

Co-ordination and Analytical Studies Of Cu(II), And Ni(II) Using Pyrocatechol Violet and CTAB As Modified Reagents

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ABSTRACT

The study of the absorption spectra of the complexes formed between metal ions selected for the present study viz. Cu(II), and Ni(II) and the dye-surfactant species (i.e. Pyrocatechol Violet and Cetyltrimethyl ammonium bromide); as ligands forms the first subject matter of the study of metal complexes. Quantitative information on complex formation is obtained by determining the composition and the stability constants of the chelates formed. Pyrocatechol Violet (PCV) is a triphenylmethane dye which forms stable complexes with CTAB and Metals under study. Dye-Surfactant complexes showed Hypsochromic Shifts while with Metal chelates a large bathochromic shift has been observed. Composition of the complexes remains unchanged in presence of CTAB as 1:1. Stability Constants has been evaluated which revealed to increase the stability of chelates in the presence of CTAB. Studies were also carried out on various analytical parameters revealed that Pyrocatechol Violet (PCV) is an effective reagent to be used for microdetermination of Cu(II) and Ni(II).

Introduction:

Reactions of surfactants in bringing a change in spectral characteristics of triphenylmethane dyes & their use in determination of metal ions was studied^(1, 2,3). The mechanism of the interaction of surfactants with Triphenylmethane Dyes used for the spectrophotometric determination of metal ions is discussed⁽⁴⁾. 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⁽⁵⁻⁹⁾. Complexation of (Cu(II), Fe (II) & Al(III) with Chrome Azurol S in the presence of non ionic surfactants was studied⁽¹⁰⁾. The present investigation undertaken involves a detail study of the interaction of surfactant CetylTrimethylAminonium Bromide with a triphenylmethane dye Pyrocatechol Violet (PCV). The dye surfactant complexes thus formed was used to study complexation reactions of Cu (II) and Ni (II) in presence as well as in the absence of surfactant CTAB.

Experimental : The absorption measurements were done on UV Shimadzu - UV240 Spectrophotometer. Distilled water blanks were used for pH measurements Elico pH meter LI-10 with glass calomel electrode system was used after standardization.

All the reagents used were of BDH Anala R grade purity. The surfactant Cetyltrimethyl ammonium bromide (CTAB) was prepared in 20% aqueous methanol in double distilled water and were standardized by usual procedures.

The dye solution of PyrocatecholViolet(PCV) was prepared in double distilled water by dissolving its purified samples and the standard solutions of heavy metals under study were prepared by dissolving analytical grade metal salts in 5% HNO₃.

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 PCV solutions which was kept for at least 20 minutes for maximum decolorizing effect to which standard metal ions solution was then added. The absorbance readings were recorded only after 30 minutes of additions of the reactants a time necessary for equilibration.

RESULTS AND DISCUSSION

Absorption Spectra :

Absorption Spectra of PyroCatechol Violet solution was recorded from pH 1.0 to 12.0. The spectral studies in the presence of ten times pH 1.0 to pH12. The λ_{max} values in the absence of, as well as in the presence of CTAB was found to be as given below in Table - 1.

For studying the absorption spectra of PCV, 1.0 ml of 1.0×10^{-3} M solution was taken in different volumetric flasks and their pH was adjusted & from 1.0 to 12.0 after which total volume was made upto 25ml with distilled water. The hypsochromic shift in the presence of CTAB was observed almost all pH values. This was attributed due to formation of dye / surfactant complex.

Table - 1
 λ_{max} of PCV at different pH values:

pH	Inabsence of (nm)	In presence of CTAB (nm)
1.0	460 nm	490
2.0	460	500
3.0	480	500
4.0	480	470
5.0	445	410
6.0	440	415
7.0	430	415
8.0	420	415
9.0	420	415
10.0	420	415
11.0	420	410
12.0	600	610

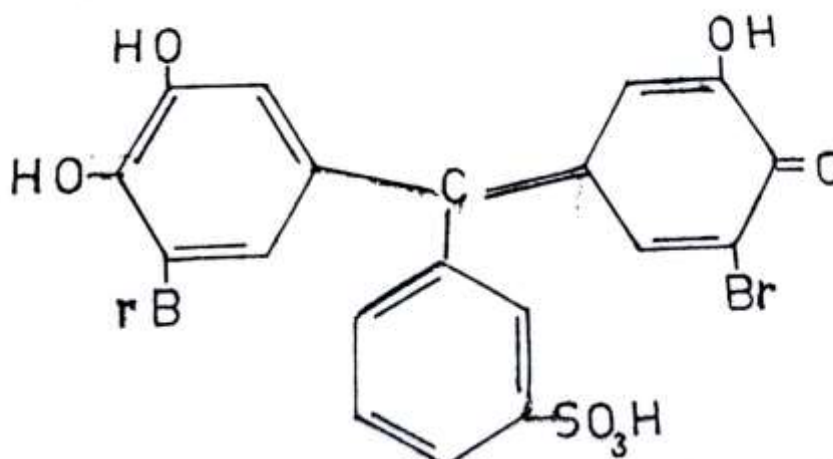
pH 5 & λ_{max} 410 nm is thus selected for further analytical studies of PCV.

