



Sensitization of Chrome Azurol-s in Presence of Cetyl dimethyl ethylammonium Bromide for the Microdetermination of Europium.

G. W. Belsare*, S. G. Badne

1. Department of Chemistry, Shri Shivaji College of Arts, Commerce and Science, Akola.

Key Words: Chrome azurol-s (CAS), Cetyldimethylethylammonium bromide (CDMEAB), Molar absorptivity, sensitivity etc.

Abstract:

Cetyldimethylethylammonium bromide (CDMEAB), a cationic surfactant has been used to decolorized Chrome Azurol-S (CAS), an anionic triphenyl methane dye. Addition of Eu^{3+} to this decolorized solution resulted into intense colour 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 (Eu-CAS-CDMEAB) as compared to binary complex (Eu-CAS). The analytical applications like Beer's law range and effective photometric range have been studied at pH 6.0 and at 540nm in absence and at 650nm in presence of CDMEAB.

1. Introduction:

There are number of advent of separation methods available for the determination of the rare earths with their growing interest in the industrial applications. In early 70's some reactions were reported in which the addition of surfactants decreases the colour intensity of organic dyes considerably. Subsequent developments demonstrated that the addition of specific metal ions to these decolourized indicators resulted in intense, water soluble highly coloured complex with greater molar absorptivity and solubility than the complex formed in the absence of surfactant and thus making these decolourized dyes suitable for the spectrometric determination of metal ions at low concentration which cannot be determined. Some of micro analytical techniques for the determination of metal ions with these dyes in presence of surfactants are discussed below. The spectrophotometric determination of the lanthanoids with chrome azurol-s in presence of cetylpyridinium bromide have been studied at pH 5.4 ($\lambda_{\text{max}} = 620\text{nm}$)¹. Both pyrogallol red and bromopyrogallol red have been studied in presence of surfactants (CPB and OP-7) by using optical methods for the determination of $\text{Mo(VI)}^{2,3}$, $\text{W(VI)}^{2,5}$, Cu(II)^2 , Ti(IV)^4 and V(V)^5 by Ivanov and coworkers. Spectrophotometric determination of Sc(III) in monazite after separation in presence of

eriochrome cyanine R and CTAB have been reported by Chan-il-Park and coworkers⁶. Applications of chrome azurol -s and benzyldodecyldimethyl ammonium bromide for Ga(III) have been studied by Buhl Franciszek and coworkers⁷. Microspectrophotometric determination of Thorium with methyl thymol blue in presence of CTAB has been studied by Upase and Zade⁸. The spectrophotometric determination of Thorium with pyrocatechol violet in presence of CTMAB by Chan-il-Park⁹. Spectrophotometric determination of some rare earths with triphenyl methane dyes in presence of cetyldimethylethyl ammonium bromide has been studied earlier¹⁰⁻¹²

2. Material and Methods:

2.1 Instrumentation and Reagent solutions:

All the spectral measurements have been carried out on Chemline model CL 133 microcontroller based spectrophotometer with glass cuvettes of light paths 10mm. distilled water has been used as a reference solution. Chemline model CL 180 pH meter with combine electrode has been used for the adjustment of pH. The scale has been standardizing every day before making the pH measurement with buffer solutions of pH 4.0, 7.0 & 9.0. The pH of the each solution has been adjusted with HCl and NaOH solution of suitable concentration.

The Chrome azurol-s and Cetyldimethylethyl ammonium bromide were used in this work were of analytical grade purity and supplied by Sigma-Aldrich chemical company, USA. The Europium oxide of analytical grade purity was supplied by Indian Rare Earth Company. The solution of both the reagents have been prepared by using distilled water using ethanol. The stock solution of all reagents have been prepared in the concentration $1.0 \times 10^{-2} \text{M}$. The HCl and NaOH used was supplied by SD fine chemical laboratories.

2.2 General Procedure:

All experiments are carried out at room temperature $30 \pm 2^\circ\text{C}$. The CDMEAB solution was first added to the CAS solution and kept for equilibration for half an hour. The metal solution was then added in the dye- surfactant solution and kept for half an hour for complete equilibration. This order of mixing of solution was maintained throughout the investigation.

3. Result and Discussion:

It has been considered necessary to have prior information on the nature of interaction between CAS and CDMEAB before evaluating the CAS as sensitive reagent for the estimation of Eu(III) in the presence of CDMEAB. Therefore, absorption spectra of CAS in absence and presence of CDMEAB, composition of dye-surfactant complex, absorption spectra of Eu (III) in absence and presence of CDMEAB, effect of pH, composition of the chelates in absence and presence of CDMEAB, have been studied.

