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Research Article

A Study of Metal – CTB Charge Transfer Complexes with Spectrophotometric Descriptors

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Abstract

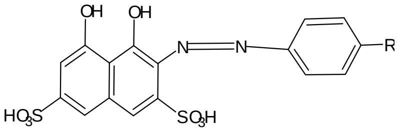
Chromotrope 2B is a very important azo dye used in number of analytical and clinical applications. Its complexation with metal ions is a key for its applicatory uses. Using spectrophotometric descriptors, stability of its charge transfer complexes with various metal ions viz, Sc(III), Y(III), Sm(III), Dy(III), Er(III), were studied. With the help of a novel graphical method, molar absorptivity coefficient of the complexes were determined simultaneously with the stability constant. The presence of azo group and lone pair on $-NO_2$ group in CTB increases the length of conjugation in its structure which in-turn intensifies the colour of CT complex making a red shift in the absorption spectra.

Key words: Chromotrope 2B, stability constant, molar absorptivity, CT complex.

INTRODUCTION

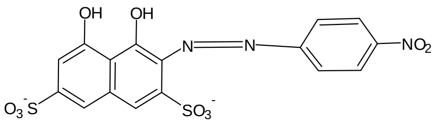
Dyes are well known complexometric and colorimetric reagents. They were widely used in the microdetermination and analysis of number of metals, in pharmaceutical formulations and applied in the determination of some drugs[1-4]. The reactions of p-nitrobenzene azochromotropic acid disodium salt, which is commonly known as chromotrope 2B (CTB), have attracted much attention due to their capability of formation of charge transfer complexes. The interactions of CTB with many substances such as metals, drugs, proteins, chitosin etc. have been studied with the help of various analytical tools. Ivanov et al have used Chromotrope 2B reagent as an analytical reagent for the direct determination of nitrite ions by sorption chromaticity measurements, diffuse reflectance spectrometry, and solid-phase spectrophotometry[5]. In most samples, metals are generally present at levels lower than the limits of detection of common analytical methods. Başbuğ and Tokalıoğlu[6] have used Coprecipitation methods using Al(III) and Fe(III) as carrier elements and chromotrope 2B as coprecipitative reagent were described for the pre-concentration of Cr(III), Pb(II), Zn(II), Cd(II) and Mn(II) ions. Different oxidants regulate the staining ability. Weixing et al[7] have developed a simple and sensitive fading spectrophotometric method for the determination of chitosan taking advantage of the reaction between chitosan and chromotrope 2B in Clark-Lubs buffer medium. Sun et al[8] have studied the interaction of chromotrope 2B with proteins by the electrochemical method. Datta [9] discussed the analytical aspects of some azo dyes derived from chromotropic acid . Chattopadhyaya et al determined stability constant of 1:1 Lanthanum(III)-Chromotrope 2B Complex by a graphical method novel membrane and coated wire electrodes by ion-selective electrode[10].

The general structure of the chromotropic acid can be shown as following scheme-1, in which R stand for -H, $-SO_3H$, -COOH, $-NO_2$, -OH, $-OCH_3$, $-OC_2H_5$, $-CH_3$, or $–NH_2$ etc.

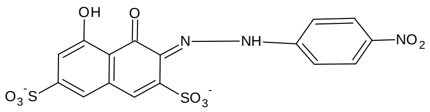


Scheme-1. Substituted azo-chromotropic acid

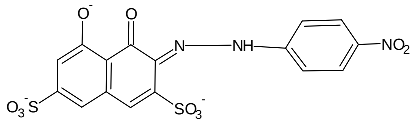
Structure of chromotrope 2B in different media is given in following scheme-2.



(i) In acidic medium



(ii)In Mildly acidic to neutral medium



(iii) In Alkaline medium

Scheme-2

When the concentration of CTB reaches beyond the limiting concentration, the formation of a new complex would be possible which would cause a reduction in the absorbance. Therefore, it is important to decide to choose optimum concentraton as ~10^{-5} µg/ mL of CTB. Our present work throws an idea on the stability of the complex, which could be utilized for the various analytical applications. We have studied the charge transfer spectra of various metal-CTB complexes by determining their stability constant and molar absorptivity constant simultaneously providing a comparatively less tedious method using a novel graphical approach.

