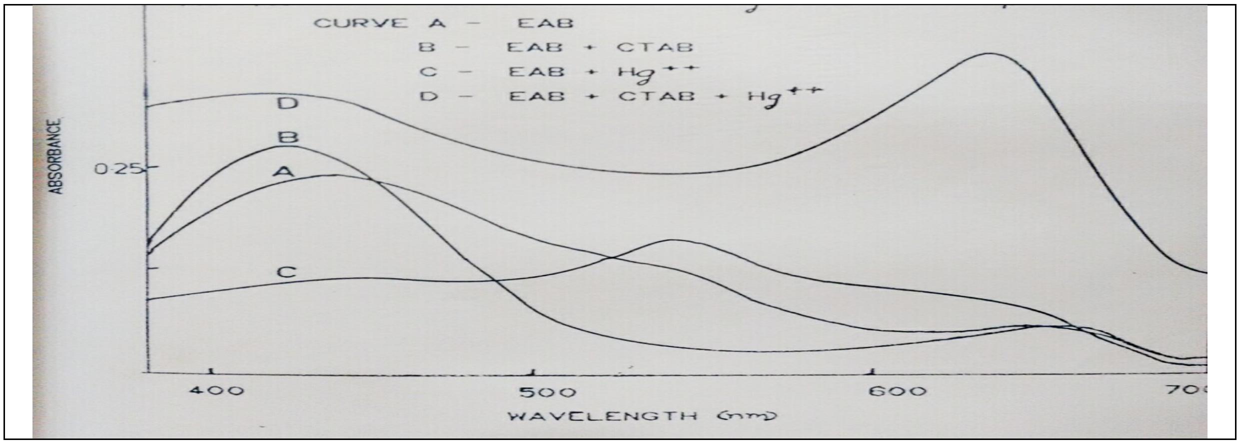

Fig.-1: Absorption Spectra Of Cd(II) in Absence and Presence of CTAB

Dissociation Constant (pK Values) of EAB

Table-2: Dissociation Constants of EAB

pK values	In absence of surfactant	In presence of CTAB	In presence of TX-100
pK_1	3.20	2.70	2.90
pK_2	5.69	5.04	5.60
pK_3	11.13	10.84	11.00

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

Absorption Spectra of the Complexes

Absorption spectra of EAB, EAB- metal ion, EAB - CTAB and EAB - metal ion - CTAB and that in presence of TX-100, were recorded at the pH of study. The nature of complexes formed 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 the 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 and TX-100. The bathochromic shift and increase in the absorbance of complexes are attributed due to the dissociation of phenolic protons of the dye in presence of a surfactant.

Table-3: λ max of EAB and its Chelates in the Absence as well as the Presence of CTAB at pH 5.0 and with M : L as 1:2

System	λ max
EAB	460
EAB+ CTAB	440
EAB + Hg(II)	540
EAB +CTAB + Hg(II)	630
EAB + Pb(II)	540
EAB+ CTAB + Pb (II)	630
EAB + Cd (II)	540
EAB+ CTAB + Cd (II)	640
EAB + Cr(III)	540
EAB + CTAB +Cr(III)	640
EAB + TX+ Cd	590
EAB +TX+ Hg	630

The composition of the Chelates

The stoichiometry of complexes is ascertained by Job's method of continuous variation at the pH 5.0 & λ max and at the wavelength of study. The composition of the complexes at metal ions under study with EAB remains the same in the presence and in the absence 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. The composition of the complexes formed in presence as well as in the absence of TX changes in case of Cd, and Hg complexes. This change in nature of the complexes may be attributed due to the involvement of cationic micelles attachment to the neutral micelles attachment to the chelating positions of EAB.As these positions are already occupied by TX, another anion of the ligand must be involved in the complexation to fulfill the coordination sphere of the metal ion thus changing the composition from 1:1 to 1:2.

Stability Constant

The values of stability constants obtained as log K values of chelates of metal ions under study are reported in Table-4.

Table-4: Composition and Stability Constant (LogK) of Chelates

Chelates	λmax (nm)	Composition M:EAB:CTAB	Log K value 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 + Cd (II)	540	1:2	9.7
EAB+CTAB+Cd(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
EAB + TX + Hg(II)	630	1:1:1	10.72
EAB + TX + Cd (II)	590	1:1:1	11.20

The results showed that the values of log K in the presence of surfactants are greater than that in the absence. This is associated with the tendency of decrease in pK values, dissociation constants of dye EAB, in the presence of surfactants.

Analytical Applications

In all the experiments, a surfactant solution was added to EAB solution; which was then kept for at least 0.5hr for complete formation of dye - detergent complex, to which the metal ion solution was added. This sequence was fixed by carrying out an 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 color intensity from 25^0C to 60^0C and color was stable up to 3 to 4hrs.

pH Range of Stability

A series of solutions of metal : reagent in ratio were prepared at different pH values. In the presence of surfactants, the ratio of EAB : Surfactant was kept in proportion 1:10. The absorbance was noted at the wavelength of the study of the systems. The pH- range within which the absorbance values do not change significantly is taken as the pH range of stability. It is reported in Table 5

Beer's Law and Photometric Ranges

The linearity between the absorbance of the chelates in the absence as well as in the presence 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 which are a plot of the log of metal ion concentration Vs. % transmittance.

