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Complexation and Coordination Studies of Micelle Forming Surfactant Sodium Lauryl Sulphate with Eriochrome Azurol B.

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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 λmax. The absorption spectra of Eriochrome AzurolB ,EAB; a triphenylmethane dye , has been studied in the presence as well as in the absence of sodium lauryl sulphate, SLS . 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; the nitrates i.e KNO_3, $NaNO_3$, NH_4NO_3;andsulphatesi.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 EAB-SLS.
Keywords : Triphenylmethane Dye EAB, Surfactant SLS, Modified reagent, Hypsochromic Shift.

Introduction

The colour intensity of the triphenylmethane dyes decreases on addition of surfactants. The newly formed dye-surfactant reagent termed as modified reagent found to be suitable for the sensitization of the colour reactions of many chelates.The addition of metal ions to these modified reagent give rise to a deeply colored complex,which has much greater molar absorptivity & stability in comparison to the complex formed in the absence of surfactants.This indicates that probably it is the micelle formation which decreases the absorbance of the dye alone & increases the sensitivity of the color reaction. The stability & sensitivity are found to be greater when greater is the colour change. Some reactions were reported by Ramanuskasetal**(1)** which showed decrease in the color intensity of organic dyes on the addition of surfactants. The addition of quaternary salts to the

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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 formed at Critical Micelle Concenteration. Studies on CMC of surfactants is studied by interacting azo dyes and surfactants by Khamaisetal(2) .The purpose of addition of surfactants to the dyes is thus to decolorize them. It is followed by Sign Rule (**3,**) which is an empirical statement. The interesting property of the aggregates formed is their ability to form colored complexes with various cations.When the charge on the surfactant micelle is opposite to that of the indicator ions, the greatest is the color change observed. Reactions of triphenylmethane dyes with some heavy metal ions have been a subject matter of study by several workers (**4-8**).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 (**9**) prevents the micelle formation due to occurrence of inorganic anions which displace dye as counter ions.Hence effect of mineral salts has also been studied by addition of chlorides, nitrates and sulphates of sodium, potassium and ammonium. This unusual property has applied for microdetermination of Transition metal ions, Heavy metal ionsand even Rare Earths in several studies.With this aim present studies has been undertaken and involves a detail study of the interaction of surfactant, SLS with a Triphenylmethane Dye, EriochromeAzurol-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, Sodium Lauryl Sulphate (SLS), 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, SLS solution was added to the reagent solution which was for atleast 20min for maximum decolorizing effect and equilibration of color. 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 SLS were also recorded from pH1.0 to 12.0. The λmax values in the absence as well as in the presence of SLSare summarized below.

Table-1 λmax of Eab at Different pH Values

pH	λmax nm in absence of SLS	λmax nm in presence of SLS
1.0 – 2.0	470	460
3.0	460	495
4.0	460	495
5.0	450	420
6.0 -9.0	420	425
10.0- 11.0	425	595
12.0	595	595