3.1.1 Absorption spectra of CAS in the absence and presence of CDMEAB.

The color of CAS has been found to be different at different pH values. The addition of CDMEAB brings about a slight change in color of CAS at the same pH value. The absorption spectra of CAS, has been therefore,

studied at different pH values (3.0 to 10.0) in the absence and presence of CDMEAB. The wavelength of maximum absorbance of CAS in the absence and presence of CDMEAB are summarized in table 1.

Absorption spectra of alkaline CAS solution at pH 8.0 show a characteristics maximum at 600 nm and above in presence of CDMEAB with the increase in the absorbance value. This may be due to the formation of dye-detergent complex.

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

CAS		CAS + CDMEAB	
pH	λ_{\max} (nm)	pH	λ_{\max} (nm)
3.0-3.5	500	3.0-4.5	520
4.0-5.0	480	5.0-10.0	430
5.5-10.0	420		

3.1.2 Composition of CAS-CDMEAB Complex.

The effect of varying CDMEAB concentration on the absorbance of CAS has been studied in basic medium at pH 10.0, at λ_{\max} , 420nm where the maximum discoloration takes place. The absorbance of different concentrations of CAS is plotted against the variable concentration CDMEAB. It has been observed that the two times higher concentration of CDMEAB required for complete decolourization of CAS. Thus, the ratio of CAS: CDMEAB will be 1:2 The modified reagent species thus formed, may therefore, be written as [CAS (CDMEAB)₂].

3.1.3 Absorption Spectra of Eu (III)-CAS Chelates in Presence and Absence of CDMEAB

A series of solutions were prepared keeping the ratio of Eu (III)²⁺: CAS: CDMEAB as 1:1:5 and 4:1:5. A number of sets were prepared for each ratio and pH was adjusted to 3.0 to 10.0 The absorption Spectra were recorded in the entire visible region from 400nm to 700nm. Absorbance maxima of CAS and its complexes with Eu (III) in the absence and presence of CDMEAB have been summarized at different pH values in table 2.

Table 2: Absorbance Maxima (nm) of CAS and its Chelates in the Absence and presence of CDMEAB at different pH.

System/pH	4.0	4.5	5.0	5.5	6.0	6.5	7.0
CAS	480	480	420	420	420	420	420
CAS + CDMEAB	430	430	430	430	430	430	430
CAS + Eu (III)	540	540	540	540	540	540	540
CAS + CDMEAB + Eu (III)	650	650	650	650	650	650	650

The absorption spectra of CAS shows peak at 430nm in the presence of CDMEAB in the pH range 3.0 to 5.0 but shows peak at 580nm in the pH 8.0 to 10.0. In the pH range 4.0 to 7.0, in absence and presence of CDMEAB, the wavelength maxima of CAS shows change in λ_{\max} but small change in absorbance values; indicating poor complexation. But, huge change in the absorbance value in pH range 6.0 to 7.0 show complex formation in absence and presence of CDMEAB. By comparing the absorption spectra and the absorbance values of the reagent and complex in presence of CDMEAB, it has been observed that the maximum complexation takes place at pH 6.5. Thus bath chromic shift of 120 nm in absence and 220nm in the presence of CDMEAB have been observed for Eu (III).

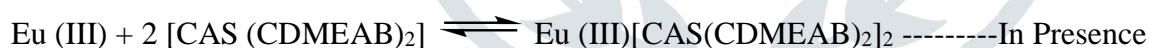
3.2 Effect of pH

Effect of pH on λ_{\max} and on the absorbance, of the Eu (III) complexes of CAS 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 4.0 to 7.0 indicating pH range of stability of complex formation in presence and absence of CDMEAB.

3.4 Composition of Chelates

The composition of the chelates has been studied by the Mole ratio method. solutions of Eu (III) and CAS have been taken in two equimolar concentrations of 2.0×10^{-5} M and, 4.0×10^{-5} M; Five times excess of CDMEAB has been then added for studying the composition in the presence of surfactant.

The stoichiometric composition between the Eu (III) and CAS in the absence and presence of CDMEAB have been found to be 1:1 and 1:2 respectively. It has been observed that CAS reagent at pH 8.0 exists as $[\text{CAS}(\text{CDMEAB})_2]$ and therefore, the composition of complexes in the presence of CDMEAB may be written as Eu (III) $[\text{CAS}(\text{CDMEAB})_2]_2$ for Eu (III).



