MICRODETERMINATION OF Ce(IV) AND Y(III) WITH CHROME AZUROL-S IN PRESENCE OF CETYLDIMETHYLETHYLAMMONIUM BROMIDE

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Abstract

Complexation reaction of Ce(IV) and Y(III) with Chrome azurol-s (CAS), a member of triphenylmethane dye in absence and presence of cetyldimethylethylammonium bromide (CDMEAB), a cationic surfactant have been studied. The intense blue coloured complexes of Ce(IV) and Y(III) in presence of cetyldimethylethylammonium bromide show shift in the λmax with increased sensitivity and molar absorptivity. The change in the properties of chrome azurol-s in presence cetyldimethylethylammonium bromide utilized for the Microdetermination of Ce(IV) and Y(III).

Keywords: Cetyldimethylethylammonium bromide (CDMEAB), complexation, microdetermination, Chrome azurol-s, Wavelength maxima etc.

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 grater 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 spectrphotometric determination of the lanthanoids with chrome azurol-s in presence of cetylpyridinium bromide have been studied at pH 5.4 (λmax= 620nm)[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 Mo(VI)[2,3], 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 coworkers[6]. Applications of chrome azurol -s and benzyldodecyldimethyl ammonium bromide for Ga(III) have been studied by Buhl Franciszek and coworkers[7]. Microspectrophotolmetric determination of Thorium with methyl thymol blue in presence of CTAB has been studied by Upase and Zade[8]. The spectrophotometric determination of Thorium with pyrocatechol violet in presence of CTMAB by Chan-il-Park[9]. Spectrophotometric determination of some rare earths with triphenyl methane dyes in presence of cetyldimethylethyl ammonium bromide has been studied earlier[10-12].

Very little work as discussed above has been reported for microdetermination of Ce (IV) and Y(III) ternary complexes, hence present study has been planned to suggest really simple metal ion at low concentration, using reported reagent chrome azurol-S(CAS) as a binary complex and sensitizing the reagent with CDMEAB as ternary complex using spectrophotometer.

2. Materials and Methods:

2.1 Experimental part

All the spectral measurements have been taken 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 is 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 & 9.2. The pH of the each solution has been adjusted with HCl and NaOH solution of suitable concentration.

2.2 Reagent solution:-

The chrome azurol-S and cetyldimethylethylammonium bromide were used in this work was of analytical grade and supplied by Sigma chemical company, USA. The solution of the reagent has been prepared by using distilled water and ethanol. The stock solution of reagents has been prepared in the concentration 1.0×10^{-3}M. Yttrium Nitate and Ceric Nitrate were used in this work was supplied by Indian Rare earth company. The HCl and NaOH used were supplied by SD fine chemical laboratories.

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 microderemination of Ce (IV) and Y (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 Ce (IV) and Y (III) in absence and presence of CDMEAB, effect of pH, composition of the chelates in absence and presence of CDMEAB, have been studied.

3.11. Absorption spectra of CAS in the absence and presence of CDMEAB[7].

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 12.0) 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 430nm 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)
3.0-4.5	500	3.0-4.0	520
5.0	480	4.5	450
5.5-11	420	5.0-10.0	430
12.0	630	11.0-12.0	410

3.12. Composition of CAS-CDMEAB Complex.

The effect of varying CDMEAB concentration on the absorbance of CAS has been studied in basic medium at pH 5.0 in acidic medium and pH8.0 in basic medium have been studied. 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 decolorization of CAS. Thus, the ratio of CAS: CDMEAB was found to be 1:2. The modified reagent species thus formed, may therefore, be written as [CAS (CDMEAB) $_2$].

3.13. Absorption Spectra of Ce (IV) and Y (III) Chelates in Presence and Absence of Surfactant.

A series of solutions were prepared keeping the ratio of M^{n+}: 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 Ce (IV) and Y (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	4.0	5.0	6.0	7.0
CAS	500	480	420	420
CAS +CDMEAB	520	430	430	430
CAS+Y^{3+}	540	540	540	540
CAS+CDMEAB + Y^{3+}	650	650	650	650
CAS+Ce^{4+}	540	540	540	540
CAS+CDMEAB +Ce^{4+}	650	650	650	650

The absorption spectra shows that the change in λ_{max} and increase in the absorbance value in pH range 4.0 to 7.0 show complex formations 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 6.0. Thus bathochromic shift of 110nm in the presence of CDMEAB have been observed for Ce (IV) and Y (III).