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

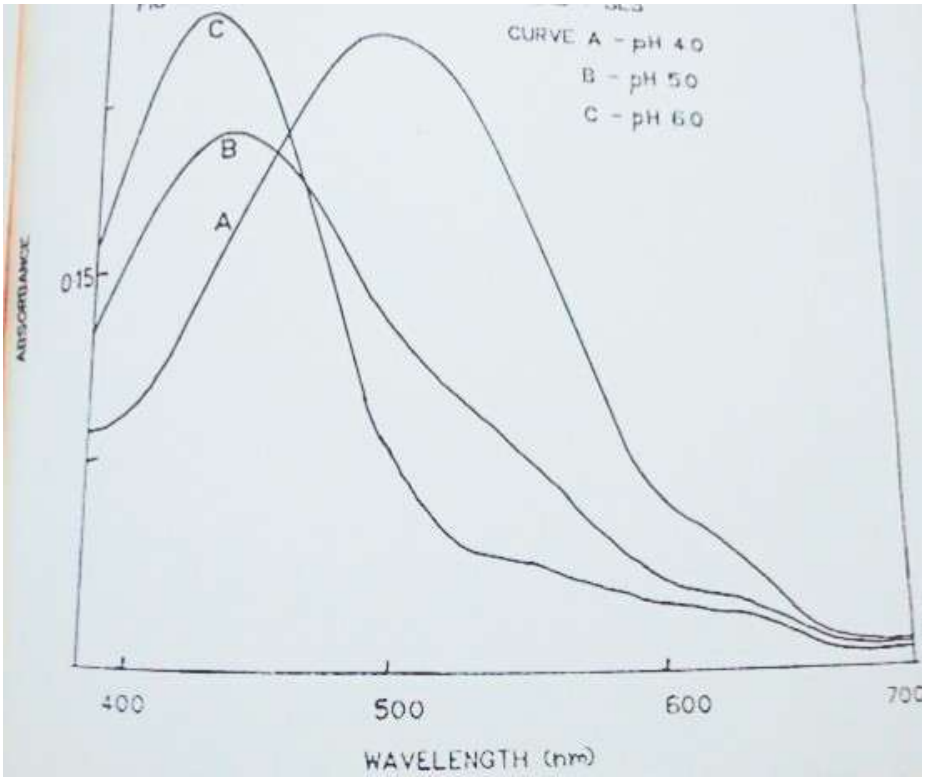

Fig.1 Absorption Spectra Of EAB in The Presence Of SLS

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 SLS. 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 SLS 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 SLS 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.

$pK = pH + \log [(A_I - A)] / [(A - A_M)]$….. equation(1)
$pK = pH + \log [(A - A_I)] / [(A_M - A)]$……..equation (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 EABIn Presence and Absence Of SLS

pK values	In absence of surfactant	In presence of SLS
pK1	3.00	2.80
pK2	5.69	5.00
pK3	11.13	10.50

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

Composition Of EAB-SLS Complex :

The effect of varying concentration of SLS on EAB absorbance was also studied at pH 5.0 and at 420nm. The absorbance of EAB decreases linearlyupto a definite ratio of EAB:SLS, 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(SLS)].It is represented in fig.

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

CURVE A : 6.0 X 10^{-5} M
CURVE B : 4.0 X 10^{-5}M
CURVE C : 2.0 X 10^{-5} M

The descending section of the curve represents the successive effect of SLS on EriochromeAzurol B upto the point at which the additional increase of SLS, 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 SLS as 1:1. After this point the further addition of increased concentration of SLS 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 (SLS)] .

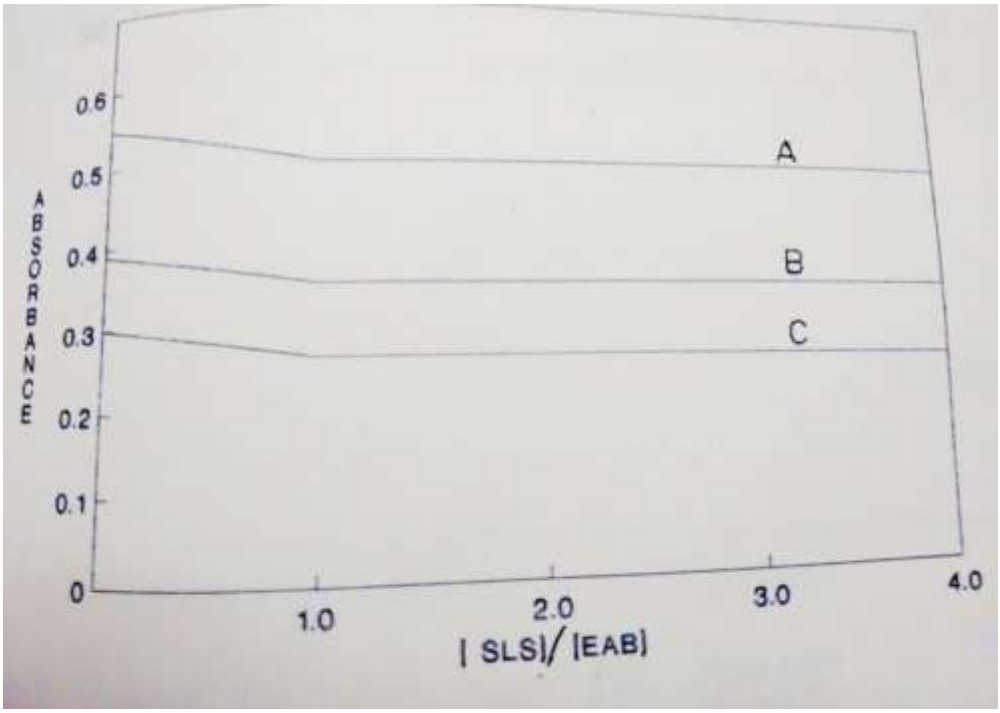

Fig. 2 Composition Of EAB-SLS Complex

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

D-H + R-X $\rightleftharpoons$ D-R + H-X ; where Dye is represented as D-H , while R-X as surfactant

