

CHAPTER – IV

STUDIES ON THE INTERACTION OF OXAZINE DYES WITH ANIONIC AND NON-IONIC SURFACTANTS

4.1 : Introduction and review of the previous work

In aqueous solution, micelle formation is usually detected by some change in the physical properties of the solution, such as surface tension, conductivity, viscosity and e.m.f.¹⁻³ or some optical or spectroscopic property of the solution.⁴⁻⁷ Hartley first noticed that the colour of sulphonaphthalein indicators changed on the addition of detergents, and this effect occurred only when the charge on the detergent aggregate was opposite in sign to that on the dissociated indicator molecule. This behaviour proved to be quite general, as azo⁸, triphenyl methane⁹⁻¹¹ and merocyanine dyes¹² all exhibited the same effect.

At concentrations below the cmc addition of a surfactant to a dye solution may bring about the formation of colloidal dye surfactant submicellar aggregates (mixed micelles) or insoluble dye surfactant salts. The actual species formed depends mainly on the nature of the dye. Bromophenol Blue and Bromocresol green solutions at low concentrations of 1-carbethoxypentadecyltrimethylammonium bromide, in acid and alkaline solution show turbidity.¹¹ Bromopyrogallol Red in solution of cetylpyridinium bromide concentration below the cmc. at pH 2-3 precipitates as a dye-surfactant salt.¹³

Formation of an insoluble salt between ionic dyes and oppositely charged detergents is most common, but is not a completely general phenomenon. In fact, some dyes, such as phenol Red¹¹ or 8-hydroxy quinoline-5-sulphonic acid produce neither turbidity nor precipitation⁵² along with the spectral change induced by addition of the cationic surfactant.

The nature of the dyes and their own tendency to aggregate¹⁵⁻¹⁷ have to be considered to explain such phenomena. Dyes are also amphiphiles, in the sense that bulky non-ionic moieties are attached to the ionic or analytical groups, but as they lack long-chain alkyl groups they have weak surface activity and do not form micelles in water. Depending on the balance between the hydrophobic and hydrophilic tendencies of any particular dye, increase in dye concentration can lead to stepwise aggregation i.e. the formation of dimers, trimers, polymers and finally colloids.¹⁸

If a surfactant is added to such a dye solution at submicellar concentrations, both the surfactant monomer and the dye aggregates can interact to form a special kind of micelle (mixed micelle)¹⁹ at concentrations far below the normal cmc characteristic of the surfactant. This dye-surfactant interaction accounts for the often observed fact that the so-called "spectral change dye method."⁴ does not provide a true cmc value. In fact in such cases, the change in absorbance or fluorescence intensity of a dye solution in the presence of increasing surfactant concentrations may not reflect the formation of micelles of the surfactant (homomicelles) but that of mixed micelles or dye-surfactant salts. The surfactant cmc values are not only influenced by the nature and concentration of the dye, but also markedly influenced by the reaction medium.

Once the surfactant concentration has reached a value close to or above the cmc neither turbidity nor precipitation is observed. Solubilization of the dye-surfactant "salt like" ion pairs in the micellar phase and or the final incorporation of the dye into the micelles (homomicelles) is taking place.

Many of the features observed in the spectral behaviour of dye-surfactant systems carrying opposite charge can often be extended to general sensitized reactions in micellar media.²⁰⁻²²

Mukherjee and Mysels⁵ using spectrophotometric and electrical conductivity measurements of the pynacyanolsodium dodecyl sulphate system

identified the presence of two types of dye-surfactant aggregates: (i) below the cmc a dye-surfactant salt which formed a coarse (visible suspension) stable slurry in the presence of more than a stoichiometric amount of surfactant and (ii) dye-rich micelles, at below and around the cmc which solubilized the water-insoluble dye-detergent salt. Malik et al²³⁻²⁵ reported that spectral changes for several dyes are due to electrostatic forces involving interactions between the anionic (or cationic) surfactant and the basic (or acidic) dye. They claimed that chemical interaction giving a stoichiometric dye-surfactant complex was very improbable.

Guha et al²⁶ attributed the changes in the absorption spectra and the decrease in fluorescence intensity of Thionine to the formation of a dye-surfactant complex at SDS concentration below the cmc. At concentration above the cmc the appearance of the dye absorption spectrum with a small red shift and increased extinction coefficient, was interpreted as due to the incorporation of the dye into the micelles.

The existence of true ion-association complexes formed at below the cmc between ionic surfactants and dyes with opposite charge is supported by most of the published data.^{11,30-33} These complexes are electrically neutral and often poorly soluble in water but readily extractable by low-polarity solvents. They have stoichiometric surface ratios. At surfactant concentrations at the cmc value and above, the solubilizing effect of the micelles begins to be important and the ion-association complexes are incorporated into the micelles.

Electrostatic interaction of anionic dyes with the surface of cationic surfactant micelles takes place through the negatively charged groups of the dye ($-\text{SO}_3^-$, $-\text{COO}^-$). However, this kind of electrostatic interaction could not explain by itself the spectral changes observed during the interaction. In fact, bulky non-micelle forming species such as diphenylguanidinium or tetra ethyl ammonium ion, have no effect *per se*. Moreover, simple ion-pairing between a

negative group such as $-\text{SO}_3^-$, or $-\text{COO}^-$, of the dye and a quaternary ammonium ion does not perturb the chromophore³¹. In the presence of cationic surfactants, aromatic compounds with sulphonic³² or carboxylic acid groups³³ do not act simply as counterions, but are incorporated into the water-rich Stern layer of the micelle in a Sandwich arrangement. This permits not only the hydration of the hydrophilic $-\text{SO}_3^-$ (or $-\text{COO}^-$) group, but also the solvation of the aromatic ring of the dye by the $-\text{N}^+(\text{CH}_3)_3$ group and the participation of vander Waals' interaction between adjacent surfactant chains and the dye organic moiety (hydrophobic forces). In this situation, the micro-environment of the chromophore has clearly changed, from that existing in the bulk aqueous phase, and this change is the cause of the spectral shifts observed. Since dyes based on aromatic rings are widely used in spectrophotometry and fluorimetry, this picture can be considered general and is probably operative in most analytical dye-surfactant systems at concentration above the cmc.

The proton release occurring during the reaction between an anionic dye and a cationic surfactant produces a change in the spectrum which is similar to that observed on increasing the pH of the dye solution. Such pKa shifts for solubilized indicators have been attributed to the influence of the surface potential of micelles.³⁴⁻³⁶ The pKa changes also appear to be related to the reduction of the difference in free energy between the acidic form of the dye and its anion in the micelle.^{33,37-39} Extensive incorporation of an anionic dye into a cationic micelle implies that the free energy of the anionic form decreases more than that of the un-ionized form, as the anion is more polarizable and firmly attached to the positive end groups of neighbouring surfactant molecules.⁴⁰

There is multiple binding in these associated micellar species; evidence has been produced indicating that hydrophobic interaction, not charge compensation, plays in the main role in binding between dyes and surfactants. The exact nature of this interaction, however, has not yet been satisfactorily

explained. Chiang and Dukton⁴¹ reported that their result on the interaction between 2-p-toluidinylnaphthalene-6-sulphonate and SDS micelles suggest that the binding force is hydrophobic. Analogously, Birdi et al³⁹ claimed that the interaction of SDS micelles with 1-anilinonaphthalene-8-sulphonate is hydrophobic in nature. The interaction between some mono-azo dyes with a series of non ionic surfactants has been shown⁴² to be hydrophobic in nature and occurs between dyes and the ethylene oxide chains of the non-ionic surfactant. Minch¹² showed, from spectral changes of Merocyanine dyes in cationic and anionic micelle, that in all cases the spectra were red-shifted when the dye was incorporated into micelles and that the magnitude of the shift increased with more hydrophobic dyes. Biedermann and Datyner⁴³ also suggested that the interactions of some azo dyestuffs with SDS micelles increased with increasing lipophilicity of the dyes.

According to the current thought⁴⁴ the inclusion of a dye molecule within a micelle is not strictly akin to placing it in a hydrophobic region in the micellar core, but is more like placing it in a hydrophobic environment where it is exposed to water. A consideration of hydrocarbon chains in micelles as disordered structures could explain why the nature of the dye may determine its binding site within the micelle assembly.⁴³ In other instances, the factors responsible for the spectral changes have been ascribed to the deaggregation of the dye molecules by association with micelles⁴⁵ to the joint effect of deaggregation and the change in the molecular environment^{46,47} or to the localization of the chromophore within the hydrophobic micellar interior.⁴⁸ Micelles are sensitive to small changes in the ionic strength of the aqueous solution. The change in the cmc of cetyl pyridinium bromide in aqueous solution with electrolyte concentration⁴⁹ reveals two trends, one occurring at low and the other at high concentrations of the added salt. Addition of salts to ionic micelle solutions reduces the mutual electrostatic repulsions of charged head groups.⁵⁰

Owing to electrostatic repulsion, the interaction between anionic dye ions and the head-groups of anionic surfactants should produce neither new spectral bands nor changes in absorbance or fluorescence intensity. Similar results are also observed in case of interaction between cationic dye ions and head groups of cationic surfactants. However, as mentioned earlier, lipophilicity may often be the driving force for interaction, rather than the electrostatic interaction^{12,39,41,43} and some spectral changes can be explained in this way. A similar explanation can also be given for non-ionic surfactant effects on the spectral behaviour of dyes. Coomassie Brilliant Blue G-250 does not show any spectral shift with anionic detergents such as sodium dodecyl sulphate or sodium deoxycholate, but does with non-ionic surfactants, probably owing to transfer of the dye from a hydrophilic to a hydrophobic micellar environment.⁵¹

If a charge-type effect can combine with the classical hydrophobic interactions then both kinds of interactions, electrostatic and hydrophobic, seem to act concurrently, bringing about the largest spectral changes, as shown for anionic dye-cationic surfactant complexes by Savvin et al³¹ or for metal chelate – cationic surfactant species by Sanz-Medel et al^{14,52}. In any case, it seems clear that the surfactant character has the decisive role in determining the observed spectral changes, since bulky ions, which are non-micelle-forming (e.g., tetra ethyl ammonium) do not give rise to effects similar to those observed in the presence of micelle-forming agents.^{13,31} The implications of a model for the interactions in micelles are significant not only for micelles in water but also for related assemblies, since the principles of organization are thought to be quite general.⁵³

The surfactant interactions in non-aqueous media have been investigated less⁵⁴ than those in aqueous surfactant systems. The surfactant aggregates in organic solvents are described as having a “reverse micellar structure”, in which

the hydrocarbon tails are in contact with the solvent and the polar head groups form the micellar core.

The aggregation number in such reverse micelles is relatively small, e.g. less than 10 for alkyl ammonium carboxylates, compared with upto 100 for aqueous micelles,⁵⁵ but it is supposed that these systems would exhibit an experimentally determinable cmc. Although many of the common methods for cmc determination in aqueous solution are not applicable to reverse micellar systems, because of the low degree of aggregation and because ionic surfactants do not ionize in organic media, the "spectral change method" has been proposed for determination of the cmc of Aerosol-OT (sodium di-(2-ethyl hexyl) sulphosuccinate)⁵⁶ with the dye 7,7,8,8-tetra cyanoquinodimethane. Breaks in the plots of absorbance against surfactant concentration were interpreted as corresponding to the surfactant cmc. However, the concept of cmc as explained for normal micelles is no longer applicable in these systems and is still subject to controversy. Reverse micelles alter the micro-environment of solubilized reactants and thus affect their stereochemistry, dissociation constants, redox potentials and reactivities.⁵⁷

In analytical chemistry scant use has been made of reverse micelles. Many organic reactions have been studied in reverse micelle systems but few studies have been made on inorganic reactions.⁵⁸⁻⁶⁰ In view of this situation, the study of analytical systems in reverse micelles is an unexploited research field.

Dye-surfactant interaction in sub-micellar concentration of surfactant:

There has been an increasing interest in the study of interaction of dyes with surfactants as the knowledge of dye-surfactant interaction is of great value in understanding the chemical equilibrium, mechanism and kinetics of surfactant sensitized colour and fluorescence reactions.⁴⁹ Many researchers had noticed the change in colour of the ionic dyes when they were dissolved in oppositely charged ionic micelles.^{61,5,46,62-69} Most of the previous studies on dye-surfactant

interaction were carried out with the concentration of the surfactants above the cmc and the color changes have been explained on the basis of the interaction between the surfactant micelles and the dyes and the equilibrium between conjugate acid and base forms of the dye. However, there is not much information available regarding the nature and mechanism of the interaction between dyes and surfactants when their concentration of the surfactants are much below the cmc. Dutta and Bhatt⁷⁰ carried out systematic spectroscopic and thermodynamic investigations in order to understand the nature of this interaction between ionic dyes and oppositely charged surfactants of very low concentrations i.e., far below their cmc's. They have investigated interactions of cationic dyes viz. phenosafranine (PSF), Safranin O (SFO) and Safranin T (SFT) with anionic surfactants, viz. Sodium dodecyl sulfate (SDS) and sodium octyl sulphate (SOS) in submicellar concentration ranges. The interaction has been shown to be an induced protonation of the dye in the dye-surfactant ion pair. Even though the opposite charges on the dye and the surfactant are the primary requirements for the ion pair formation, it is the hydrophobicity of the surfactant as well as of the dye, which induces the protonation.

As the concentration of SDS is slowly increased from 1.6×10^{-4} M (the lowest concentration at which there was detectable decrease/increase in absorbance of PSF bands) to 3.0×10^{-3} M, λ_{\max} of PSF band gradually shifted from 520 to 528 nm with a gradual decrease in intensity of the λ_{\max} band, accompanied by an increase in absorbance in the longer wavelength region of ca. 550 to ca. 700 nm. The red shift of the PSF band from 520 to 528 nm was attributed partly to a change in the environment of the chromophore of PSF and partly to the overlapping of the 520 nm band with the new band in the longer wave length region. Increasing the concentration of SDS upto 4.0×10^{-4} M, for a fixed concentration of PSF of 2.13×10^{-5} M gives a series of spectra that pass through a sharp isobestic point at 550 nm.