The absorbance of PCV is found to be reduced in the presence of surfactant.

PYROCATECHOL VIOLET :

Structure of Pyrocatechol Violet is as follow :

3,3'-4'- trihydroxy fuchstone 2" sulphonic acid.



Dissociation constant (pK values) of PCV :

PCV has 4 replaceable protons in its molecule. One of these corresponds to -SO₃H group, and other three corresponds to -OH groups while the fourth corresponds to -OH group. Thus, the following equilibrium can be written for the stepwise dissociation of PCV which represents existence of its four pK values :



Table - 2

pK values of PCV in absence & in presence of CTAB

	PCV	PCV + CTAB
pK ₁	1.90	1.42
pK ₂	5.10	4.20
pK ₃	7.65	7.20
pK ₄	11.40	11.10

The lowering of pK values in presence of CTAB indicates its action on PCV.

Composition of PCV - CTAB complex :

For determination of dye - surfactant composition, the absorption of dye was studied at pH5.0 by keeping the dye concentration constant and varying the surfactant concentration. The concentration of PCV taken was A) 8.0 x 10⁻⁵M; B) 6.0 x 10⁻⁵M & C) 4.0 x 10⁻⁵M.

The composition of dye - surfactant complex was established at a value where further addition of CTAB did not alter the absorbance of the dye. The absorbance decreases till the ratio of dye-detergent is reached to 1:1 which on further addition of CTAB remains constant. This shows a definite ratio of 1:1 of PCV:CTAB complex formed. The modified species called as dye-detergent complex & can be represented as [PCV/ (CTAB)].

Absorption spectra of the complexes :-

Absorption spectra of PCV, PCV- metal ion PCV - CTAB and PCV-metal ion-CTAB were recorded at the pH of study. The nature of complexes found between PCV and Cu(II), and Ni (II) has been studied in detail. A representative absorption spectrum is shown in the fig. 1 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 PCV 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.

