

Studies On Interaction Of Dye- Surfactant Binary Complex Of Pyrocatechol Violet and Cetyl Trimethyl Ammonium Bromide

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Abstract: Surfactants enhances complexation of triphenylmethane dyes by formation of a new dye : surfactant complex which is as an intermediate stable complex. Addition of quaternary salts of surfactants to the deeply colored solution of dyes causes a marked change in its λ_{max} . The absorption spectra of Pyrocatechol Violet, PCV; a triphenylmethane dye, has been studied in the presence as well as in the absence of cationic surfactant, Cetyl Trimethyl Ammonium Bromide, CTAB. At different pH values ranging from pH 1.00 to 12.00, the spectra is studied. Hypsochromic shift is observed in the absorption spectra in the presence of surfactant. Dissociation constant has been evaluated both in the presence and absence of surfactant. Decrease in the values of dissociation constant, pK values in the presence of surfactant is observed which indicated formation of water soluble, stable, dye-surfactant complex. Composition of stable dye-surfactant complex is determined and effect of foreign ions such as Chlorides i.e NaCl, KCl, NH_4Cl ; the nitrates i.e KNO_3 , $NaNO_3$, NH_4NO_3 ; and sulphates i.e K_2SO_4 , Na_2SO_4 and $(NH_4)_2SO_4$ has been studied in detail. It is found out that the Binary submicellar aggregates can be proposed as the active species in ternary complex formation with metal ions and hence can be termed as modified reagents, as PCV-CTAB.

KeyWords: Triphenylmethane Dye, Surfactant, Modified reagent, Hypsochromic Shift

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I. Introduction

Some reactions were reported by Ramanuskas et al(1) which showed decrease in the color intensity of organic dyes on the addition of surfactants. These newly formed dye-surfactant species are termed as modified reagents which are suitable for the sensitization of the color reactions even with metal ions. The addition of quaternary salts to the deeply colored solution of dyes, causes a marked color change with the change in 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 addition of surfactants to the dyes is thus to decolorize them. It is followed by Sign Rule (2,) which is an empirical statement. The interesting property of the aggregates formed is their ability to form colored complexes with various cations. Another advantage is that the determination of microamounts of metal ions can be done with much higher sensitivity in the presence of these long chain quaternary salts. Composition of dye-surfactant complex is determined by adding varying concentration of surfactants to the dye solutions. Higher concentration of mineral salts (3) prevents the micelle formation due to occurrence of inorganic anions which displace dye as counter ions. Hence effect of mineral salts has been studied.

This unusual property has applied for microdetermination of Transition metal ions and even rare earths in several studies. With this aim present studies has been undertaken and involves a detail study of the interaction of surfactant, CTAB with a Triphenylmethane Dye, Pyrocatechol Violet.

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), 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.

Procedure: Preparation of mixtures, measurements of absorbance, adjustment of pH etc. were carried out at room temperature. In all the experiments, TX solution was added to the reagent solutions which was for at

least 20min for maximum decolorizing effect. The absorbance readings were recorded only after 30 minutes of the addition of the reactants, a time necessary for equilibration.

II. Results And Discussion

Absorption Spectra

Absorption spectra of PCV solution was recorded from pH1.0 to 12.0. The spectral studies in the presence of ten times excess of CTAB were also recorded from pH1.0 to 12.0. The λ_{max} values in the absence as well as in the presence of CTAB are summarized below.

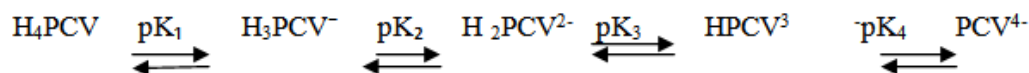
TABLE-1
 λ_{max} OF PCV AT DIFFERENT pH VALUES

pH	λ_{max} nm in absence of CTAB	λ_{max} nm in presence of CTAB
1.0 – 2.0	440	440
3.0	440	440
4.0	440	440
5.0	440	410
6.0 -9.0	440	425
10.0- 11.0	470	490
12.0	500	No Sharp Peak obtained

Hypsochromic shift is observed at pH 5.0. Hence pH of study for using PCV and CTAB is 5.0.

Dissociation Constant (pK values) of PCV

The PCV contains four replaceable protons in its molecule. The following equilibrium reaction which occurs in the stepwise dissociation of PCV can be written as follows.