3.5 Analytical Applications of Eu (III) chelates with CAS in absence and in presence of CDMEAB

3.5.1 Order of Addition of Reactants

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

3.5.2 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. The temperature was found to have no effect on color intensity of ternary complexes from 20°C to 60°C .

3.5.3 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 in presence of CDMEAB). The final

concentration of CAS taken was 2.0×10^{-5} M, of CDMEAB was 1.0×10^{-4} M. Total volume was kept constant at 25ml at pH 8.0. 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 this 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 4.

Table 4: Photometric Determination of Eu (III) with CAS in the Absence and Presence of CDMEAB.

Photometric Determination of Eu (III)-CAS Cheletes in presence and absence of CDMEAB

CAS Cheletes	pH of Study	Wavelength of Study(nm)	Beers Law Range (ppm)	Effective Photometric range (ppm)	Molar Absoptivity	Sensitivity ($\mu\text{g}/\text{cm}^2$)
CAS + Eu (III)	6.0	540	0.30-1.80	0.30-1.20	2700	0.009
CAS + CDMEAB + Eu (III)	6.0	650	0.20-1.40	0.60-1.40	5400	0.003

4. Conclusion:

The spectrophotometric determination of Eu (III) with Chrome azurol-s in the presence and absence of Cetyldimethylethyl ammonium bromide has been studied. Following are the merits of modified method. The sensitization of CAS by the addition of CDMEAB is clear from the fact that the formation of stable ternary complex with Eu (III) occurs at pH range 6.0-7.0 with bath chromic shift in the λ_{max} of Eu (III)-CAS complexes in the presence of CDMEAB. This change λ_{max} and high absorbance value is attributed due to the formation of ternary complex system in the presence of CDMEAB compared to the binary system in the absence of CDMEAB. Due to the shifted λ_{max} towards higher wavelength (From 540 nm to 650 nm) a large difference in the absorbance between the reagents blank (CAS + CDMEAB) and its ternary complex results in enhancement of the sensitivities and molar absorptivities again indicate the great sensitivity of colour reaction. Further, the modified method requires smaller molar concentration of CAS over the metal ion concentration for full colour development and is instantaneous in the presence of CDMEAB, again indicates the stability of the colour reaction. The modified reagent i.e. [CAS (CDMEAB)₂] has also been found to be extremely useful in the complexometric titration of the Eu (III). This modified reagent act as sensitive metallochrome indicator giving a very sharp colour change at the end of complexometric titration. The increase in the sensitivity and absorptivity facilitate the determination of Eu (III) in the given photometric range.

5. Acknowledgments:

Authors are thankful to Dr. A. L. Kulat, Principal, Shri Shivaji College of Arts, Commerce and Science, Akola for providing necessary facilities

6. References

1. Vekhande , C. R. and Munshi K. N. 1976 : Indian Journal of Chemistry;A14; 189-191;
2. Ivanov V. M. and Mamedova A. M.; 200 ; J. Anal. Chem.; 61,242.
3. Ivanov V. M. and Mamedova A. M and Akimedov S. A. ;2003; Moscow University Chemical Bulletin; 44, 253.
4. Ivanov V. M. and Mamedova A. M and Akimedov S. A. ; 2003 ; Moscow University Chemical Bulletin; 44, 304.
5. Mamedova A. M, Ivanov V. M. and Akimedov S. A.; 2004 ; Moscow University Chemical Bulletin; 45, 117.
6. Chan-il-Park and Ki-Won-Chan; ; 1999; Bull Koeran Chem. Soc.; 20.
7. Buhl Franciszek and Poledniok Justyna; 2002; Chemia Analityczna; 47, 153.
8. Upase A. B. and Zade A. B. ;2005; Journal of Indian Chemical Soc.;82, 853.
9. Chan-il-Park Hua Zi Haung and Ki-Won-Chan; 2001; Bull Koeran Chem. Soc.; 22.
10. G. W. Belsare, A. B. Zade, Pawan P. Kalbende and P. U. Belsare; 2012; Der Pharma Chemica ; 4 (3):1226-1238.
11. A. B. Zade, P. P. Kalbende, M. S. Umekar, and G. W. Belsare; 2012 E-Journal of Chemistry; 9(4), 2394-2406.
12. G. W. Belsare, S. G. Badne; 2018; The Pharma Innovation Journal; 7(1), 128-131