It was observed that the spectra of PSF in low concentration of SDS were similar to those of PSF in strong acidic media. Gopidas and Kamat⁷¹ had reported that PSF⁺ in HCl (2M) has absorption band at 580 nm which can be attributed to HPSF²⁺. They had noticed that with the increase in concentration of strong acids, e.g., H₂SO₄, HClO₄ etc. PSF gave rise to three bands viz. at 580, 525 and 690 nm. Similarly, with the increase of BF₃ in ether the absorption maxima of PSF were at 578, 622 and 688 nm successively. The appearance of a new band at ca. 582 nm which increases with the increase in concentration of SDS (upto ca. 3.0×10^{-3} M) and decreases with increase in temperature, and the presence of an isobestic point are indicatives of the presence of an equilibrium between the free PSF, SDS and complexed PSF (an interaction product of PSF and submicellar SDS). With the increase in concentration of SDS above cmc was (6.0×10^{-3} M in presence of 2.2×10^{-5} M PSF), the 520 nm band shifts to higher wave length, viz., 531 nm which is attributed to the associations of the dye with the surfactant micelles. There was hardly any change in the position and intensity of this band with further addition of SDS.

The colour change observed in many dyes on the addition of very small amount of oppositely charged surfactant has been attributed to ion pair formation⁶³, dye-surfactant salt formation⁵, the formation of dye dimer or higher aggregates⁷², micelle and mixed micelle formation,^{46,65} etc. However, Lewis⁷³ had pointed out that the ion pair formation, a phenomenon in itself (like PSF⁺SDS⁻), does not alter the spectral absorption of the associated ions. Moreover, in the case of cationic dyes, like Phenazinium and Thiazinium dyes, the dimerizations are known to cause hypochromic shifts in the spectra.^{74,75}

No interaction of the phenazinium dyes with N-hexadecyl pyridinium chloride (a cationic surfactant) and Triton X-100, $(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)_2 - \text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_{10}\text{OH}$ (a non ionic surfactant), in the submicellar concentration range was observed⁷⁰. This indicates that the opposite charge on the dye and the

surfactant is the primary requirement for this interaction. Therefore it can be suggested that as the oppositely charged ions, viz., PSF^+ and SDS^- , come closer to each other due to electrostatic attraction, the hydrophobic nature of the large organic ions and hydrogen-bonded water structure enforce them to form closely associated ion pairs, $\text{PSF}^+ \text{SDS}^-$.^{63,76,77}

It is clear that some more changes, in addition to the ion pair formation, occurs to the chromophore to effect the large shift of the absorption band. Gopidas and Kamat⁷¹ reported that PSF gets protonated and gives a band at 583 nm when it is bound to H^+ -Nafion, a polymer which exhibits a strong acidic environment to the dye in aqueous solution.⁷⁸ It has been shown that the PSF absorption band remains unperturbed even on lowering of the pH the aqueous PSF solution till 1.2. Only below pH of 1.2, the 580 nm band of PSF appears. On the other hand, in the entire experimental submicellar concentration range of SDS, the pH's of the aqueous SDS solutions were 6.5. Therefore, it seems that the 582 nm band of PSF in submicellar SDS may also be due to the protonated PSF, viz., HPSF^{2+} caused by a strong acidic environment exhibited by monomeric SDS^- bound to PSF^+ in the hydrophobic ion pair of $\text{PSF}^+ \text{SDS}^-$.⁷⁰ This protonation has been explained in terms of the Hamaker constant.⁷⁶

The interaction of PSF^+ with SDS^- in aqueous medium has been represented by



$$\text{Such that } K'_c = \frac{[\text{HPSF}^{2+} \text{SDS}^-]}{[\text{PSF}^+][\text{SDS}^-][\text{H}^+]} \quad (29)$$

$$\text{and } K_c = K'_c [\text{H}^+] = \frac{[\text{HPSF}^{2+} \text{SDS}^-]}{[\text{PSF}^+][\text{SDS}^-]} \quad (30)$$

(Assuming $[\text{H}^+]$ to be constant throughout the experiment

Using the Ketelaar's⁹⁰ equation -

$$\frac{[D]_0}{d - d_0} = \frac{1}{\epsilon - \epsilon_0} + \frac{1}{K'_c (\epsilon_c - \epsilon_0) [S]_0} \quad (31)$$

one can obtain the equilibrium constant, K'_c . Here d and d_0 are the observed optical densities of the dye in the presence and in the absence of the surfactant, ϵ_0 and ϵ_c are the molar extinction coefficients of the dye in the free and the associated (viz., $\text{HPSF}^{2+} \text{SDS}^-$) forms, and $[D]_0$ and $[S]_0$ are the initial concentration of the dye and the surfactant, respectively. The plots of $[PSF]_0 / (d - d_0)$ Vs $(1 / [SDS]_0)$ for various temperatures yield straight lines in a wide range of the concentration of SDS. Deviations from the straight lines are normally observed towards higher concentrations of SDS which is due to the disappearance of the protonated ion pairs as a result of solubilization of the dye by mixed micelle formation.⁶⁵

SOS has a shorter hydrocarbon chain than SDS and therefore it is expected to show weaker interactions with cations dyes (due to lesser hydrophobicity)⁷⁹ than that of SDS. From the equilibrium constants and the other thermodynamic parameters it is evident that the interaction of cationic dyes with SOS is much weaker compared to that with SDS. The slightly lower value of ΔS for PSF - SDS may be due to more ordering of the protonated ion pair in water, as SOS is relatively less hydrophobic compared to SDS.

SFO is a 2, 8 - dimethyl derivative of phenosafranine and SFT is a positional isomer of SFO. Both of these dyes have absorption maxima at 520 nm in the visible range. The spectral changes in the aqueous solutions of SFO and SFT on addition of SOS were similar to those of PSF - SDS and PSF - SOS. It seems apparent that hydrophobicity of the surfactant plays an important role in the ion pair formation as well as in induced protonation of the dye in the ion pair.

Dye-Surfactant interaction in Super micellar concentration of surfactant

As has been already discussed that changes in the colour of ionic dyes in the presence of oppositely charged ionic surfactants in aqueous solution have been observed by many workers^{5,37,80-85} and these changes have been explained by proposing dimer and multimer formation of dye molecules in the surfactant micelle. Hayashi⁸⁶ studied the interaction of Congo Red dye with cetyltrimethyl-ammonium bromide (CTAB) and Triton X-100 and interpreted the spectrophotometric data in terms of formation of a 1:2 dye surfactant complex. Matibinkov and coworker⁸⁷ studied the effect of sodium lauryl sulphate (SLS) on Xanthane dyes and observed shifts in their visible absorption maxima at lower surfactant concentrations. Recently the results of spectrophotometric studies on phenosafranin dye, a cationic phenazine dye, in aqueous solutions containing three different types of surfactants such as CTAB, SLS and Triton X-100 was reported.⁶⁴ While the formation of 1:1 dye Triton X-100 and dye-SLS observed, there was no interaction of phenosafranin with CTAB. The thermodynamic and spectrophotometric properties of these complexes suggest that phenosafranin forms strong charge transfer (CT) complex with Triton X-100 whereas the interaction with SLS is coulombic in nature. This conclusion was claimed to be confirmed by photogalvanic and photoconductivity measurements of phenosafranin in these surfactants. Since the interaction of Triton X-100, a good electron donor^{88,89} with cationic phenosafranin dye is CT in nature, it is therefore interesting to see if other cationic dyes will also form CT complexes with Triton X-100. The spectrophotometric data of the cationic dyes (Rhodamin B, Fuchin and Crystal violet) shown 1:1 complex, the equilibrium constant (K) and the molar extinction coefficient can be determined using Ketelaar's equation.⁹⁰ or Scott equation.⁹¹ The data presented⁹² provide direct Spectrophotometric evidence of molecular interactions between the cationic dyes and Triton X-100.

In the neutral surfactant micelle of Triton X-100 a cationic dye can penetrate the micelle to form a strong molecular complex at a polar site, the interaction may occur either at phenoxy group or at the polyoxyethylene chain. The absorption spectra of phenosafranin in acetonitrile, water, dioxane, acetone, ethanol and glycol exhibit absorption maxima at 518, 520, 525, 526, 532 and 535 nm respectively. The position of absorption maximum of phenosafranin-Triton X-100 complex in aqueous medium occurs at 537.5 nm. These results suggest that the positive centre of the dye molecule within the micelle is associated not with the lone pair electron on ether oxygen atom but with the lone pair electron on the oxygen of the hydroxyl group.

However, there is no indication of hydrophobic interaction between the dyes and Triton-X-100 in non aqueous media as the absorption spectra of the dyes do not show any characteristic change in the absorption maxima in non-aqueous media containing Triton X-100. This molecular interaction between the dyes and Triton X-100 in aqueous media is considered to be CT interaction. This is confirmed by the fact that absorption spectra of the dye-surfactant systems in the presence of small amount of NaCl are not affected.

Thiazine dyes are structurally similar to phenosafranin; the former dyes are the substituted phenothiazines, while the latter is the substituted phenazine. It is, therefore, expected that thiazine dyes behave similarly to phenosafranin towards Triton X-100. The thionine shows absorption maximum at 597 nm. A spectacular change is noticed when the Triton X-100 concentration is above the cmc, where all spectra show shifted absorption band at longer wave length, 608 nm, being a function of the concentration of Triton X-100. The visible absorption spectra of other thiazine dyes (such as Azure A, Azure B, Azure C and methylene blue) in aqueous solution of Triton X-100 behave similarly. Spectrophotometric data were employed to calculate the thermodynamic as well as spectrophotometric properties of dye surfactant interaction. For 1:1 complex,

the equilibrium constant (K) and molar extinction co-efficient (ϵ) can be determined using the Benesi Hildebrand equation⁹³ or Scott equation.⁹¹

From the thermodynamic and spectrophotometric properties of these complexes, the abilities of dyes to accept an electron are in the order azure C > thionine > azure A > azure B > methylene blue values of K , ΔG° , ΔH° and ΔS° are found to vary from 21.16 to 52.63 dm³ mol⁻¹, 7.61 to 9.88 kJmol⁻¹, 19.00 to 29.25 kJmol⁻¹, and 38.22 to 65.00 Jmol⁻¹ deg⁻¹ respectively for these dyes. Using Scatchard⁹⁴ and Scott⁹¹ equations, the almost identical values of K and ϵ were obtained. Triton X-100 in carbon tetrachloride solution can not even solubilize the dye; it is expected that the hydrophilic part of Triton X-100 interacts with the dye whereas there is no hydrophobic interaction between the dyes and Triton X-100. The absorption spectra of Thionine in different solvents such as acetonitrile, water dioxane, acetone, ethanol, and tert-butanol exhibit absorption maxima at 593, 597, 520, 598, 600 and 607 nm respectively. Although the absorption maximum of thionine- Triton X-100 complex appears at 612 nm, the shifted band of thionine in Triton X-100 solution exhibits at 608 nm. These results suggests that the positive centre of the dye molecules within the micelle is associated not with the lone pair electron on the ether oxygen atom, but with the lone pair of electron on the oxygen of the hydroxyl group for comparatively higher electron density. This molecular interaction between the dyes and Triton X-100 in aqueous medium is again considered to be a CT interaction. This is also confirmed by the fact that the absorption spectra of the dye-surfactant system are not affected by the presence of a small amount of NaCl.

The visible absorption spectra of Thionine along with the difference spectra of mixed solutions with a fixed concentration of Thionine and varying concentrations of Tween - 80 in aqueous media at 298K, are studied.⁹⁵ Thionine shows an absorption maximum at 597 nm. A remarkable change was noticed

when the Tween-80 concentration was above the cmc, where the difference spectra showed shifted absorption band at longer wave length, i.e. 616 nm with an isobestic point at 600 nm, the magnitude of the absorbance at 616 nm being directly proportional to the concentrations of Tween-80. The visible absorption spectra of thionine in aqueous solutions of others surfactants except CTAB above their cmc behaved similarly. In the presence of CTAB, the Thionine spectra were not perturbed at all, indicating no interaction between thionine and CTAB, whereas the presence of sharp isobestic point and spectral shift in other cases indicated 1:1 molecular complex formation between thionine and the surfactants. The equilibrium constant (K) as well as, molar extinction coefficient of the thionine – surfactant interaction, were evaluated using the Benesi-Hildebrand equation⁹³ /Ketelaar's equation (Equation No 31).

Mukhopadhyay et al⁹⁵ shown the spectra for the thionine-Tween-80 complex at three different temperatures (287, 298, 313K) and calculate the Equilibrium constant and other thermodynamic parameters also. They have recorded the spectra of thionine (Th)-Tw 60, Th – Tw 40, Th – Tw 20, Th – Tx 100 and have determined the thermodynamical parameters.

The cationic dye thionine is expected to form a strong complex with anionic surfactant SLS Mukhopadhyay et al⁹⁵ have shown that thionine forms stronger complexes with all the non-ionic surfactants compared to SLS. The nature of interaction of this dye with the non-ionic surfactants is therefore different than that with SLS. The thermodynamic and spectrophotometric parameters, ΔH° , and ΔS° for thionine complexes with non-ionic surfactants are also higher. Since all these surfactants can not even solublize the dye in carbon tetrachloride solution, it is plausible that the hydrophilic part of surfactants interacts with the dye in aqueous medium. A cationic dye can penetrate the non-ionic micelles to form a strong molecular complex at a polar site on the oxygen of the hydroxyl group for having comparatively higher electron density. The

molecular interaction between the thionine and non-ionic surfactants in aqueous medium is considered to be CT interaction. On the other hand, with a the negatively charged micelles of SLS, the cationic dye will be held in the stern region due to coulombic interaction, and the dye will be repelled by the positively charged micelles of CTAB.⁹⁶

According to Mulliken's CT theory⁹⁶ the CT-complex for the present system may be represented by a resonance hybrid of a non-ionic ground state structure and an ionic excited state structure. For thionine (Th) and non-ionic surfactant (S), these two states are represented as Th S and Th⁻.....S⁺. The excited or CT state is formed by the transfer of an electron from the non ionic surfactant, an electron donor to the dye, an electron acceptor on light absorption of suitable energy. It is shown that upon light excitation of the dye-non ionic surfactant systems, the primary charge separation takes place, forming a negatively charged dye and a positively charged surfactant and this charge separation causes photovoltage development when the illuminated and dark compartments of the cell containing dye-surfactant are connected to the electrometer. In the case of Thionine-SLS system, the interaction is ionic in nature, so no new ionic species are generated when the system is illuminated. The prominent interaction of thionine with surfactants above their cmc in aqueous medium indicates that the surface formation in micelle is a necessary criterion for complex formation. The interfaces (micelle/water) catalyse the CT complex formation due to absorption of thionine from solution and thus increase the concentration of CT complex. Mukhopadhyaya et al⁹⁵ concluded that the electron donating abilities of the non ionic surfactants towards the dye are in the order: Tween - 80 > Tween - 60 > Tween - 40 > Tween - 20 > Triton X - 100 and this is in accordance with the increasing alkyl hydrocarbon chain length, which in turn, increases the electron density at the electron-donating centre of the molecule, due to inductive effect. The presence of an aryl group in Triton X - 100 results in an opposite effect. They concluded that the nature of interactions

of thionine with different types of surfactants is different. Thionine undergoes CT interaction with non-ionic surfactants, ionic interaction with negatively charged SLS, and no interaction with positively charged CTAB.