3.14. Composition of Chelates

The composition of the chelates has been studied by the Mole ratio method. solutions of Ce (IV) and Y (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 Ce (IV) and Y (III) and CAS in the presence and absence of CDMEAB has been found to be 1:2. It has been observed that CAS reagent exists as [CAS (CDMEAB)$_2$] and therefore, the composition of complexes in the presence of CDMEAB may be written as M^{n+}[CAS(CDMEAB)$_2$]$_2$ where M^{n+} is Ce (IV) or Y (III).

$$M^{n+} + 2 [CAS (C D E A B)_2] \rightleftharpoons M^{n+} [CAS(CDMEAB)_2]_2 \quad M^{n+} = Ce (IV), Y (III)$$

3.2. Analytical applications of Ce (IV), Y (III) chelates with CAS in absence and in presence of CDMEAB

3.21. 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, M^{n+} solution was then added which again kept for 30 minutes for complete formation of the ternary complex.

3.22. 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 20^0 C to 60^0 C.

3.23. 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 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 50ml at pH 6.0. 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 3 in absence and presence of CDMEAB. The effective range for photometric determination was also calculated from this data by Ringbom[9-10] 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 3.

3.24. Sensitivity and Molar absorptivity:

Molar absorptivity of complexes was determined by taking constant amount of metal ion and different amount of excess of CAS. The values of molarabsorptivities and sensitivities of metal complexes in absence and presence of CDMEAB have been recorded in table 3. The increase in the molar absorptivity and sensitivity of ternary complexes show the sensitization of colour reactions in presence of CDMEAB

Table 3: Photometric Determination of Y(III) and Ce (IV) with CAS in the Absence and Presence of CDMEAB.

Chelates CAS	pH of study	Wavelength of study, (nm)	Beer's law Range (ppm)	Effective Photometric range (ppm)	Molar Absorptivity	Sensitivity ($\mu g/cm^2$)
$CAS+Y^{3+}$	6.0	540	0.17-1.065	0.35-1.065	27000	0.003
$CAS+CDMEAB + Y^{3+}$	6.0	650	0.11-1.06	0.35-1.065	54000	0.0016
$CAS+Ce^{4+}$	6.0	540	0.028 -0.56	0.22-0.53	35000	0.0040
$CAS+CDMEAB +Ce^{4+}$	6.0	650	0.028-1.68	0.084-1.12	45000	0.00311

4. Microdetermination of Metal Ion:

The pH of the solution containing 23.70 μg/50ml of Y(III) and 56.04 μg/50ml of Ce (IV) has been adjusted at 6.0. The two fold excess of modified CAS reagent has been added in the metal ion solution. The solution mixture has been then kept for 30 minutes for complete equilibration. The absorbance measurement has been recorded at 650 nm against the reagent blank prepared in the same manner. The absorbance has been then compared with the calibration curve obtained under similar conditions. The results of microderemination have been recorded in table 2.

Table 4: Microdetermination of Individual Metal Ion

Metal Ion	Amount Taken (μg/50ml)	Amount Found (μg/50ml)	Standard Deviation
Y(III)	23.70	23.77	±0.035
Ce(IV)	56.04	55.47	±0.285

5. Conclusion

The spectrophotometeric determination of Y(III) and Ce (IV) with chrome azurol-S in the presence and absence of cetyldimethylethylammonium 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 complexes with Y (III) and Ce (IV) occurs at pH 6.0 with bathochromic shift in the λ_{max} of CAS-M^{n+} complexes in the presence of cationic surfactant. This change λ_{max} and high absorbance value is attributed due to the formation of ternary complex system in the presence of CDMEAB at pH 6.0 compared to the binary system in the absence of CDMEAB. Due to the shifted λ_{max} towards higher wavelength (From 430 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 sensitization of color reaction.

Further, the modified method requires smaller molar concentration of CAS over the metal ion concentration for full color development and is instantaneous in the presence of CDMEAB, again indicates the stability of the color reaction.

The modified reagent i.e. [CAS (CDMEAB)$_2$] has also been found to be extremely useful in the photometric determination of the metal ions understudy. The increase in the sensitivity and absorptivity facilitate the microdetermination of metal ion understudy in the given photometric range.

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