The above equilibrium reaction shows three pK values of PCV. Experiments were carried out for the determination of pK values of PCV in the presence and absence of surfactant CTAB. 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 pK values were determined both in absence as well as in the presence of CTAB using equation given below. The color changes corresponding to a shift of pH values towards acidic and alkaline ranges was studied. This has been related to an early dissociation of protons of triphenylmethane dyes in the presence of surfactants showing a decrease in the value of their constants. The lowering of pK values in presence of CTAB indicates their action on PCV. The pK values were determined on the basis of eq. I or eqn. II. If the absorbance of the ionized species is greater than the absorbance of the molecular species, equation II is used.

$$pK = pH + \log [(A_I - A)] / [(A - A_M)] \dots \dots \text{equation(I)}$$

$$pK = pH + \log [(A - A_I)] / [(A_M - A)] \dots \dots \text{equation (II)}$$

The terms in equations are

A_M = Absorbance of molecular species,

A_I = Absorbance of ionic species, and

A = Half point absorbance

TABLE - 2
Dissociation Constants of PCV

pK values	In absence of surfactant	In presence of CTAB
pK ₁	5.40	2.70
pK ₂	6.30	5.04
pK ₃	8.32	8.15
pK ₄	11.02	10.81

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

Composition Of PCV-CTAB Complex :

The effect of varying concentration of CTAB on PCV absorbance was also studied at pH 5.0 and at 410nm. The absorbance of PCV decreases linearly upto a definite ratio of PCV:CTAB, as 1:2, is reached. After this point the addition of surfactant , even in excess amount did not alter the absorbance of PCV to any significant extent. Thus the complex formed can be represented as $[PCV(CTAB)_2]$. It is represented in fig.

The concentration of the solution of PCV for studies is taken as follows :

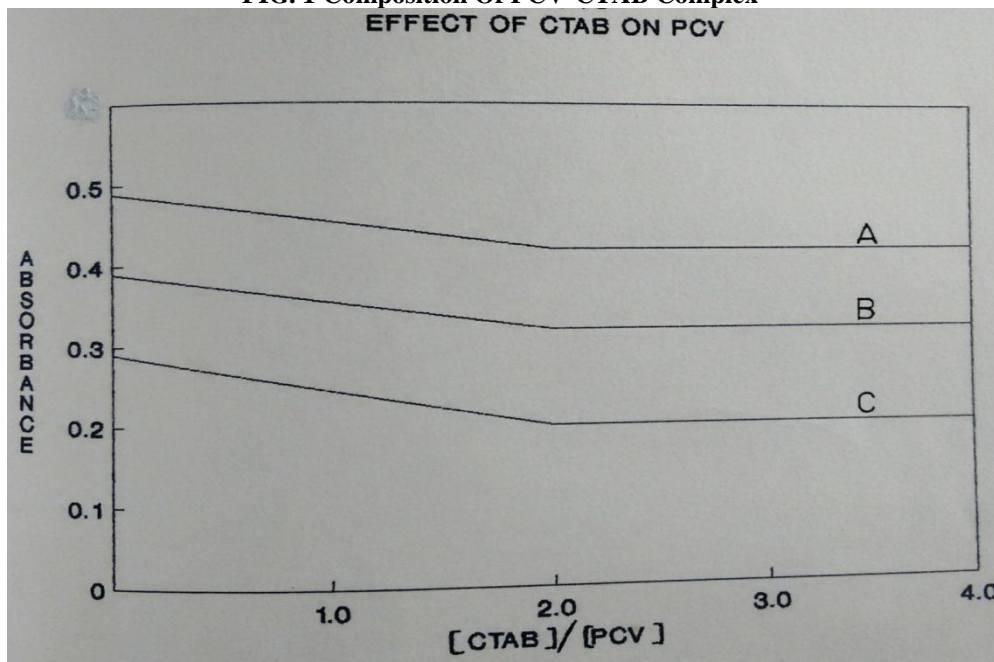
CURVE A : $3.2 \times 10^{-5} M$

CURVE B : $2.40 \times 10^{-5} M$

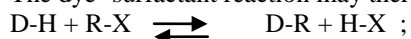
CURVE C : $1.60 \times 10^{-5} M$

The descending section of the curve represents the successive effect of CTAB on Pyro Catechol Violet upto the point at which the additional increase of CTAB, concentration does not further diminish the absorbance of Pyrocatechol Violet. Thus, it may be concluded from the curves that this point and hence the maximum decolorizing effect is reached at the minimal ratio of PCV to CTAB as 1:2. After this point the further addition of increased concentration of CTAB to PCV, does not alter the absorbance of PCV. Thus, at this point it was concluded that, the modified reagent species of PCV complex can be represented as $[PCV(CTAB)_2]$.