Sandell's Sensitivity and Molar Absorptivity of the System

The sensitivity of color reaction of the metal ion with EAB given by log Io/It =0.0001, as defined by Sandell are listed below.

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

System	pH range	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
Cd(II)-EAB-TX	5.– 6.5	0.75 – 3.99	2.82 – 4.46	4.9	16.7	590
Hg(II)-EAB-TX	4.– 6.0	2.1 – 8.02	3.23 – 5.49	9.8	18.5	630

Procedure for the Microspectrophotometric Determinations of Pb(II), Cr(III), Cd (II) and Hg(II) with EAB in the presence of surfactant CTAB and TX-1OO

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 up to 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 a blank. The amount of metal ion present in the 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 to 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 is further increased that would subsequently decrease the value of $t\alpha$. Consequently, a point would be reached when an increase in precision will be too small to justify the expenditure of labor, time and reagents involved in an increased number of determinations. On the basis of root mean square deviation(σ); the most probable error(ε), the difference between the 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 the 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-6: Precision Data For Absorbance Measurement

System	$\dot{X}$	σ	ε	$\dot{X} - \varepsilon$	$\dot{X} + \varepsilon$
EAB + Hg(II)	0.793	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
EAB+ TX + Cd	0.024	0.001	0.0012	0.023	0.025
EAB+ TX + Hg	0.027	0.003	0.0035	0.024	0.030

Table-7: Accuracy Data For Absorbance Measurement Expressed as ($\Delta < \varepsilon$)

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
EAB+ TX + Cd	0.024	0.024	0.000	0.0012
EAB+ TX + Hg	0.027	0.028	0.001	0.0035

CONCLUSION

The mean absorbance, mean deviation, and relative mean deviation are calculated by taking ten repeated analysis with aliquots containing metal ions under study. Also, i) the Root Mean Square deviation, ii) the Most Probable Analytical error, and iii) the Difference Between Arithmetic Mean, and the true or Most Expected Value of the absorbance for the systems are studied. The Precision and Accuracy data recorded revealed that the method proposed is both precise as well as accurate. It is observed that the stabilities of the complexes have increased in the presence of surfactants. One of the most important applications of the colored complexes is its use in the spectrophotometric determination of the metal ions with organic dyes. The use of micelle-forming surfactants in increasing the sensitivity of the color reactions is one of the important aims of the 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.

REFERENCES

1. C. F. Hartley and A.A Downay, *J. Phys. Chem*., **85**, 835 (1984)
2. M. Jarosz, *Wydawn Politech. Warsaw Pol*., 53(1988)

3. M. N. Shtykov, *Organ Reactivity. Analize*., **3**, 36, (1979)
4. R. K. Chernova, L. M. Kudrytseva, V. V. Belousova, L. K. Sukhova, *Organ Reactivity Analize*, **3**, 16, (1979)
5. L. Cerkova, *Surfactants Solution*, **4(2)**, 1217, (1982)
6. T.S. West, R. M. Dognali, J. E. Chester and W. Bailay, *Talanta,* **51**, 1359, (1968)
7. A.B. Zade; K. N. Munshi, K.L. Mitttal (ed) Proceedings International Conference *on Surfactants in Solution, Plenum Press,* 5 *(Part II),* 713,(1988).
8. C. R. Vekhande, K. N. Munshi, *J. Indian Chem.. Soc*., **50**,384(1973).
9. A. S. Mahakalkar, K. N. Munshi, *Asian Journal of Chemistry*, **6**, 56(1994)
10. A. Ringbom, Zh. *Analyt.Chem*., **115**, 332(1939), **DOI:** 10.1016/B978-0-444-98882-9.50007-4
11. V. Svoboda, V. Chromy, *Talanta*, **12**, 431(1965), **DOI:** 10.1016/0039-9140(65)80259-4
12. Caiwen, Guo and Wang Quingyne, *Huaxue Shiji,* **6**, 26(1985).
13. Juan A. Ocana, Manuel Callejon and Francisco Jose Barragan, *Anal.*, **125,** 1851(2000), **DOI:** 10.9790/5736-1106012934
14. M. Z.Salma Al-Kindy and Fakhr Eldin O. Suliman, *Luminescence* , **22(4)**, 294(2007).
15. I. S. Ahmed , A.S. Amin , Y.M. Issa , *Spectrochimica Acta Part A*, **64**, 246(2006), **DOI:** 10.1016/j.saa.2005.06.044
16. Mohsen Keyvanfard, *PWASET*, **33**, 2070, (2008)
17. A. S. Dhepe, A.B. Zade, *E- Journal Of Chemistry*, **8(3)**,1264(2011), **DOI:** 10.1155/2011/871685
18. H. Dezhampanah and R Firouzi, *Int. Res. Phys. Chem*., 45(2012), **DOI:** 10.1016/j.arabjc.2015.09.009
19. Renu Sharma, Ajar Kamal and Rakesh Kumar Mahajan, *RSC Advances*, **75(6)**,71692(2016), **DOI:** 10.1039/C6RA12056C

[RJC-4007/2018]