



COMPLEXOMETRIC STUDIES ON BINARY SYSTEMS OF TPM DYE AND SURFACTANTS

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ABSTRACT

The absorption spectra of Chrome Azurol S, triphenylmethane dye, are studied in the presence as well as in the absence of cationic surfactants; cetyl trimethyl ammonium bromide and sodium lauryl sulphate. Dissociation constant has been evaluated both in the presence and absence of surfactants. Decrease in the values of dissociation constant, pK values in the presence of surfactants 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, NH₄Cl; the nitrates i.e KNO₃, NaNO₃, NH₄NO₃; and sulphates i.e K₂SO₄, Na₂SO₄ and (NH₄)₂SO₄ 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.

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INTRODUCTION

Interactions between various surface active agents and many substances including dyes have been studied for contribution to the elucidation of fundamental properties of surface active agents to extend their applications. Subsequent developments showed that the addition of detergent solution to a triphenylmethane organic dye solution forms a new modified reagent species as dye: surfactant complex. These modified species are used for determination metals in solution as they can form complexes. It is found out that when metal ion solution is added to these modified species it resulted in soluble, highly colored complexes with much greater molar absorptivities and sensitivity too. This increased sensitization of color reactions of metal ions with these dye-surfactant modified species is most advantageous for analysis.

The basic principle involved in surfactant behavior is the clustering of monomeric units to form colloidal aggregates also called as micelles. Micelles are formed in surfactant solutions at or above or within narrow range of concentrations called as critical micelle concentration. The CMC is inversely proportional to the surface activity(1) The selection of appropriate surfactant is done on the basis of Sign Rule proposed by Hartley(2). In accordance with the Sign rule, the effect has been observed for the interaction between an indicator with several charged points and oppositely charged micelles.(3). CAS is anionic dye while CTAB is a cationic surfactant. Corrin and Harkins (4) developed a method for the determination of CMC on the postulate that the surfactants

and dye interact to form a complex which is adsorbed or absorbed by the micelles as it is formed upon the addition of more surfactant. This leads to the spectral shift of dye solution. Surfactants used were found to increase the color contrast intensity, selectivity, and sensitivity of the spectrophotometric determinations. With this aim, present studies have been carried out for studying complexation of Chrome Azurol-S with cationic, namely, Cetyl trimethyl ammonium bromide. Formation of modified species at different pH ranging from pH1.0 to pH12, their dissociation constants, stability, and interference of various ions are studied in detail. There is a considerable amount of data available as studied by Berzin T, *et al*; Mukerjee P, *et al*; and Underwood A.L., *et al*; for micellar systems which indicates that micellar system do indeed shift pK values. Zade, A.B., and Munshi. K.N, (5) has found out that the solubilisation in cationic micelles causes the pK value of organic dyes to shift in opposite direction from solubilisation in anionic micelles. The ionic, submicellar, and micellar phenomenon of substituted triphenylmethane dyes mainly Chrome azurolS, Eriochrome azurol B, Eriochrome Cyanine R, and Pyrocatechol Violet with cationic surfactants has been examined by Jarosz (6). The effect of TPM dyes on the hydrophobic properties of cationic surfactants on the absorption spectra and the dissociation constants of dyes, and CMC was studied. Binary submicellar aggregate is proposed as the active species in ternary complex formation with metal ions. Surfactants used in the present studies were found to decrease dissociation constants of the dye, increase the color contrast intensity, selectivity, and sensitivity of the spectrophotometric determinations. With this aim, present studies have been carried out for studying complexation of

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Chrome Azurole- S with cationic, namely, Cetyl trimethyl ammonium bromide and Sodium Lauryl sulphate. Formation of modified species at different pH ranging from pH1.0 to pH12, their dissociation constants, stability, and interference of various ions are studied in detail.

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 Cetyl trimethyl ammonium bromide (CTAB) was prepared in 20% aqueous methanol in double distilled water and were standardized by usual procedures. The dye solution was also prepared in double distilled water by dissolving its purified samples.