The absorption spectra of methyl violet, a cationic dye, were investigated in aqueous solution containing anionic, non-ionic and cationic surfactants above their cmc. The dye forms 1:1 electron donor acceptor or charge transfer complexes with different non ionic surfactants. The dye acts as the electron acceptor and the surfactants as the electron donors. The length of the alkyl hydrocarbon chain of the non-ionic surfactants influences the stability of the complex.⁹⁷ Recently association constant for the formation of cresyl violet surfactant complex and the binding constant for the micellization of the dye, both in the absence and presence of electrolyte have been determined. From these studies, the dielectric constant experienced by cresyl violet within the SDS micelles has been found to decrease due to micellization of the dye. The environment arounds cresyl violet in the anionic micelle of SDS is highly polar and electrostatic attraction between cresyl violet and anionic micelle favour location of dye close to the head groups of the micelle.⁹⁸

Investigations of photoinduced electron transfer reactions in surfactant solutions are not only inherently interesting and relevant to the understanding of photobiology but they are also potentially important for efficient energy conversion and storage. Surfactant solutions help to achieve the separation of photoproducts by means of hydrophilic-hydrophobic interaction between the products and the interface.⁹⁹⁻¹⁰³

The surfactants are drawing the attention of analytical chemists in recent years, due to their uses in analytical methods which provide an increase in selectivity and sensibility.¹⁰⁴ Surfactants increase the solubility of organic compounds in water¹⁰⁵ and also catalyse some reactions, modifying the microenvironment in which the reactants are produced.⁵⁵ The nature and

mechanism of interactions of surfactant with chemical systems are still not clearly understood.¹⁰⁶ Electrostatic interactions and/or hydrophobic interactions may take place.¹⁰⁷ The dye surfactant interactions are also interesting due to their complex nature.^{49,62,108-113} Molecular complexes having specific and characteristic physico-chemical features may be formed. The dye phenosafranine in normal micelle⁶⁴ and Methylene blue in reverse micelle¹¹⁴ are reported to form 1:1 molecular complexes with both the non-ionic and the anionic surfactant, while congo red is reported to form 1:2 dye-surfactant complexes with CTAB and Triton X-100⁸⁶ The metachromatic dye Acridine Orange has been observed to undergo complicated interactions with normal and reverse micelle.^{115,116} The acid base behavior of indicator dyes are significantly influenced by reverse micellar solution.¹¹⁷⁻¹¹⁹ Micellar media is being considered as simple biological mimetic system.¹²⁰

4.2. Experimental

Interaction of Oxazine dyes with Surfactant

Dye-surfactant interaction is of great value in understanding the chemical equilibrium, mechanism, and kinetics of surfactant sensitized colour and fluorescence reactions. Most of the previous studies on dye-surfactant interactions are carried out with the concentration of the surfactants above the cmc. However, there is not much information available regarding the nature and the mechanism of the interaction between dyes and surfactant when the concentrations of the surfactants are much below the cmc. Systematic spectroscopic and thermodynamic investigations have been carried out in the present study in order to understand the nature of this interaction between ionic dyes and oppositely charged surfactants of very low concentration. The dyes chosen for such studies are Brilliant Cresyl Blue (BCB) Cresyl Violet Acetate (CVA), Cresyl Fast Violet (CFV) and Nile Blue A (NBA) and the surfactant is sodium dodecyl sulfate (SDS), an anionic surfactant.

The mechanism of interaction in the micellar solution of non ionic surfactants with dyes involves Charge Transfer or electron donor acceptor (EDA) interaction. The surfactants for such studies were Triton X-100 and Tween - 80.

Sources and purification of oxazine dyes used for the present study are described in chapter III. The surfactants sodium dodecyl sulphate (SDS), cetyl trimethyl ammonium bromide (CTAB), poly oxyethylene sorbitan - mono Oleate (Tween - 80) and octyl phenyl polyoxyethylene ether (Triton - X-100) are either Aldrich or sigma (USA) products. The surfactants were stirred overnight in ether separately and recrystallised from ethanol. Double distilled water was used as solvent. The electronic absorption spectra were recorded with double beam UV-VIS spectrophotometer (Shimadzu, model UV - 240, Japan) using a matched pair of 1 cm path length cells in a thermostated cell holder. The temperatures were maintained within $\pm 0.1K$

4.3 Results and Discussion

4.3.1. Interaction of Nile Blue A (NBA) in aqueous solution with SDS, Triton X -100 and Tween - 80.

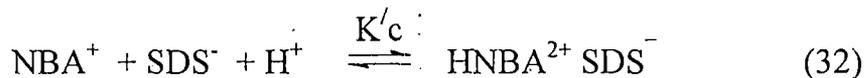
Aqueous NBA - SDS System (below cmc)

The electronic absorption spectra of NBA (1×10^{-5} M) alone and in the presence of varying concentrations of SDS (from 0.4×10^{-5} M to 2.5×10^{-5} M) much below the cmc in aqueous solutions were recorded. Representative spectra are shown in Fig. (37a, 37b, 37c). In the visible region, NBA has an absorption band with λ_{\max} of 633 nm. Values of monomer fractions as given in chapter - III (Table 1-4) for NBA at conc 1.0×10^{-5} M shows that dyes are present in solution mostly in monomeric form. As the concentration of SDS is slowly increased from 0.4×10^{-5} M to 2.5×10^{-5} M, the absorbance of NBA band

gradually decreases, accompanied by an increase in absorbance in the longer wave length region of 690 to 800 nm.

It can be seen from fig. (37a, 37b, 37c) that increasing the concentration of SDS upto 2.5×10^{-5} M, gives a series of spectra that pass through an isobestic point at 670 nm. The appearance of new broad band at ~ 710 nm, which increases with the increase in concentration of SDS (upto 2.5×10^{-5} M) and decreases with increase in temperature becomes apparent on inspection of the differences in absorbance of the NBA bands in the presence and absence of SDS. It has been shown that cationic dyes viz. Phenosafranine, Safranine O and SafranineT interact with anionic surfactants viz., SDS and sodium octylsulfate in sub-micellar concentration ranges which is an induced protonation of the dye in the dye – surfactant ion pair.⁷⁰ This protonated ion pair absorbs at a higher wave length similar to present observation at submicellar concentration ranges of SDS. The presence of an isobestic point is indicative of the presence of an equilibrium between the NBA, SDS and “Complexed NBA” (as interaction product of NBA and submicellar SDS). When the concentration of SDS increased further, above the cmc, the nature of the spectra started changing. A new band starts appearing at 640 nm. At a concentration of 3.0×10^{-3} M SDS, full spectrum reappear with λ_{\max} at 640 nm and the band at 633 nm is disappeared completely (fig. 39a). Therefore, with the increase in concentration of SDS above cmc, the 633 nm band shifts to higher wave length at 640 nm; which is attributed to the association of the dye with surfactant micelles (Discussed in further detail under “General Discussion”)

Spectral properties at different temperatures are shown in Table 13. The interaction of NBA^+ with SDS^- in aqueous medium can be represented by:



$$\text{or } K'/c = \frac{[\text{HNBA}^{2+} \text{SDS}^-]}{[\text{NBA}^+][\text{SDS}^-][\text{H}^+]} \quad (33)$$

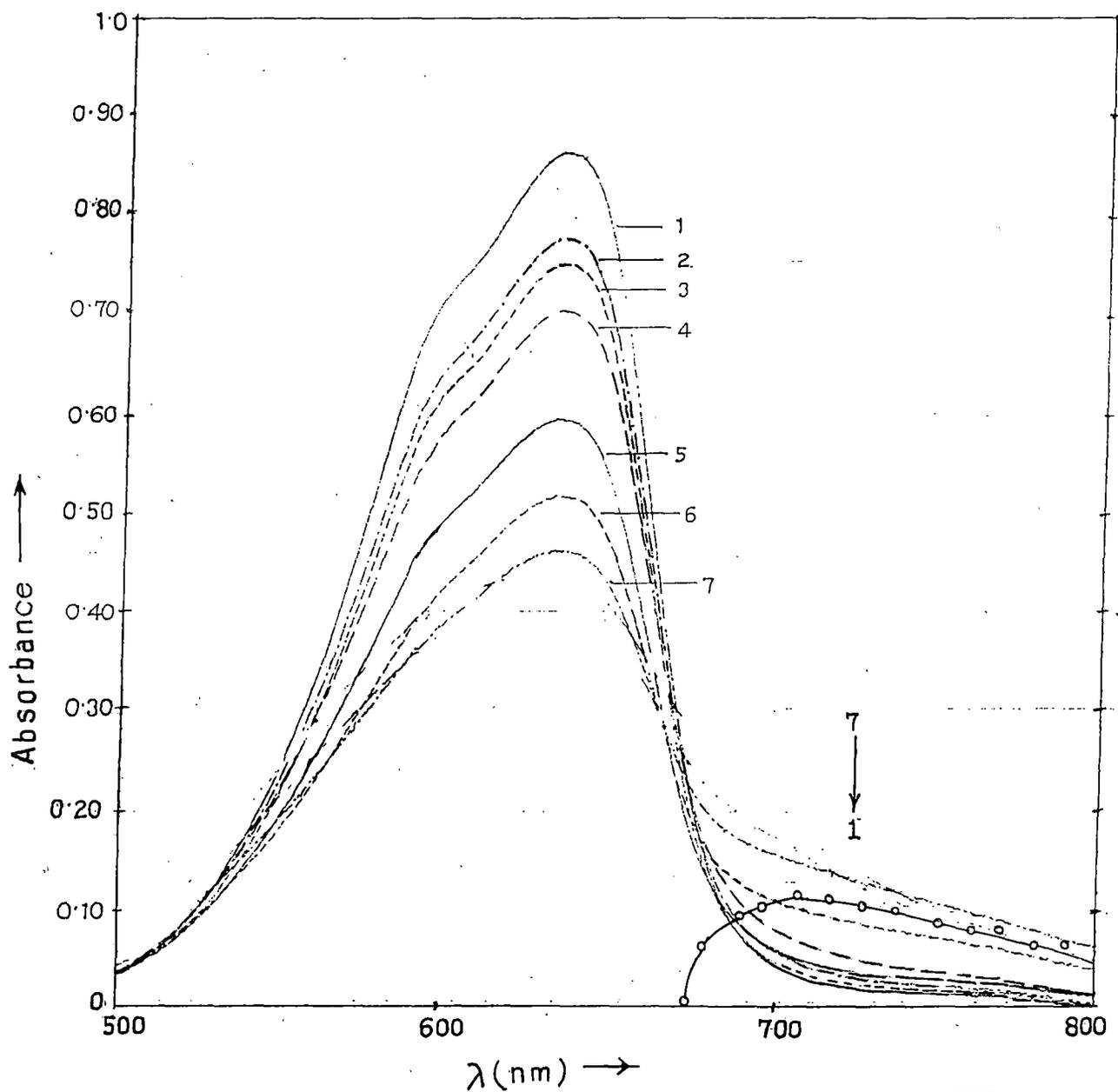


Fig. 37(d). Effect of variation in concentration of SDS on the Spectra of NBA at 30°C ; $[\text{NBA}] = 1 \times 10^{-5}\text{M}$; $[\text{SDS}] \times 10^5\text{M} = (1) 0.00 (2) 0.40 (3) 0.90 (4) 1.00 (5) 1.50 (6) 2.00 (7) 2.50$; $\circ-\circ-\circ$, difference spectra of (7) and (1).

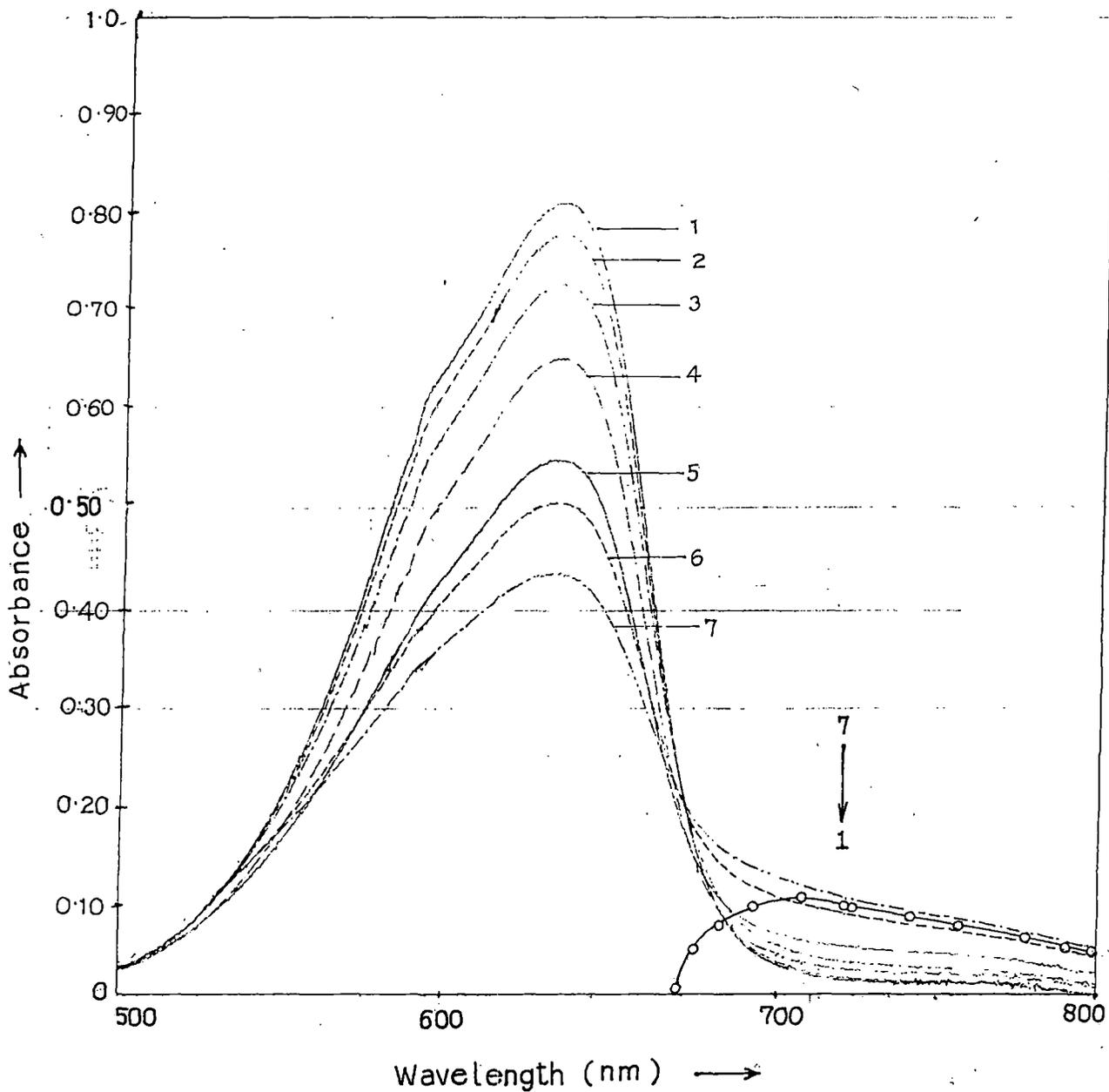


Fig. 37(b). Effect of variation in concentration of SDS on the Spectra of NBA at 40°C; $[NBA] = 1 \times 10^{-5} M$; $[SDS] \times 10^5 M = (1) 0.00 (2) 0.40 (3) 0.90 (4) 1.00 (5) 1.50 (6) 2.00 (7) 2.50$; o-o-o difference spectra of ⑦ and ①