EXPERIMENTAL

All experiments involving absorbance measurements have been performed at fixed hydrogen-ion concentrations, because the chelates are found to change their colour with variations in pH of the medium. The ionic strength has also been kept constant, wherever cited, by the addition of suitable non-reacting electrolytes($NaClO_4$).

Standard solution of Chromotrope 2B (both from E.Merck), Scandium Chloride, Yttrium Chloride, Samarium Chloride, Dysprosium Chloride and Erbium Chloride (all from BDH) were prepared in doubly distilled water. Freshly made solution were always used and care was taken to exclude carbon dioxide from the double distilled water used for preparing the same.

The pH measurements were carried out using Orion Research Microprocessor Ionalyzer/901 and spectrophotometric data were obtained using a digital UV-Visible spectrophotometer (Systronic) with 10 mm quartz cuvettes. The work was carried out at room temperature $30^0 \pm 2^o$C.

Determination of Wavelength of Maximum Absorption:

A solution was prepared by mixing 10 mL of 2.5 × 10^{-4} mol dm^{-3} solution of Chromotrope 2B (CTB) in 10 mL of 2.5 × 10^{-4} mol dm^{-3} different metal solutions, viz. Sc (III), Y (III), Sm (III), Dy (III), Er (III) followed by diluting the solution to 50 mL. The colour appeared instantaneously. The absorption maxima of each solution was measured in the wavelength range 480-580 nm taking water as blank. It was found that value of absorbance does not change even after for long time. The composite spectra of metal-CTB are shown in fig. 1 .

RESULTS AND DISCUSSION

A series of solutions were prepared by mixing said metal ions and dye solutions in 1:1 ratio. The absorbance of each solution was recorded in the range 480-580 nm. For the simultaneous determination of molar absorptivity and the apparent stability constants .following theory was used.

Consider the formation of 1:1 species according to the equation (1)

$$M + L = ML \qquad (1)$$

for which the stability constant can be expressed as equation (2),

$$K = \frac{[M]}{\{[M^0] - [ML]\}\{[L^0] - [ML]\}} \qquad (2)$$

M^0 and L^0 are the analytical concentration of metal ion and ligand respectively. If metal ion, ligand and complex absorb light in the region of study the absorbance for unit path length can be expressed as equation (3),

$$A = \{[M^0] - [ML]\}\epsilon_M + \{[L^0] - [ML]\}\epsilon_L + [ML]\,\epsilon_C \qquad (3)$$

Where, ϵ_M , ϵ_L and ϵ_C are the molar extinction coefficient of the species M, L and ML respectively.

Combining equations (2) and (3) and rearranging we get equation (4),

$$\frac{M^0L^0}{A - \epsilon} + \frac{A - \epsilon}{\epsilon_0^2} = \frac{M^0 + L^0}{\epsilon_0} + \frac{1}{K\,\epsilon_0} \qquad (4)$$

$$\epsilon = M^0 \epsilon_M + L^0 \epsilon_L \qquad (5)$$

and

$$\epsilon_0 = \epsilon_C - \epsilon_M - \epsilon_L \qquad (6)$$

If the left hand side of equation (4) is plotted against $M^0 + L^0$, one will get a slope as $1/\epsilon_0$ and intercept as $1/K\epsilon_0$. From these one can calculate K. Usually the value of ϵ_C is not known initially, nor the value of ϵ_0. In such case, a trial value of ϵ_0 can be taken and approximate values of ϵ_0 and K calculated. The approximate value of ϵ_0 can be refined by successive approximation using method of least squares. The results are summerised in table-1.

Azo dyes provide an extra chelating site along with the presence of other donor groups like, –OH , –O etc in a dye. The presence of azo group increases the length of conjugation in its structure which in-turn intensifies the colour of charge transfer complex due to red shift in the absorption spectra(Fig.1). Moreover, the presence of $-NO_2$ group in CTB promotes $n \rightarrow \pi^*$ transitions more facile due to the presence of lone pair on the nitrogen .

