RESEARCH ARTICLE

COMPLEXOMETRIC STUDIES ON DYE- SURFACTANT BINARY COMPLEX OF ERIOCHROME AZUROL B AND CETYL TRIMETHYL AMMONIUM BROMIDE

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ARTICLE INFO	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 Eriochrome Azurol B EAB; 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.eNaCl, KCl, NH_4Cl; Nitrates i.e $NaNO_3$,KNO_3, NH_4NO_3; and Sulphatesi.eNa_2SO_4, K_2SO_4, $(NH_4)_2SO_4$ 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 EAB-CTAB.

INTRODUCTION

Some reactions were reported by Ramanuskas *et al.* (1969) 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 (Hartley and Downay, 1984) 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 micro amounts 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 (Svoboda *et al.,* 1965) prevents the micelle formation due to occurrence of inorganic anions which displace dye as counter ions. Hence effect of mineral salts has been studied.

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This unusual property has applied for micro determination 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, Eriochrome Azurol-B.

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.

RESULTS AND DISCUSSION

Absorption Spectra: Absorption spectra of EAB 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 λmax values in the absence as well as in the presence of CTAB are summarized below.

**Table 1. λmax OF EAB at different pH values**

pH	λmax nm in absence of CTAB	λmax nm in presence of CTAB
1.0 – 2.0	470	480
3.0	460	510
4.0	460	450
5.0	450	420
6.0 -9.0	420	425
10.0- 11.0	425	610
12.0	595	610

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

Dissociation Constant (pK values) of EAB

The EAB contains three replaceable protons in its molecule. Two of it correspond to-COOH groups while the third corresponds to-OH group. The equilibrium reaction which occurs in the stepwise dissociation of EAB can be written as follows.

$$H_3EAB \xrightleftharpoons{pK_1} H_2EAB^- \xrightleftharpoons{pK_2} HEAB^{2-} \xrightleftharpoons{pK_3} EAB^{3-}$$
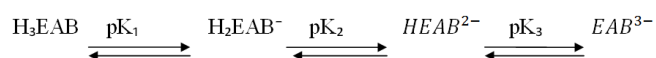
The above equilibrium reaction shows three pK values of EAB. Experiments were carried out for the determination of pK values of EAB in the presence and absence of surfactant CTAB. From the results, pK values obtained are recorded in Table 2. Several sets of solutions of suitable concentrations of dyes 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 maxs 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 EAB. 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.

$$pK = pH + \log [(A_I - A)] / [(A - A_M)] \qquad \text{.............. (1)}$$

$$pK = pH + \log [(A - A_I)] / [(A_M - A)] \qquad \text{.............. (2)}$$

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 EAB

pK values	In absence of surfactant	In presence of CTAB
pK1	3.00	2.70
pK2	5.69	5.04
pK3	11.13	10.84

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

Composition of EAB-CTAB Complex

The effect of varying concentration of CTAB on EAB absorbance was also studied at pH 5.0 and at 420nm. The absorbance of EAB decreases linearly upto a definite ratio of EAB: CTAB, as 1:1, is reached. After this point the addition of surfactant, even in excess amount did not alter the absorbance of EAB to any significant extent. Thus the complex formed can be represented as [EAB(CTAB)]. It is represented in Fig.

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

CURVE A: 8.0 X 10^{-5} M
CURVE B: 6.0 X 10^{-5}M
CURVE C: 4.0 X 10^{-5} M

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

Composition of EAB-CTAB Complex
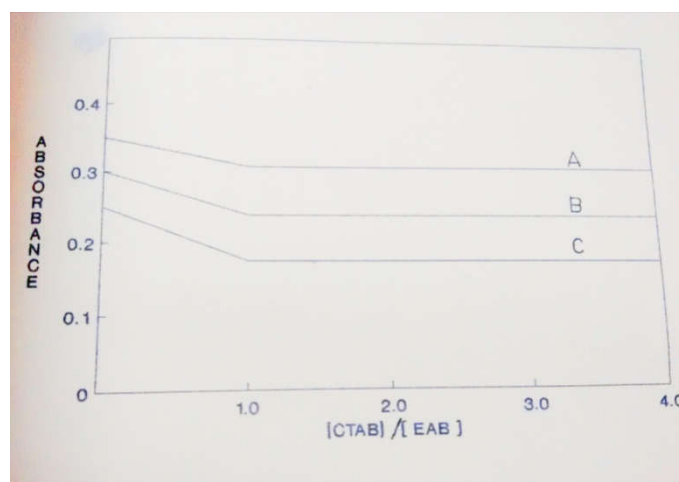
Fig. 1. Composition of EAB: CTAB Complex

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

$$D\text{-}H + R\text{-}X \rightleftharpoons D\text{-}R + H\text{-}X \; ;$$

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**.**

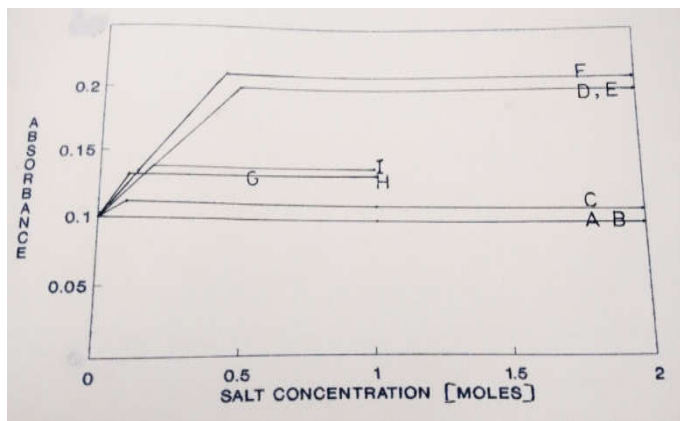## Effect of Mineral Salts on EAB-CTAB Complex

Fig. 2. Effect of Mineral Salts on EAB-CTAB Complex

The effect of mineral salts on the absorption spectrum of EAB 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 EAB solution containing 1.0×10^{-2} M CTAB into it.

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, Eriochrome Azurol B. This color change is caused by the short range electrostatic forces on the surface of the micelle double layer. EAB 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 occured when the charge on the surfactant micelle is opposite to that of reagent ions. As a consequence this modified reagent (EAB-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 Eriochrome Azurol B and surfactant, CTAB, is a stable, water soluble and effective to be used for further micro determination with greater sensitivity.

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