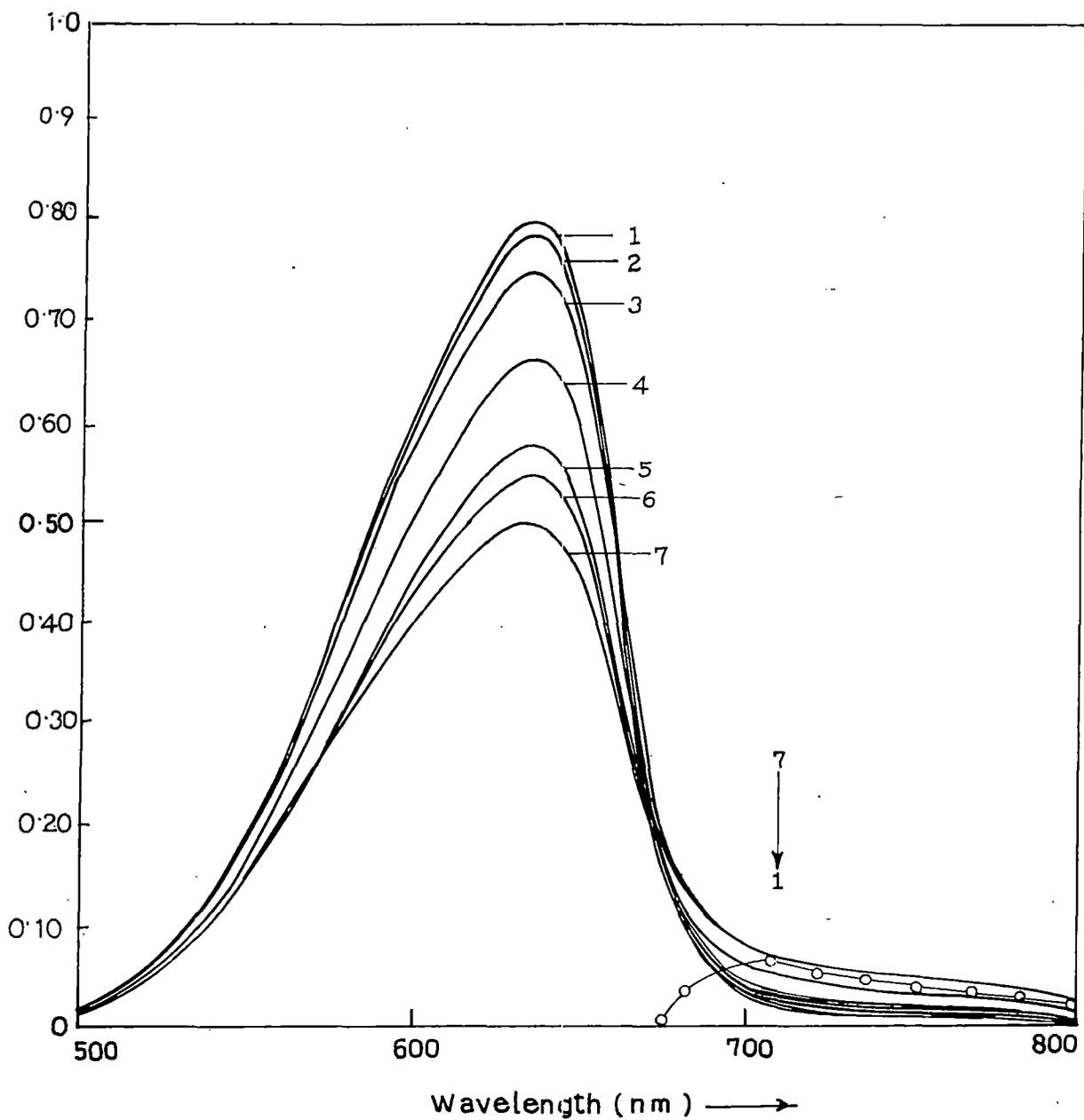


Fig.37(c).Effect of variation in concentration of SDS on the Spectra of NBA of 50°C $[NBA] = 1 \times 10^{-5} M$; $[SDS] \times 10^5 M = (1) 0.00 (2) 0.40 (3) 0.90 (4) 1.00 (5) 1.50 (6) 2.00 (7) 2.50$; o-o-o difference spectra of ⑦ and ①.

The pH of the mixed solution (i.e., of NBA and SDS) remain at 4.75 (within the sub-micellar experimental concentration range of SDS). Therefore, assuming that $[H^+]$ virtually remains constant, the above equation can be written as:

$$K_c = K'_c [H^+] = \frac{[HNBA^{2+} SDS^-]}{[NBA^+][SDS^-]} \quad (34)$$

Using the Ketelaar's equation⁹⁰ (equation no. 31) the equilibrium constant K_c may be obtained from the slope of the straight line of the plot of $[D]_0 / d - d_0$ Vs $1/[S]_0$. Here d and d_0 are the observed optical densities of the dye in the presence and in the absence of the surfactant, ϵ_0 and ϵ_c are the molar extinction coefficients of the dye in the free and the associated (viz. $HNBA^{2+} - SDS^-$) forms, and $[D]_0$ and $[S]_0$ are the initial concentration of NBA and the surfactant, SDS respectively. In order to know the nature of bonding between the dyes and surfactant molecules, some important thermodynamic functions are determined. Using Van't Hoff equation the enthalpy of dimerization ΔH° is calculated. The changes produced on the standard free energy and entropy are evaluated from the equations:

$$\Delta G^\circ = -RT \ln K \quad \text{and}$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ) / T \quad \text{respectively.}$$

In the foregoing calculation it is assumed that ΔG values are linear between 30°C and 50°C. The true equilibrium constant and thermodynamic parameters are shown in table 14 and plots of $[D]_0 / d - d_0$ Vs $1/[S]_0$ at different temperatures are shown in fig. 38.

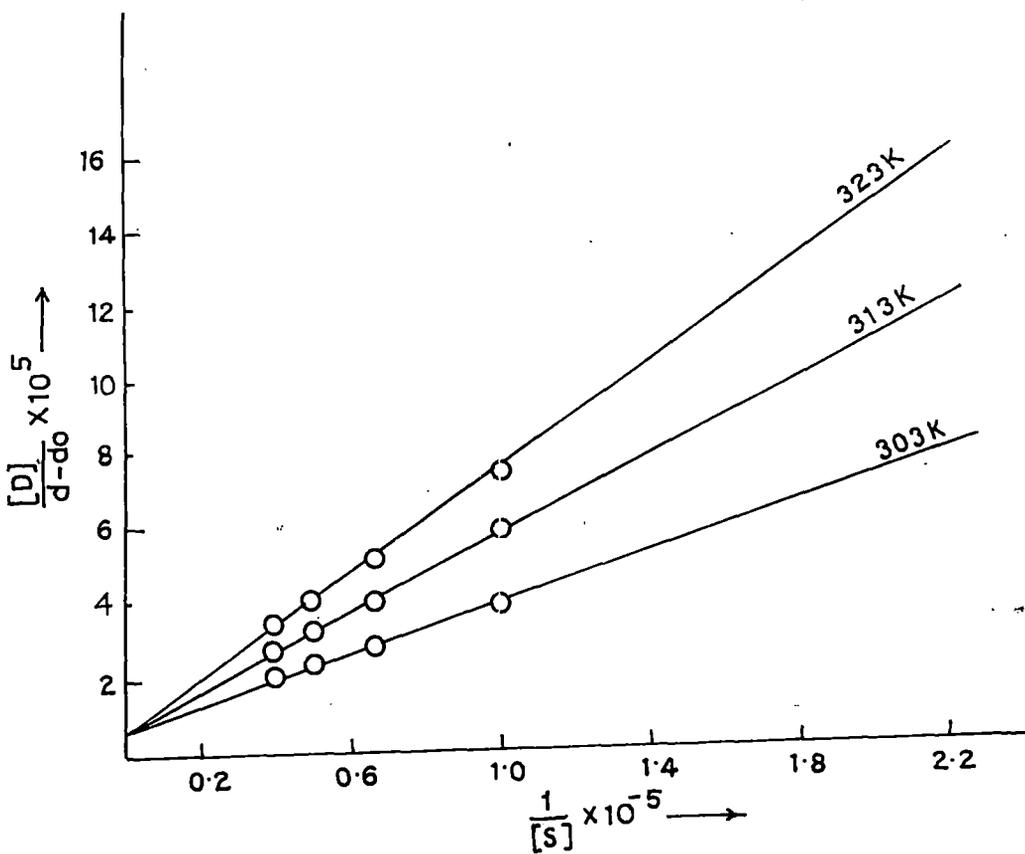


Fig. 38

Spectral determination of Equilibrium constant and molar extinction coefficient of Nile Blue A - SDS Complex in water at 303K, 313K, 323K using Eqn. (31). These plots were made by least squares method with standard deviation of 5%.

Table 13 : Spectral properties of oxazine dyes and their protonated ions pairs (complexes) with SDS in sub micellar concentration ranges at different temperatures.

Dye	Temperature (K)	λ_{\max} of the dye (± 1) nm	ϵ_{\max} of the dye (± 50) m^2M^{-1}	λ_{iso} of the complex (± 1) nm	$\epsilon_{\text{iso}}(\pm 100)\text{m}^2\text{M}^{-1}$	λ_{\max} of the complex (± 2) nm	ϵ_{\max} of complex (± 100) m^2M^{-1}
NBA	303	633	8600	670	2500	710	1800
	313	633	8100	670	2000	710	1200
	323	633	8000	670	1800	710	1000

Table 14: Equilibrium constants and the other Thermodynamic parameters of the sub micellar interaction product of oxazine dye with an anionic surfactant.

Dye	Surfactant	PH	Temperature (K)	K_c (M^{-1})	$K^{\prime}C = K_c/[H^+]$ (M^{-2})	$-\Delta G$ kJM^{-1}	$-\Delta H$ kJM^{-1}	ΔS $JM^{-1}K^{-1}$
			303	25.5×10^3	1.434×10^9	53.15		
NBA	SDS	4.75	313	17.0×10^3	0.956×10^9	53.85	22.67	100.0
			323	14.0×10^3	0.796×10^9	55.07		

Aqueous NBA – SDS System (above cmc)

The visible absorption spectra of NBA (10^{-5} mol. dm^{-3}) in aqueous solution exhibits an absorption maximum at 633 nm with an extinction coefficient ϵ of $86000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 303K. In the presence of increasing SDS concentration below cmc, the absorption spectra of NBA are indicative of the presence of monomers only.

In the presence of SDS above its cmc, a spectacular change occurs. The intensity of the band at 633 nm gradually diminishes with the appearance of a new band at 640 nm whose intensity increases as the SDS concentration increases. The difference spectra of NBA – SDS against NBA in water at various temperatures are shown in figure (39a, 39b, 39c). Two sharp isobestic points at 600 nm and 670nm have been attributed to a 1:1 complex formation between NBA (10^{-5}M) and SDS. The magnitude of the absorbance at 640 nm is directly proportional to the concentration of SDS. The experimental concentrations of SDS were from $3.5 \times 10^{-3}\text{M}$ to $1.5 \times 10^{-2} \text{ M}$. The spectral properties are shown in Table 15. The equilibrium constant (K_c) as well as, molar extinction coefficient of the NBA – surfactant interaction, have been evaluated using the Ketelaar's equation (equation no 31). It is assumed that Eq.31 is valid when $[S] \gg [D]$ and the complex absorbs at a wavelength where the surfactant is completely transparent. The plot of $[D]_0 / (d-d_0)$ against $1/[S]_0$ was found to be linear in all cases confirming 1:1 complex formation. Plots are shown in fig. (40) for the NBA-SDS complex at three different temperatures (303K, 313K, 323K). From the slopes and the intercepts, K_c and ϵ_c of the NBA – SDS complexes in aqueous medium are calculated. The thermodynamic functions are calculated from the temperature dependence of the equilibrium constant at 303K, 313K and 323K by the usual method. The results are presented in the Table 16. It is to be noted that as the temperatures increases, intensity of spectrum decreases indicating breaking of dye-surfactant complexes at high temperatures.