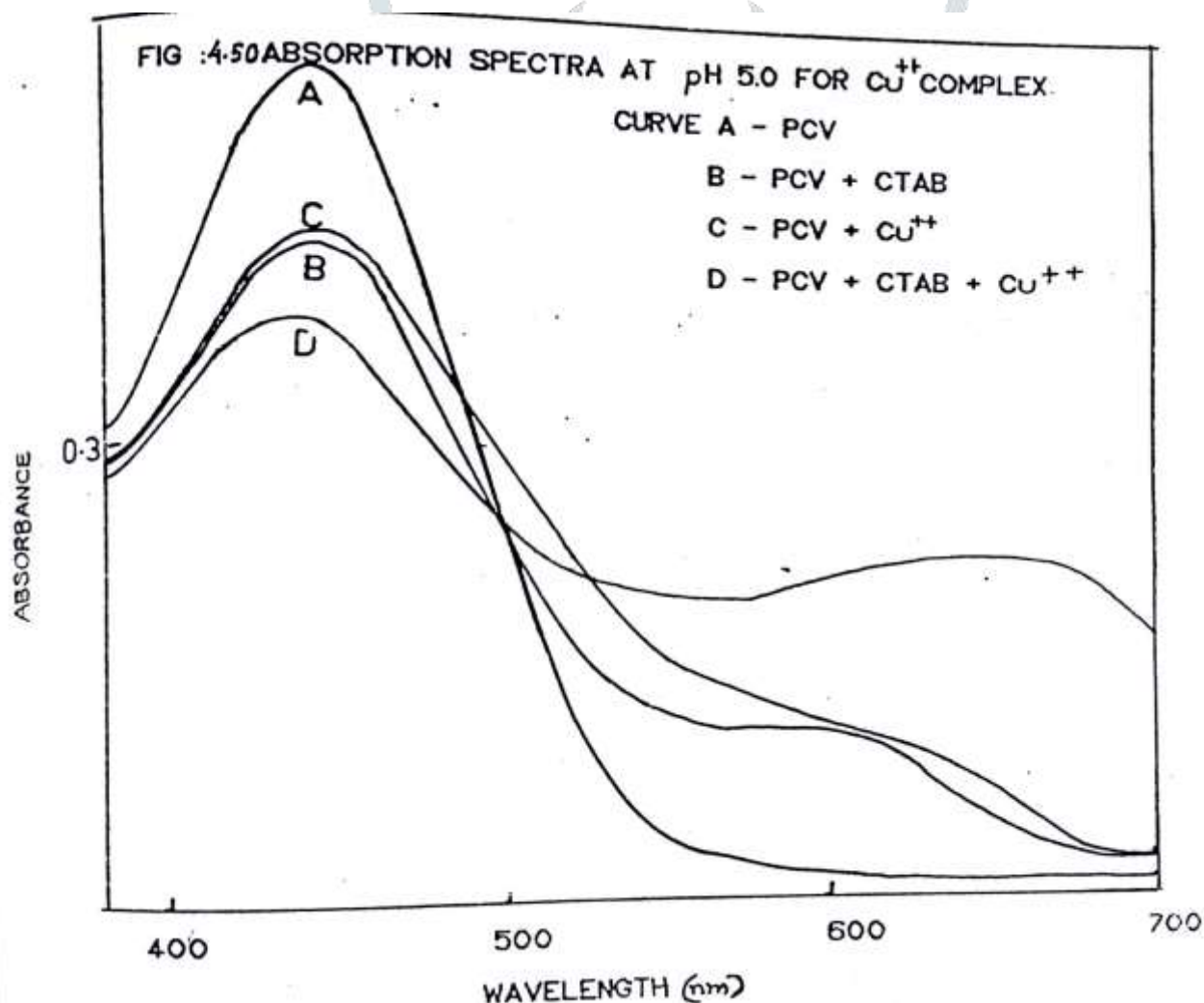


Fig.The absorption spectra of Cu (II) complex of PCV.

Table 3

**λ_{\max} of PCV AND ITS CHELATES WITH AND WITHOUT CTAB
AT pH 5.0 M : L as 1:1**

System	λ_{\max} (nm)
PCV	430
PCV + CTAB	420
PCV + Cu (II)	540
PCV+CTAB + Cu (II)	625
PCV + Ni (II)	540
PCV+ CTAB + Ni (II)	615

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 PCV 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 PCV forms complexes M:L ratios either at 1:1 with metal ions Cu(II) & Ni (II) in presence as well as in absence of CTAB.

Similarly spectral characteristics shows that PCV forms only one complex with Cu(II), in the presence 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 3

**Table 3.
Composition And Stability Constant Values**

Chelates	λ_{\max} (nm)	Composition M: CAS:CTAB	LogK value By Job's method
Cu(II) -PCV	540	1:1	5.7
Cu(II)- PCV-CTAB	625	1:1:1	6.5
Ni (II) - PCV	540	1:1	5.2
Ni(II)-PCV-CTAB	615	1:1:1	6.4

The results showed that the values of log K in the presence of CTAB are greater than that in the absence. This may be because of CTAB reacting with PCV to allow an early dissociation of protons from the phenolic group 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. This is also due to the tendency of decrease in pK values of dye PCV in the presence of surfactants.

Analytical applications :

In all the experiments, CTAB solution was added to PCV 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 color intensity from 25°C to 60°C in absence or presence of surfactants in all the systems reported here. The color was stable up to 3 to 4 hrs after which it 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 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 (11) a plot of log of metal ion concentration Vs. % transmittance.

Table - 4

pH range of stability, Concentration Range for Beer's Law & effective Photometric Range. **pH of study = 5.0**

System	$\lambda_{\max}(\text{nm})$	pH range of stability	Range of Beer's law	Photometric Range.
Cu(II)-PCV	540	4.6-5.6	0.38-0.63	0.27-0.36
Cu(II)-PCV-CTAB	625	4.5-6.4	0.1-0.35	0.14-0.21
Ni (II) - PCV	540	5.0-6.2	0.31-0.49	0.46-0.32
Ni (II)-PCV-CTAB	615	4.5-6.5	0.22-0.57	0.39-0.42

Sandell's Sensitivity and Molar Absorptivity of the System

Sensitivity of colour reaction of metal ion with PCV for $\log I_0/I_t = 0.0001$, as defined by Sandell are listed below

TABLE 5.0

Systems	wavelength of study (nm)	pH of study	Sandell Sensitivity SX10-2	Molar absorptivity EmX10-3
Cu(II)-PCV	540	5.0	1.13	10.70
Cu(II)-PCV-CTAB	625	5.0	0.74	14.94
Ni(II)-PCV	540	5.0	2.78	9.20
Ni(II)-PCV-CTAB	615	5.0	1.74	16.46

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

pH of the PCV solution is adjusted containing that concentration of metal ion as mentioned under the effective photometric determination in Table 4 is also adjusted to pH 5.0 and added to the PCV solution or modified PCV solution (the modified Dyes is prepared by adding five fold excess of CTAB solution to PCV 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.

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 colored 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 color formation, specificity of color reactions and the sensitivity of color reaction. The use of TPM dyes especially, Pyrocatechol Violet, has its origin only because of these desired properties. The use of micelle forming surfactants in increasing the sensitivity of the color 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 Cu(II) and Ni(II) using triphenylmethane dye, Pyrocatechol Violet as reagent. These metal ions when present in water at ppm level as a pollutant thus may be detected by using this method.

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