From the stability constant and molar extinction coefficient determinations it can be assumed in the case of metal - dye chelates, there are two alternative positions for the chelate ring. The metal ion most likely be co-ordinated between two phenolic oxygen, which will give a stable six membered chelated charge transfer complex. On the other sites(with other donating groups) there is no probability of the formation of 5-6 membered ring to give any stable chelate. On the basis of the decrease in the pH when hydrogen ions are liberated as a result of the chelation , it is inferred that the hydroxyl oxygen participates in the chelation. Moreover, broad hydroxyl group band in the infrared spectra of CTB(Fig-2) indicates intramolecular and inter molecular hydrogen bonding in free acid but in the metal-CTB spectra, the narrowing of this band indicated the site of chelation occurs at the above said juncture.

The expediencies of the used novel graphical method are, firstly, no term is omitted in the above used linear equation, secondly, only 1:1 complex is formed since equimolar amounts of metal and ligand is taken, hence there is no possibility of the formation of 1:2 complex and lastly the most important advantage of this method is that stability constant and molar absorptivity can be determined simultaneously.

CONCLUSION

Charge transfer spectra of metal ion[Sc (III), Y (III), Sm (III), Dy (III), Er (III)] – CTB was studied spectrophotometrically and determined their stability constant and molar absorptivity simultaneoulsy with the help of a novel graphical method.The reason for the red shift observed in the absorption spectra is also discussed and shown that the increase in the length conjugation of double bond in the structure is the major cause of the shift.

Table 1. Experimental data and results; temperature : Sc(III)-, Y(III)-, Sm(III)- Dy(III)- , Er(III)-CTB at 30°C

System	Concentration Range x10^5 (M)	pH ± 0.2	Ionic Strength (M)	λ_{max} (nm)	$\in_0$ x 10^{-4} ($L.M^{-1}.cm^{-1}$)	Log K_1
Sc(III)-CTB	2.00-5.00	4.5	0.1	530	2.306	4.66
Y(III)-CTB	2.00-5.00	6.0	0.1	530	3.231	4.49
Sm(III)-CTB	1.25-3.12	6.0	0.1	530	7.770	5.10
Dy(III)-CTB	1.00-2.50	6.0	0.1	535	1.193	4.92
Er(III)-CTB	1.00-2.50	6.0	0.1	540	1.088	4.96

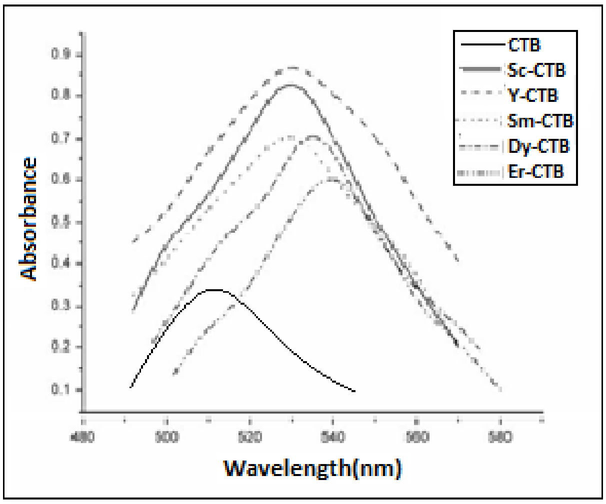


Figure 1. Absorption spectra of various metal – CTB complexes

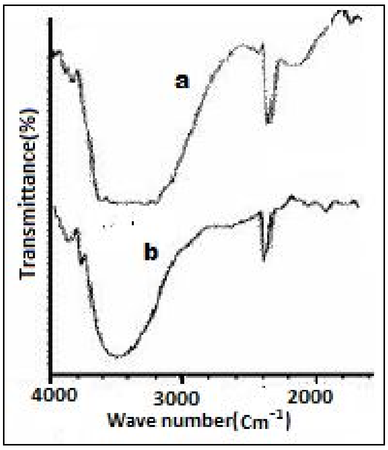


Figure 2. Infra red spectra of CTB(a) and metal – CTB (b) complex

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