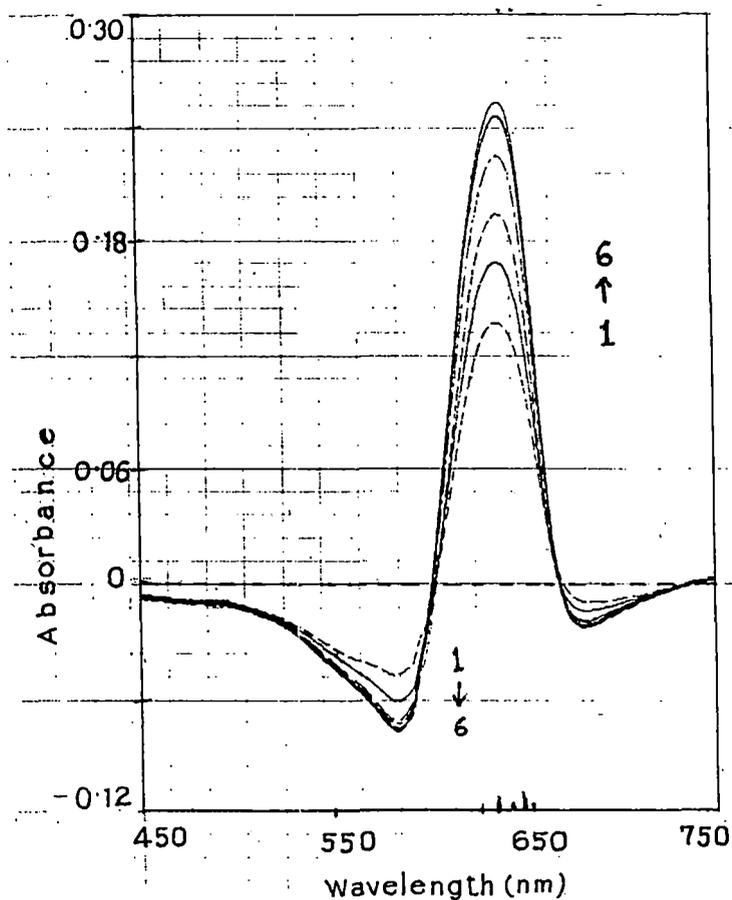


Fig. 39(a). The difference Spectra of Nile Blue A and SDS against NBA in water at 30°C. Concentration of NBA : 1×10^{-5} mol. dm^{-3} and concentration of SDS (10^{-2} mol. dm^{-3}) : (1) 0.35 (2) 0.40 (3) 0.50 (4) 0.60 (5) 1.00 (6) 1.50. The broken line represents the set of curves when the concentration of SDS is below 5×10^{-4} mol. dm^{-3} .

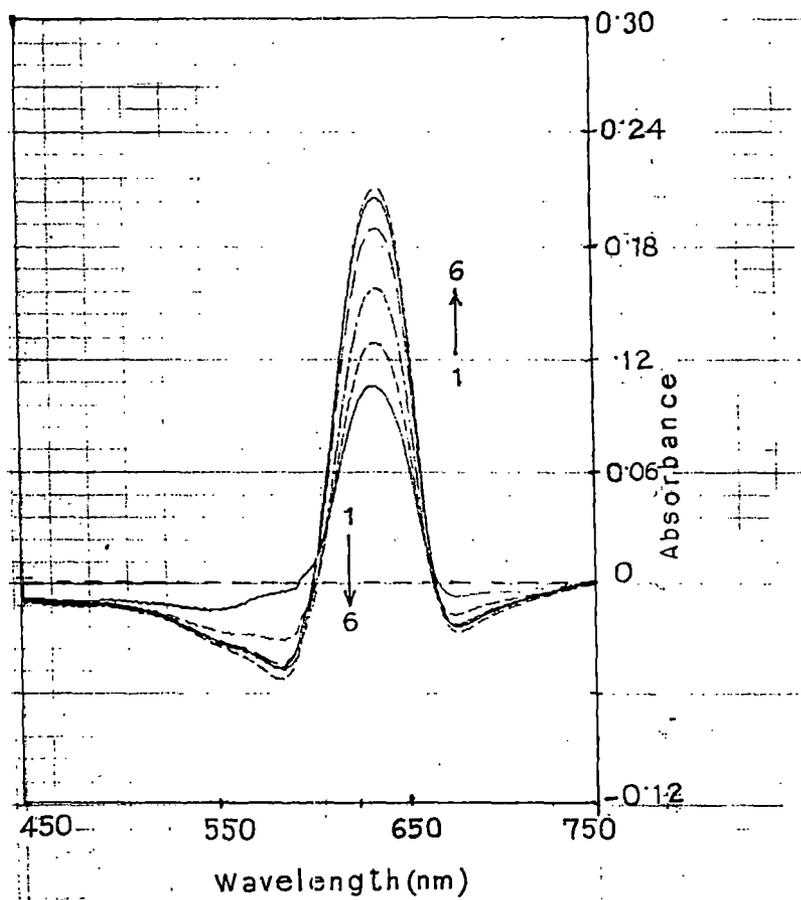


Fig. 39(b). The difference Spectra of Nile Blue A and SDS against NBA in water at 40°C . Cocentration of NBA : $1 \times 10^{-5} \text{ mol. dm}^{-3}$ and concentration of SDS ($10^{-2} \text{ mol. dm}^{-3}$) : (1) 0.35 (2) 0.40 (3) 0.50 (4) 0.60 (5) 1.00 (6) 1.50. The broken line represents the set of curves when the concentration of SDS is below $5 \times 10^{-4} \text{ mol. dm}^{-3}$.

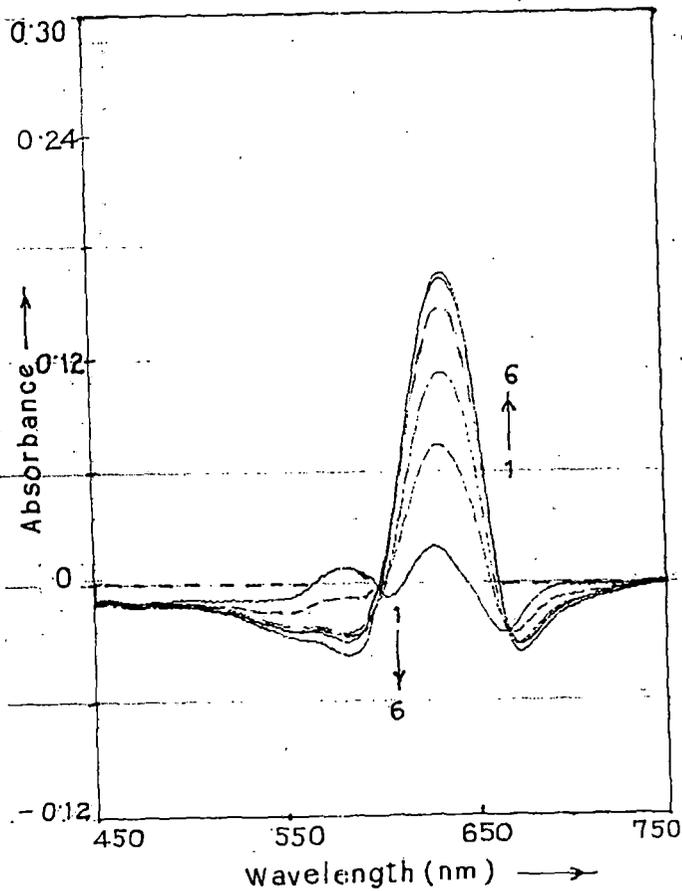


Fig. 39(c) . The difference Spectra of Nile Blue A and SDS against NBA in water at 50°C. Concentration of NBA : 1×10^{-5} mol. dm^{-3} and concentration of SDS (10^{-2} mol. dm^{-3}) : (1) 0.35 (2) 0.40 (3) 0.50 (4) 0.60 (5) 1.00 (6) 1.50. The broken line represents the set of curves when the concentration of SDS is below 5×10^{-4} mol. dm^{-3} .

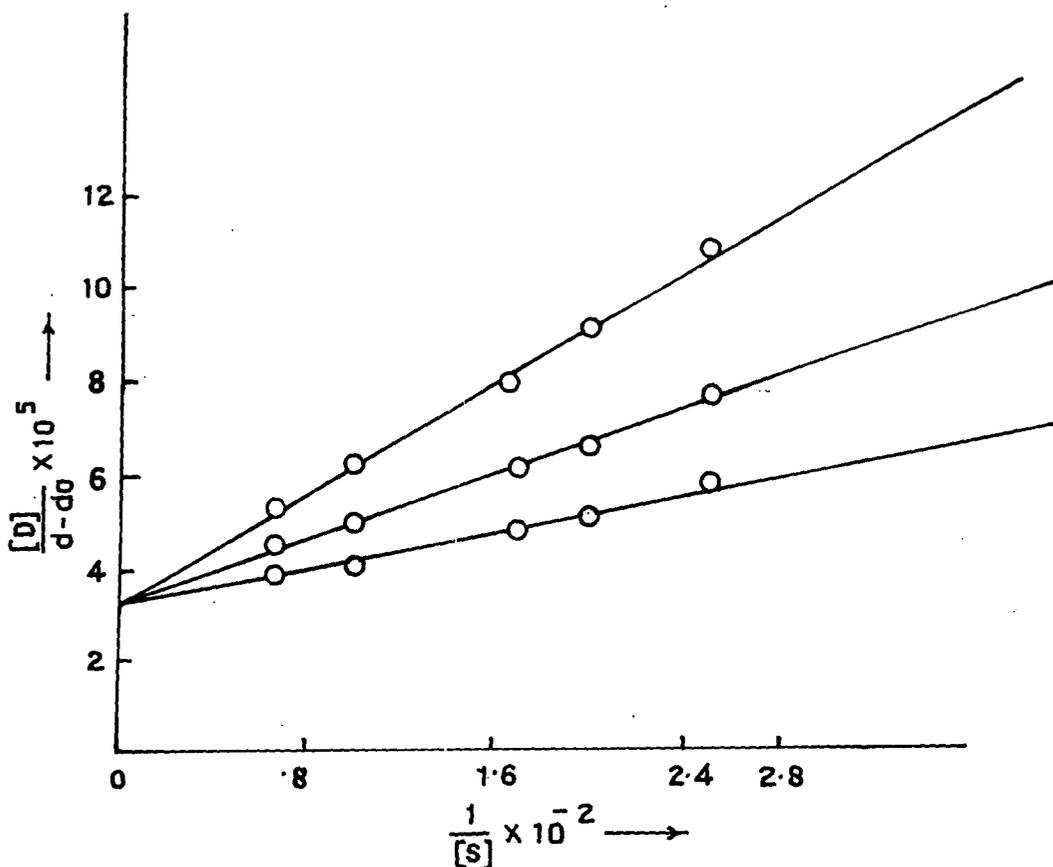
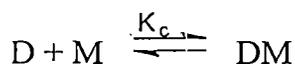


Fig. 40 . Spectral determination of equilibrium constant and molar extinction co-efficient of NBA - SDA Complex in water at 303K, 313K, 323K using Eqn (31). These plots were made by least squares method with standard deviation of 5%.

Aqueous NBA – Triton X - 100 System (above cmc)

The nonionic surfactant Triton x 100 does not affect the spectra of NBA below its cmc value indicating absence of any molecular interaction between surfactant and the dye at low concentration of the surfactant. In the presence of Triton X – 100, above its cmc, spectacular change occurs as before, the spectral band shifts from 633 nm to 650 nm and intensity increases with the Triton X – 100 concentration and decreases with temperatures (fig 41). The spectrum of the dye due to the interaction with Triton X – 100 passes through two Isobestic points viz. 610 nm and 675 nm respectively, supporting the view of the formation of a complex above the cmc. The spectral properties are shown in Table 15. Dye-surfactant complex formation can be assumed to follow the equilibrium:



Where D, M, DM and K_c represent the dye, micelle, dye-micelle complex and complexation constant respectively. For a 1:1 complex, the equilibrium constant K_c , and molar extinction co-efficient ϵ_c have been determined by using the Ketelaar's Equation (equation no. 31) at three different temperatures (303K, 313K, 323K). The plot of $[D]_0 / (d-d_0)$ against $1/[S]_0$ at three different temperatures were found to be linear in all cases confirming 1:1 complex formation. K_c and ϵ_c of NBA – Tx –100 complexes were calculated from the slope and intercept respectively (fig. 42). The thermodynamic quantities of the complexes were obtained from K_c values at three different temperatures (Table 16). The thermodynamic and spectrophotometric properties of these complexes suggest the formation of a strong charge-transfer (CT) or electron donor-acceptor (EDA) complex with Triton X – 100 (Discussed in further detail under 'General Discussion').

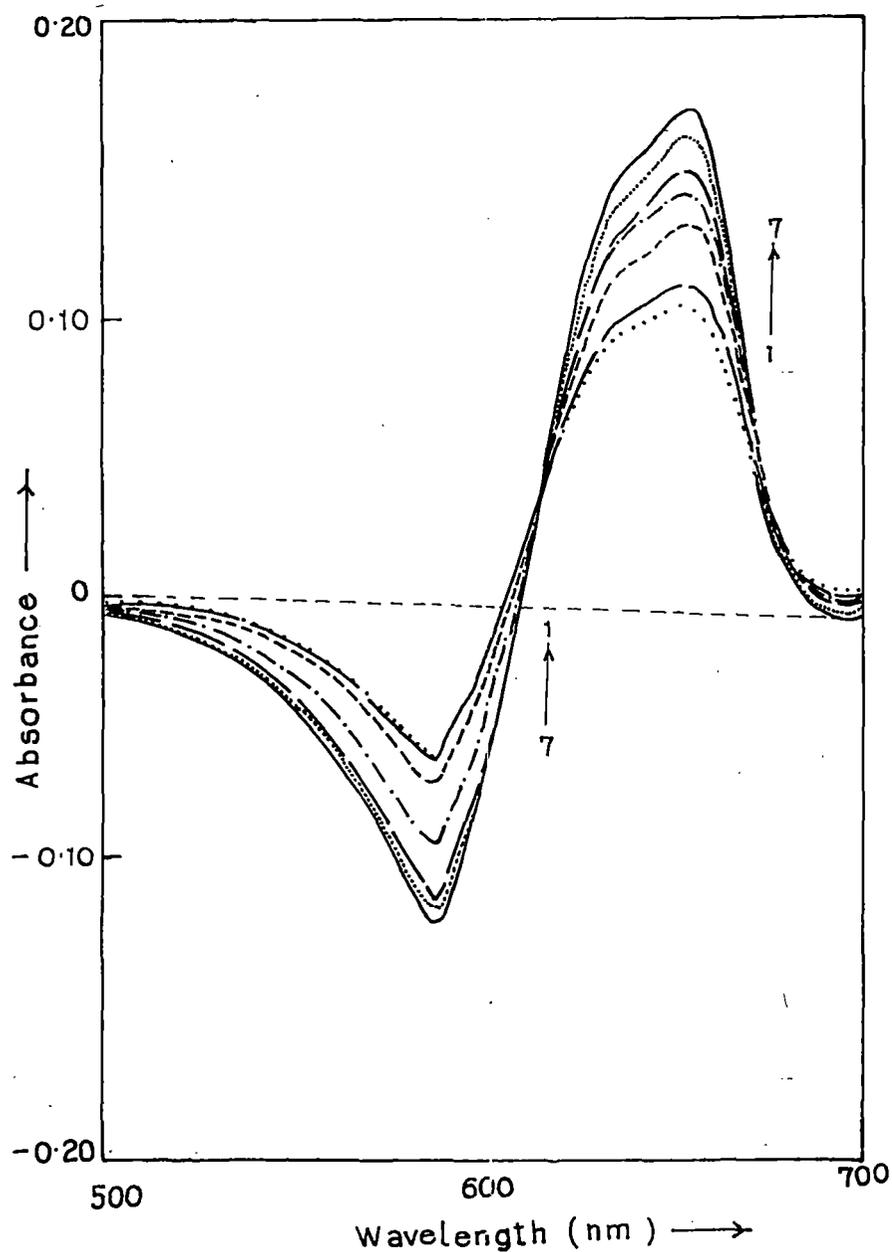


Fig. 41.