Effect of Mineral Salts :

The effect of mineral salts was studied by adding different concentration of salts in the $1.0x10^{-3}$ M EAB solution containing $1.0x10^{-2}$ SLS. The results are plotted at pH5.0 and at λ_{max}425nm in the presence of SLS. The curves A, B, C represents the effects due to KCl, NaCl, and NH_4Cl respectively. Curves D, E and F represents the effect on the absorbance of EAB due to addition of KNO_3, $NaNO_3$ and NH_4NO_3 respectively while curves G, H,and I represent the effect of addition of K_2 SO_4, Na_2SO_4, and $(NH)_2SO_4$ respectively. Chlorides and sulphates has shown no significant change in the absorbance of EAB in the presence of SLS, while nitrates has shown some effect as after addition of nitrates at pH 5.0, the absorbance goes on increasing upto a certain extent after which it remains unaltered.Caiwen and Quingyue**(10)** 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**.**

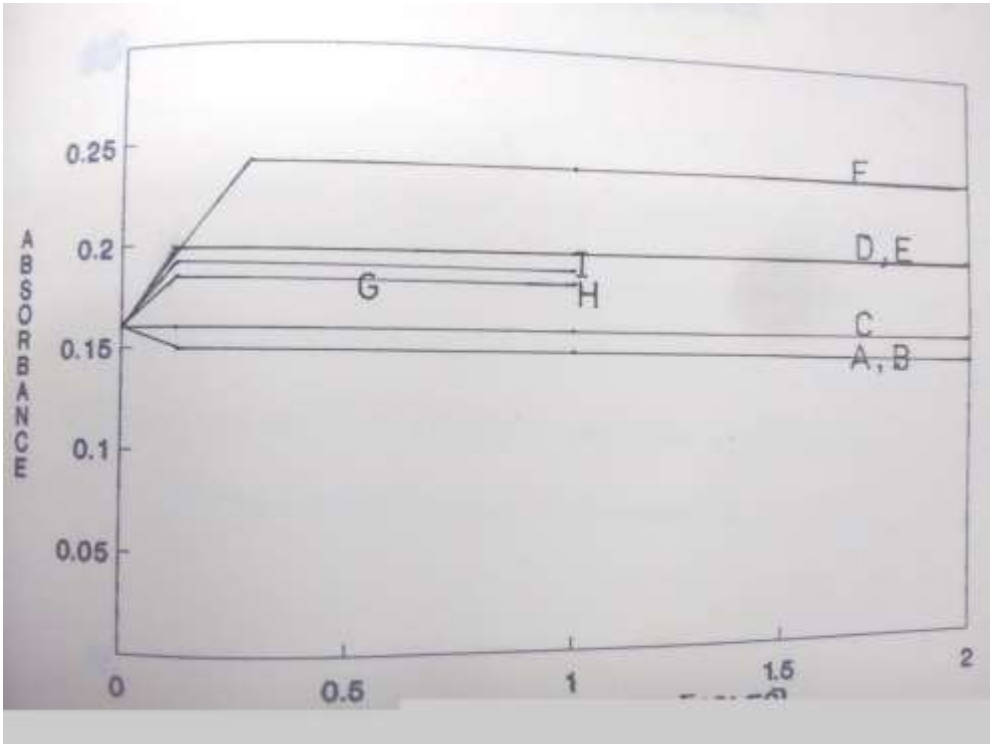

Fig. 3 Effect Of Mineral Salts On EAB-SLS Complex

The effect of mineral salts on the absorption spectrum of EAB in the presence of SLS has been studied at pH 5.0. To study this in detail, different concentration of salt solutions were added to $1.0x10^{-3}$ M EAB solution containing $1.0x10^{-2}$ M SLS into it.

Conclusion :

The addition of surfactants changes maximum wavelength of absorption. It has been observed that addition of a cationic surfactant Sodium Lauryl Sulphate 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 at Critical Micelle Concenteration. 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 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-SLS) 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, SLS, is a stable, water soluble and effective to be used for further microdetermination of metals present at microamounts with greater sensitivity.

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