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 reagent solutions which was kept for at least 20 minutes for maximum decolorizing effect. 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 CAS solution was recorded from pH 1.0 to 12.0. The spectral studies are carried out in the presence of ten times concentration of Cetyl Trimethyl Ammonium Bromide as well as Sodium Lauryl Sulphate for pH range from pH 1.0 to pH12. For adjustment of pH, 0.1M NaOH, and 0.1M HCl was used. The λmax values in the absence of, as well as in the presence of CTAB and SLS was found to be as given below in Table - 1. For studying the absorption spectra of CAS, 1.0 ml of 1.0 x 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. Spectral studies then also carried out in the presence of surfactants by adding 1.0x10⁻² ml of surfactant solutions to it in the entire visible range that is from 380nm to 700nm. The hypsochromic shift in the presence of CTAB was observed in almost all pH values. This was attributed due to formation of dye / surfactant complex.

Table 1 λmax of CAS at different pH values in presence and absence of surfactant

pH	In absence of CTAB (nm)	In presence of SLS (nm)	In presence of CTAB (nm)
1.0	470 nm	460	490
2.0	470	470	500
3.0	490	490	500
4.0	490	490	470
5.0	435	430	420
6.0	430	425	415
7.0	420	425	415
8.0	420	425	415
9.0	420	425	415
10.0	420	425	415
11.0	420	425	415
12.0	600	600	610

The addition of ten fold excess of surfactants alters λmax of CAS at almost all pH values. The absorbance values of CAS also were found to be changed in the presence of surfactants. The values of absorbances decreases in the presence of surfactants.

The wavelength chosen for further studies is an analytical wavelength at which the greatest difference between the absorbance of the two species is observed. Accordingly, pH5.0 has been selected for further studies for both binary systems.

Dissociation constant (pK values) of CAS

The complex is formed in a stepwise manner through a series of equilibria. These stepwise equilibria were first shown by Bjerrum and Leden working independently. CAS has 4 replaceable protons in its molecule. One of these corresponds to - SO₃H group, two corresponds to - COOH groups while the fourth corresponds to -OH group. Thus, the following equilibrium can be written for the stepwise dissociation of CAS which represents existence of its four pk values:



Table 2 pK values of CAS in absence & in presence of CTAB

	CAS	CAS + CTAB	CAS+SLS
pK ₁	1.80	1.57	1.70
pK ₂	4.70	4.00	4.45
pK ₃	7.50	7.20	6.82
pK ₄	11.50	11.20	11.0

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 λmaxs 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 CAS & due to hypsochromic effect of CTAB on CAS. 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

Composition of CAS-CTAB and CAS-SLS complex

A convenient method for determination of composition of solutions were studied by Dey and coworkers and they were able to develop the method for colored reactants and colored complexes formed. According to their studies mixtures were prepared according to the method of continuous variations

and their absorbances were measured at fixed wavelength. Graph is plotted as Absorbance against $[M]/[M]+[Ke]$. For determination of dye - surfactant composition, the absorption of dye was studied at pH5.0 by keeping the dye concentration same and varying the surfactant concentration. The concentration of CAS selected were for system A : $8.0 \times 10^{-5} M$; system B : $6.0 \times 10^{-5} M$ & system C : $4.0 \times 10^{-5} M$. 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 CAS: CTAB complex formed. The modified species called as dye - detergent complex & may be represented as $[CAS(CTAB)]$.

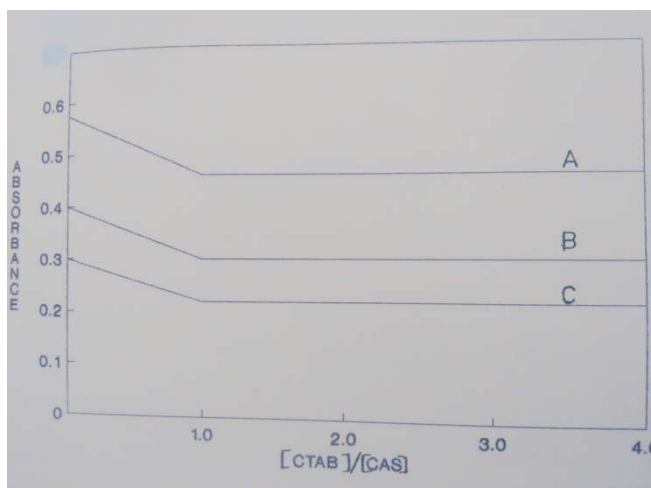


Fig 1 Effect of Ctab on Cas

The effect of varying SLS concentration on CAS is also studied. The final concentrations of CAS solution are; Curve A : $6.0 \times 10^{-5} M$; Curve B : $4.0 \times 10^{-5} M$; and Curve C : $2.0 \times 10^{-5} M$. At first the absorbance decreases upto the point where the ratio of CAS: SLS as 1:1 is achieved. After this point, the absorbance of dye remains unaltered after further addition of SLS. Thus this modified reagent formed at this point can be represented as $[CAS(SLS)]$.