The difference Spectra of Nile Blue A (NBA) and Triton X - 100 against NBA in water at 30°C. Concentration of NBA 10^{-5} mol. dm^{-3} and Concentration of Triton x - 100 (10^{-3} mol. dm^{-3}) : (1) 0.40 (2) 0.60 (3) 0.80 (4) 1.00 (5) 2.00 (6) 3.00 (7) 6.00. The broken line represents the set of curves when the concentration of Triton x - 100 is below 1.5×10^{-4} mol. dm^{-3} .

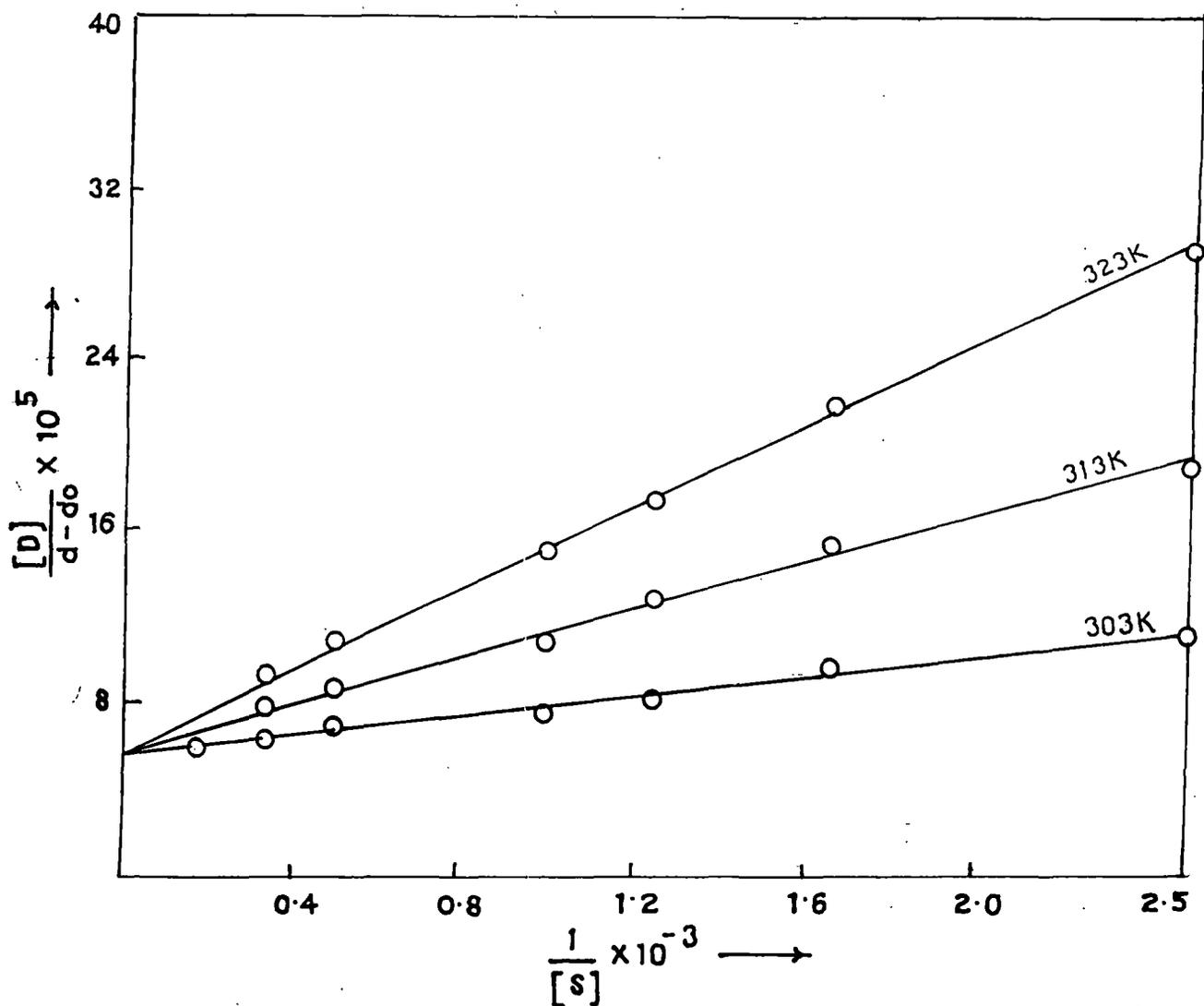


Fig.42 . Spectral determination of equilibrium constant and molar extinction co-efficient of NBA - Triton X - 100 complex in water at 303K, 313K, 323K using eqn (31). These plots were made by least squares method with standard deviation of 5%.

Aqueous NBA – Tween-80 System (above cmc)

The nonionic surfactant Tween-80 does not affect the spectra of NBA below its cmc value indicating absence of any molecular interaction between surfactant and the dye. In the presence of Tween-80, a non ionic surfactant, above its cmc, the spectral band shifts at longer wave length from 633 nm to 635nm. The spectra exhibit two humps at 635 nm and 655 nm and also two isobestic points at 610 nm and 675 nm. The intensity of spectrum increases with concentration of Tween-80 and decreases with temperatures(fig. 43a, 43b; 43c). The experimental concentrations of Tween-80 were varied from 2×10^{-4} M to 2×10^{-2} M at various temperatures viz., 293 K, 303 K, and 313 K. The spectrum of the dye due to the interaction with Tween-80 passes through two isobestic points, supporting the view of the formation of a dye-micellar complex. The spectral properties are shown in Table 15. The equilibrium constant K_c , and molar extinction coefficient ϵ_c are calculated by using the Ketelaar's equation (Equation no 31) at three different temperatures (293K, 303K, 313K) . The plots of $[D]_0 / (d-d_0)$ against $1/[S]_0$ were found to be linear in all cases, confirming 1:1 complex formation. A representative plot is shown in Fig. 44 for the NBA – Tween – 80 system at three different temperatures (293K, 303K, 313K). The thermodynamic parameters were calculated from the temperature dependence of the equilibrium constants and the results are shown in Table 16.

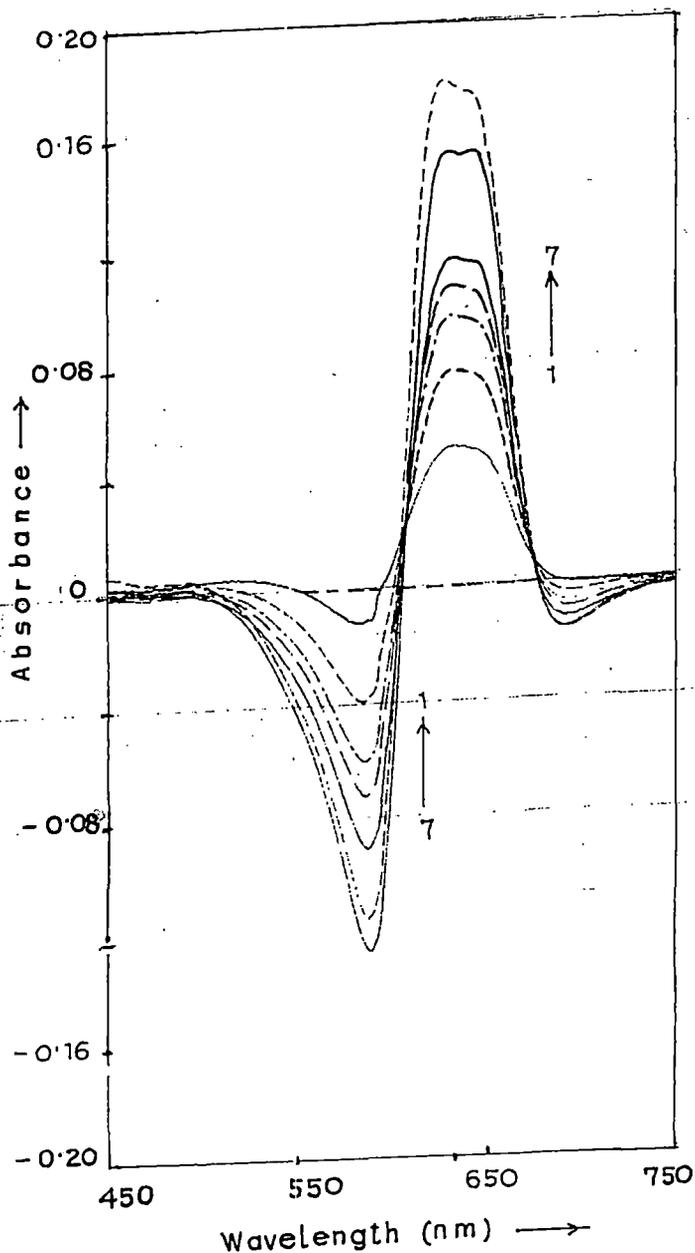


Fig. 43(a). The difference Spectra of NBA and Tween - 80 against NBA in water at 20°C. Concentration of NBA 10^{-5} mol. dm^{-3} and Concentration of Tween-80 (10^{-3} mol. dm^{-3}); (1) 0.20 (2) 0.40 (3) 0.60 (4) 0.80 (5) 1.00 (6) 10.00 (7) 20.00. The broken line represents the set of curves when the Concentration of Tween-80 is below 1.0×10^{-5} mol. dm^{-3} .

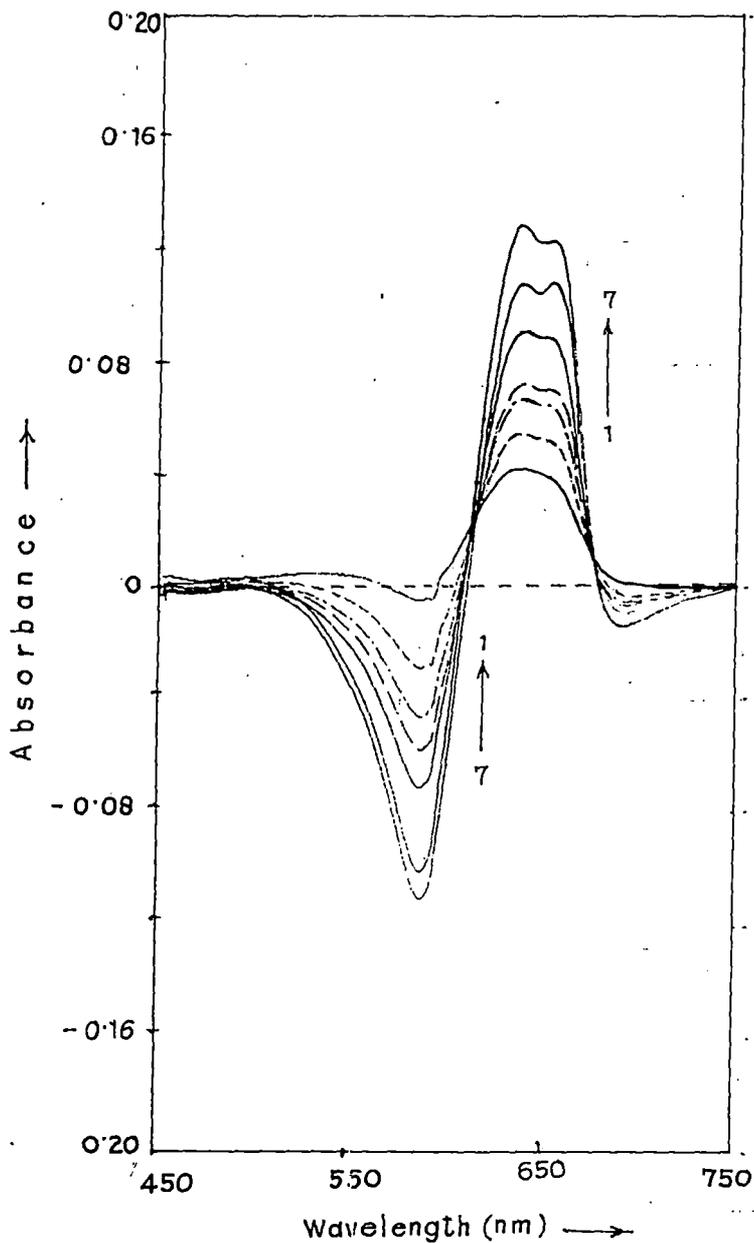


Fig. 43(b) The difference Spectra of NBA and Tween - 80 against NBA in water at 30°C. Concentration of NBA 10^{-5} mol. dm^{-3} and Concentration of Tween-80 (10^{-3} mol. dm^{-3}): (1) 0.20 (2) 0.40 (3) 0.60 (4) 0.80 (5) 1.00 (6) 10.00 (7) 20.00. The broken line represents the set of curves when the Concentration of Tween-80 is below 1.0×10^{-5} mol. dm^{-3} .