FIG. 1 Composition Of PCV-CTAB Complex



The dye- surfactant reaction may therefore be written as follows:

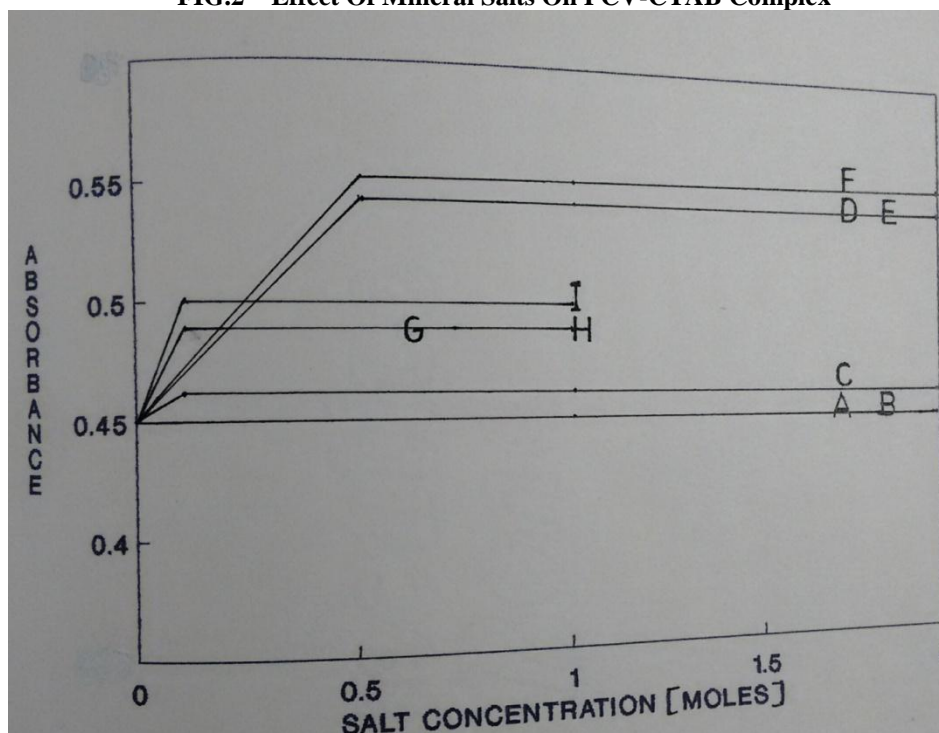


where Dye is represented as D-H , while R-X as surfactant

Effect Of Mineral Salts :

Caiwen and Quingyue(4) 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 color complex formation between TPM dyes and surfactants.

FIG.2 Effect Of Mineral Salts On PCV-CTAB Complex



The effect of mineral salts on the absorption spectrum of PCV in the presence of CTAB. The cations K^+ , Na^+ , NH_4^+ did not show any effect on the absorbance of dye-detergent solution. Nitrates has shown some effect at pH 5.0, as the absorbance goes on increasing upto 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 sulphates K_2SO_4 , Na_2SO_4 , $(NH_4)_2SO_4$. To study this in detail, different concentration of salt solutions were added to 1.0×10^{-3} M PCV solution containing 1.0×10^{-2} M CTAB into it.

III. Conclusion :

The addition of surfactants changes maximum wavelength of absorption. It has been observed that addition of a cationic surfactant CTAB causes a considerable decrease in the color intensity of organic dye, Pyrocatechol Violet. This color change is caused by the short range electrostatic forces on the surface of the micelle double layer. PCV changes its color after reaction with surfactants is due to the dissociation different chromogenic groups in it. As the dissociation is dependent on the change in hydrogen ion concentration of the solution of the dye, these are bound to show different absorption spectra at different pH values. The effect of surfactants on the dye solution was hence studied at different pH values varying from pH 1.0 to 12.0 by recording the absorption spectra in the entire visible range. Thus, the purpose of addition of surfactants to the deeply colored solutions of organic dyes is to produce some hypsochromic shift. As a consequence of this , the pK values of the dyes showed a decreasing trend in the presence of surfactants. This property arises due to the formation of dye – surfactant complexes. It was observed that maximum color change occurred when the charge on the surfactant micelle is opposite to that of reagent ions. As a consequence this modified reagent (PCV-CTAB) become very much suitable for sensitive microdetermination of different metal ions. It has been also found out that high concentration of some of the mineral salts for instance; nitrates, prevent the formation of dye- surfactant complex because of the inorganic anion displacing the dye as counter ion , and hence is to be avoided for such studies. From the present studies it can be concluded that, the binary complex formed by the interaction of Pyro Catechol Violet and surfactant, CTAB, is a stable, water soluble and effective to be used for further microdetermination with greater sensitivity.

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