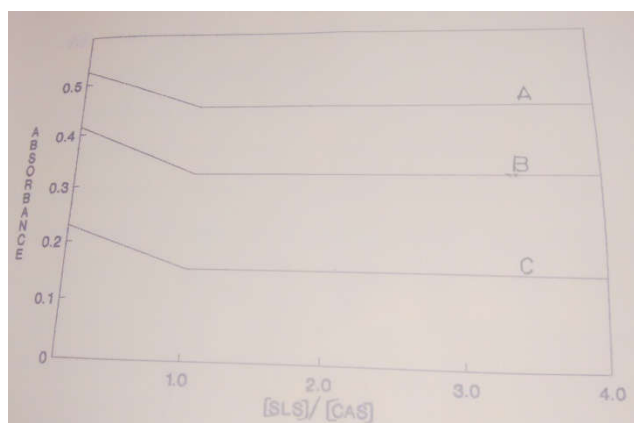
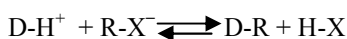


Fig 2 Effect of Sls on Cas

The dye-surfactant interaction may therefore be written as;



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

Effect of Mineral Salts

The effect of mineral salts on the absorption spectra of reagents in the presence of CTAB and SLS was studied in acidic and alkaline ranges. 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 $4.0 \times 10^{-5} M$ CAS solution containing $4.0 \times 10^{-4} M$ CTAB and SLS into it.

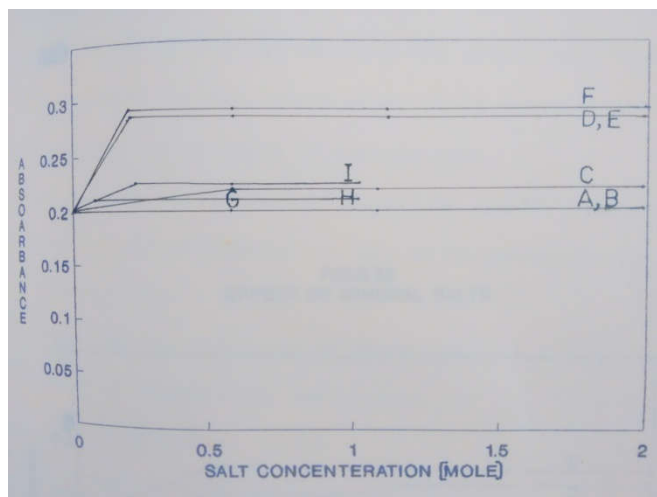


Fig.3 Effect of Mineral Salts on Cas-Ctab Complex

The results are plotted for salt concentration vs. absorbance. The curves A, B, C represent the effects due to KCl, NaCl, and NH_4Cl , curves D, E and F represent effect due to addition of nitrates KNO_3 , $NaNO_3$, $(NH_4)NO_3$, while G, H and I reflects the effect of addition of sulfates K_2SO_4 , Na_2SO_4 , $(NH_4)_2SO_4$. When the electrolytic solution of chlorides were added to dye-detergent solution, at pH5.0, no significant change in the absorbance is observed. Similarly, the sulfates of K^+ , Na^+ and NH_4^+ does not show significant change in the presence of CTAB and SLS both. However, by the addition of nitrate ions at pH5.0, absorbance goes on increasing upto certain extent after which further addition does not show any interference of nitrate ions. In all cases, the cations K^+ , Na^+ and NH_4^+ appear to have no effect on the absorbance CAS in the presence of CTAB and SLS.

CONCLUSION

The addition of surfactants has been observed to cause a considerable decrease in the colour intensity of organic dye, Chrome azurol-S. This color change is caused by the short range electrostatic forces on the surface of the micelle double layer. CAS 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 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 (CAS-CTAB and CAS-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. On the basis of the results discussed it may be concluded that Chrome Azurol S shows substantial effects on addition of cationic surfactants and hence can be effectively used as a sensitive spectrophotometric reagent for microdetermination of metal ions.

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