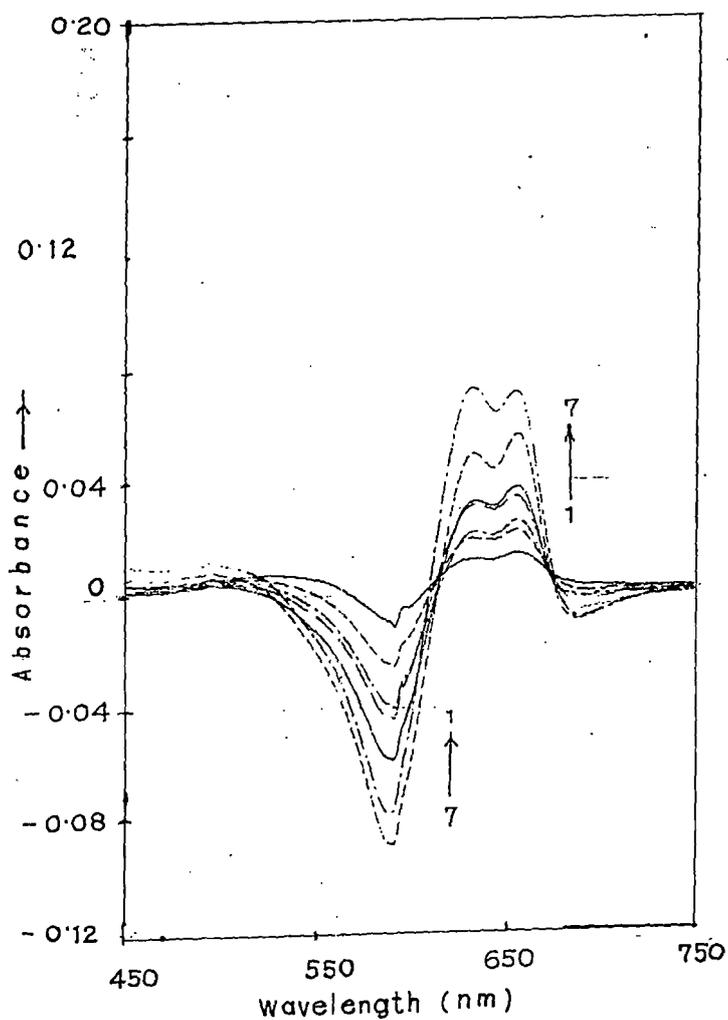


Fig. 43(c). The difference Spectra of NBA and Tween - 80 against NBA in water at 40°C. Concentration of NBA 10^{-5} mol. dm^{-3} and Concentration of Tween-80 (10^{-3} mol. dm^{-3}): (1) 0.20 (2) 0.40 (3) 0.60 (4) 0.80 (5) 1.00 (6) 10.00 (7) 20.00. The broken line represents the set of curves when the Concentration of Tween-80 is below 1.0×10^{-5} mol. dm^{-3} .

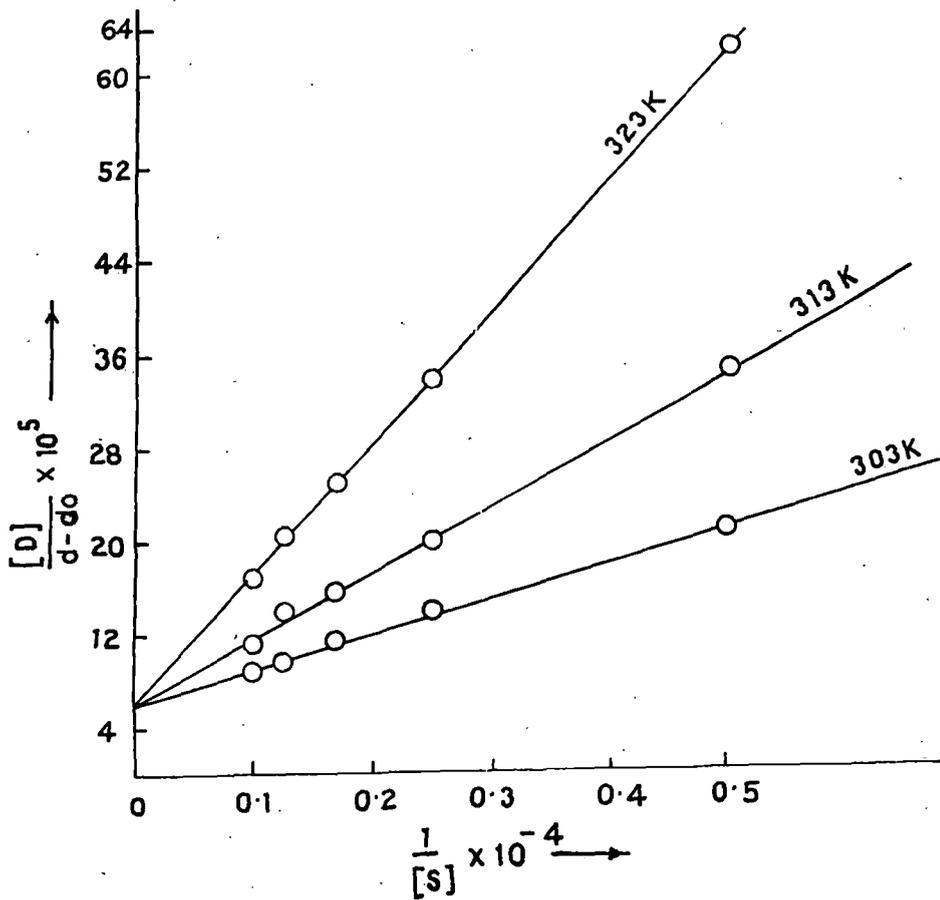


Fig. 44 . Spectral determination of equilibrium constant and molar extinction co-efficient of NBA - Tween - 80 complex in water at 293K, and 313K using eqn (31) These plots were made by least squares method with standard deviation of 5%.

Table-15: Spectral properties of Oxazine dyes and their complexes with an anionic and non ionic surfactants in supermicellar concentration ranges.

Dye	Surfactant	Temperature (K)	λ_{\max} of the dye (± 1) nm	ϵ_{\max} of the dye (± 50) $m^2 M^{-1}$	λ_{\max} of the complex(± 2)nm	λ_{iso} of the complex (± 1)nm
	SDS	303	633	8600	635	650
NBA	Triton X-100	303	633	8000	650	610nm and 675nm
	Tween-80	293	633	8000	635	610 nm and 675nm

Table –16: Equilibrium Constants and other thermodynamic parameters of the supermicellar interaction products of Oxazine dyes with Anionic and non-ionic surfactants.

Dye	Surfactant	pH	Temperature (K)	Shifting of λ_{\max}	$K_c (M^{-1})$	$-\Delta G$ kJM^{-1}	$-\Delta H$ JM^{-1}	$-\Delta S$ $JM^{-1}K^{-1}$
NBA	SDS	4.80	303	633nm to 640nm	363.0	14.85	43.38	94.47
			313		198.0	13.76		
			323		118.8	12.81		
NBA	Triton X-100	4.20	303	633 nm to 650nm	2610.0	19.82	55.43	117.89
			313		1160.0	18.36		
			323		638.0	17.34		
NBA	Tween-80	5.40	293	633 nm to 655nm	2000.0	18.51	37.27	65.27
			303		1080.0	17.60		
			313		533.0	16.34		

4.3.2 Interaction of cresyl violet acetate with SDS, Triton X-100 and Tween 80.

Aqueous CVA-SDS System (below cmc)

The visible absorption spectra of Cresyl violet acetate, CVA, (2.0×10^{-5} M) alone and in the presence of varying concentrations of SDS (much below the cmc) in aqueous solutions are shown in fig 45. In visible region, CVA has an absorption band with λ_{\max} at 585nm (ϵ at 585nm = $47000 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$ at 303K). As the concentration of SDS is slowly increased from 0.3×10^{-5} M (the lowest concentration at which there was no detectable decrease/increase in absorbance of CVA) to 2.0×10^{-5} M, the λ_{\max} of CVA band gradually shifted from 585 nm to 590nm with a gradual decrease in intensity of the λ_{\max} band, accompanied by an increase in absorbance in the longer wave length region of 630nm to 700 nm. Unlike NBA, another peak appears near 520nm as the concentration of SDS is increased.

The new peaks at 520nm and 590nm may be attributed to the complex formed between the dye and SDS molecule. The enhancement in the absorbance on the higher wave length side of the CVA band is quite pronounced and increases with the increase in the concentration of SDS. It can be seen from Fig. 45 that increasing the concentration of SDS upto 2.0×10^{-5} M, for a fixed concentration of CVA of 2×10^{-5} M, gives a series of spectra that pass through a sharp isobestic point at 622 nm (Table 17). Unlike NBA, CVA gives well defined peak at 650nm in presence of SDS below the cmc due to protonation. The presence of an isobestic point is indicative of the presence of an equilibrium between the free CVA, SDS and "Complexed CVA" (an interaction product of CVA and submicellar SDS). At the concentration of SDS from 4×10^{-5} M to 1×10^{-3} M slight precipitation occurs due to the insoluble salt formation. With the increase in concentration of SDS above cmc i.e. above 2.0×10^{-3} M the precipitates dissolve again.

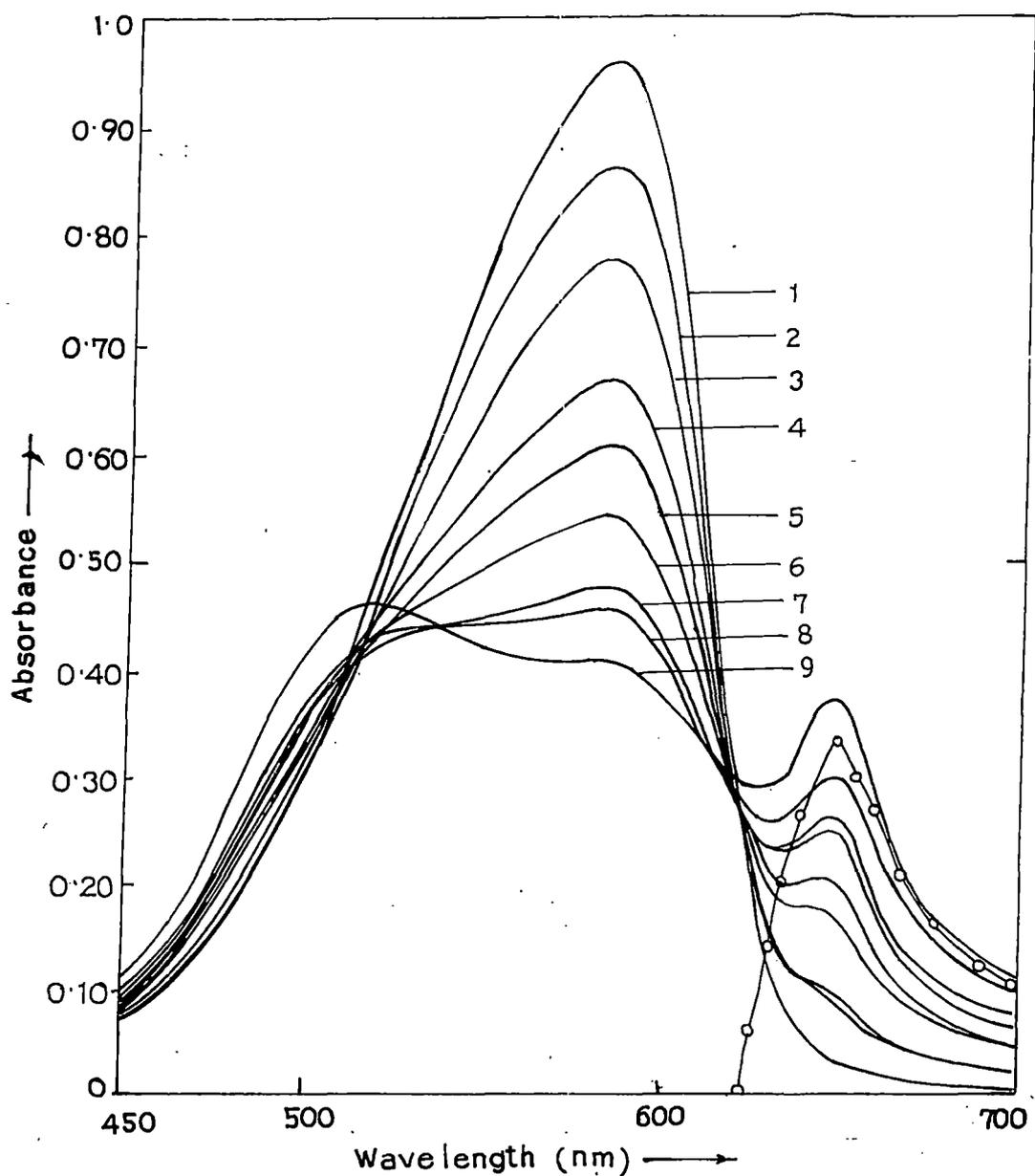


Fig. 45. Effect of variation in concentration of SDS on the spectra of CVA at 30°C $[CVA] = 2 \times 10^{-5}$; $[SDS] \times 10^5 M =$ (1) 0.00 (2) 0.30 (3) 0.50 (4) 0.70 (5) 0.90 (6) 1.20 (7) 1.40 (8) 1.50 (9) 2.00; o-o-o, difference spectra of ⑨ and ①.

Study of the Equilibrium:

The interaction of CVA^+ with SDS^- in aqueous medium can be represented by:



$$\text{Where, } K'_c = \frac{[\text{HCVA}^{2+} \text{SDS}^-]}{[\text{CVA}^+][\text{SDS}^-][\text{H}^+]} \quad (35)$$

$$\text{i.e. } K_c = K'_c[\text{H}^+] = \frac{[\text{HCVA}^{2+} \text{SDS}^-]}{[\text{CVA}^+][\text{SDS}^-]} \quad (36)$$

$$\text{Using the Ketelaar's equation, } \frac{[D]_0}{d - d_0} = \frac{1}{\epsilon_c - \epsilon_0} + \frac{1}{K_c (\epsilon_c - \epsilon_0) [S]_0} \quad (31)$$

one can obtain the equilibrium constant, K_c . ϵ_0 and ϵ_c are the molar extinction co-efficients of the dye in the free and the associated (viz., $\text{HCVA}^{2+} \text{SDS}^-$) forms, and $[D]_0$ and $[S]_0$ are the initial concentration of the dye and the surfactant, respectively.

The plots of $[\text{CVA}]_0/d - d_0$ vs $1/[\text{SDS}]_0$ at various temperatures yielded straight lines for a range of the concentration of SDS (fig. 46). Deviation from the straight line was observed towards higher concentrations of SDS which was due to the disappearance of the protonated ion pairs as a result of solubilization of the dye by mixed micelle or micelle formation.¹⁰⁰

The apparent equilibrium constant values K_c , obtained from the plot of $[\text{CVA}]_0/d - d_0$ Vs $1/[\text{SDS}]_0$ were found to be 49.60×10^3 , 28.50×10^3 , $11.20 \times 10^3 \text{ dm}^3\text{M}^{-1}$ at 303, 313 and 323K respectively. These high values of the apparent equilibrium constants are comparable to those reported for the interaction of cationic dyes with large organic anions⁹⁶. The values of the equilibrium constant, K'_c (where $K'_c = K_c / [\text{H}^+]$), alongwith the thermodynamic parameters are given in Table 18.

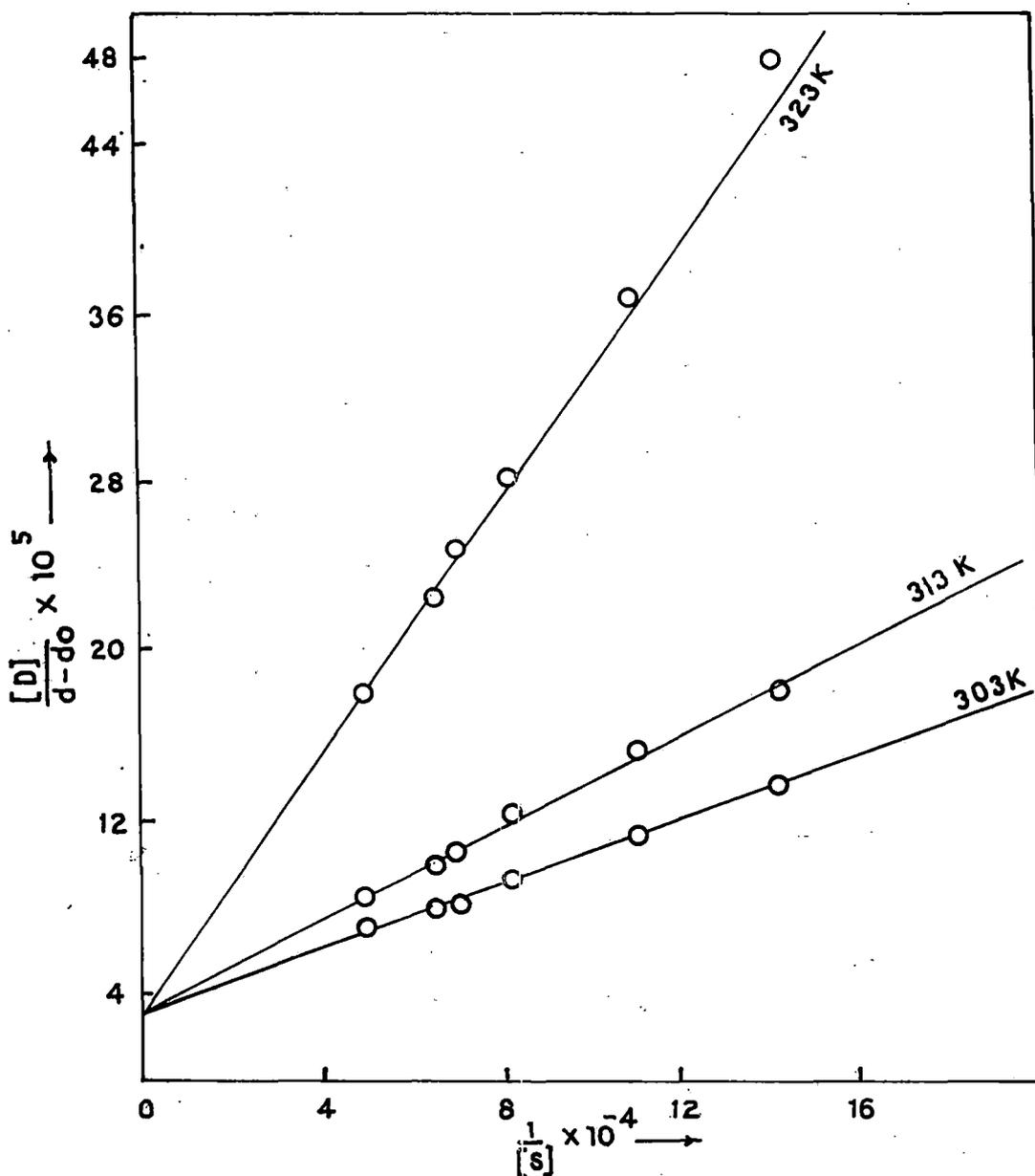


Fig. 46. Spectral determination of Equilibrium constant and molar extinction coefficient of CVA - SDS Complex in water at 303K, 313K, 323K using Eqn (31). These plots were made by least squares method with standard deviation of 5%.

Table -17 : Spectral properties of oxazine dyes and their protonated ions pairs (complexes) with SDS in sub micellar concentration ranges at different temperatures.

Dye	Temperature (K)	λ_{\max} of the dye (± 1) nm	ϵ_{\max} of the dye (± 50) m^2M^{-1}	λ_{iso} of the complex (± 1) nm	$\epsilon_{\text{iso}}(\pm 100)\text{m}^2\text{M}^{-1}$	λ_{\max} of the complex (± 2) nm	ϵ_{\max} of complex (± 100) m^2M^{-1}
CVA	303	585	2400	622	750	650	765
	313	585	2300	622	700	650	600
	323	585	2100	622	600	650	350

Table –18: Equilibrium constants and the other Thermodynamic parameters of the sub micellar interaction product of Oxazine dye with an anionic surfactant.

Dye	Surfactant	pH	Temperature (K)	K_c (M^{-1})	$K'C = K_c/[H^+]$ (M^{-2})	$-\Delta G$ kJM^{-1}	$-\Delta H$ kJM^{-1}	ΔS $JM^{-1}K^{-1}$
CVA	SDS	4.88	303	49.60×10^3	3.76×10^9	55.54		
			313	28.50×10^3	2.16×10^9	55.93	46.19	30.83
			323	15.20×10^3	1.15×10^9	56.04		

Aqueous CVA – SDS System (above cmc)

The visible absorption spectra of CVA ($2.0 \times 10^{-5} \text{M}$) in aqueous solution exhibit an absorption maximum at 585nm. The intensity of the band at 585 nm gradually diminishes with the appearance of a new band at 610nm with increasing intensity as the SDS concentration increases above its cmc value. The difference spectra of CVA and SDS against CVA in water at different temperatures are shown in figures 47a, 47b and 47c. The spectra are assigned to the incorporation of the dye in the surfactant micelles. The binding constant of the micellization of the dye are determined. The spectral properties are shown in table 19. This equilibrium constant K_c , as well as molar extinction coefficient of the CVA – surfactant interaction were evaluated using the Ketelaar equation (Benesi – Hildebrand' equation in the modified form) (Eqn. 31). The plot of $[D]_0/d-d_0$ against $1/[S]_0$ was found to be linear in all cases confirming 1:1 complex formation. K_c and ϵ_c were calculated from the slope and intercept, one such plot is shown in fig. 48 for the CVA – SDS complex at three different temperatures 303K, 313K, 323K. The thermodynamic parameters were calculated from the temperature dependence of the equilibrium at by the usual method. The results are presented in the Table 20 which shows the evidence of molecular interaction between CVA and surfactant in aqueous medium.

Aqueous CVA-Triton X - 100 System (above cmc)

The visible absorption spectra of CVA is not affected in presence of non ionic surfactant Triton X-100 below its cmc. However, in the presence of Triton X - 100, above its cmc a red shift in λ_{max} is observed from 585nm to 615nm and the intensity increases as the Triton X-100 concentration increases (from $2 \times 10^{-3} \text{M}$ to $8 \times 10^{-2} \text{M}$). The difference spectra of CVA in Triton X-100 (above cmc) against CVA in water at different surfactants concentrations are shown in figures 49a, 49b. Spectral investigations with non ionic surfactants above their cmc indicate some interesting features. The spectra of the dye in presence of

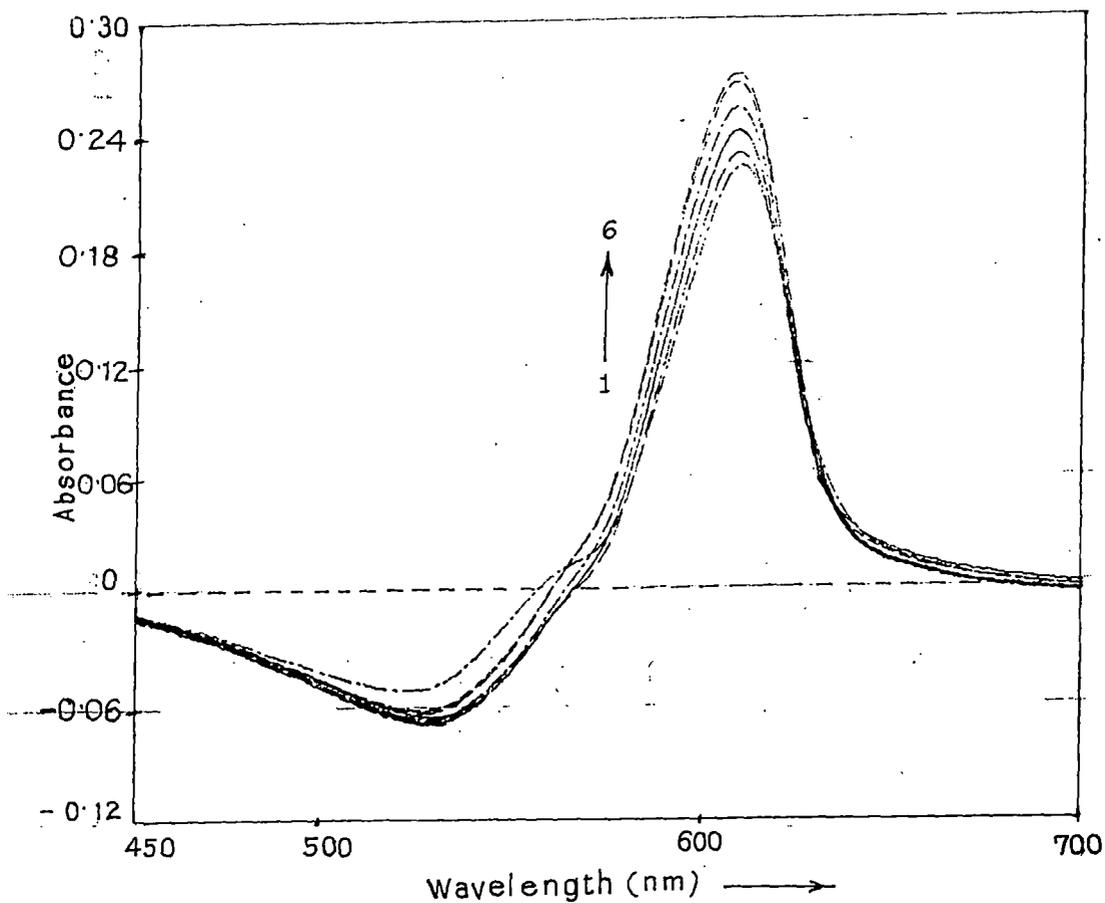


Fig. 47(d). The difference Spectra of Cresyl violet Acetate and SDS against CVA in water at 30°C. Concentration of CVA $4 \times 10^{-5} \text{ mol. dm}^{-3}$ and concentration of SDS ($10^{-2} \text{ mol. dm}^{-3}$): (1) 0.40 (2) 0.60 (3) 1.00 (4) 1.50 (5) 2.00 (6) 3.00. The broken line represents the set of curves when the concentration of SDS is below $5 \times 10^{-4} \text{ mol. dm}^{-3}$.

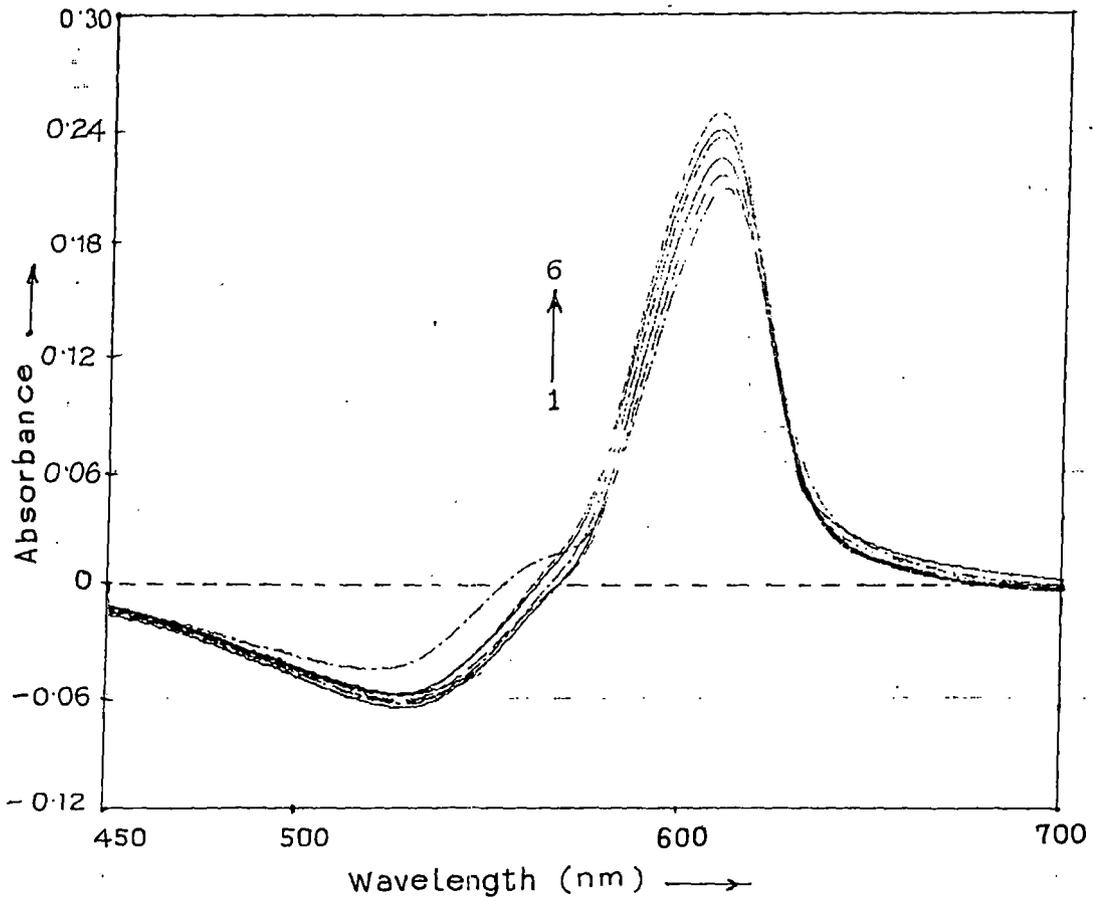


Fig. 47(b). The difference Spectra of Cresyl violet Acetate and SDS against CVA in water at 40°C . Concentration of CVA $4 \times 10^{-5} \text{ mol. dm}^{-3}$ and concentration of SDS ($10^{-2} \text{ mol. dm}^{-3}$) : (1) 0.40 (2) 0.60 (3) 1.00 (4) 1.50 (5) 2.00 (6) 3.00. The broken line represents the set of curves when the concentration of SDS is below $5 \times 10^{-4} \text{ mol. dm}^{-3}$.

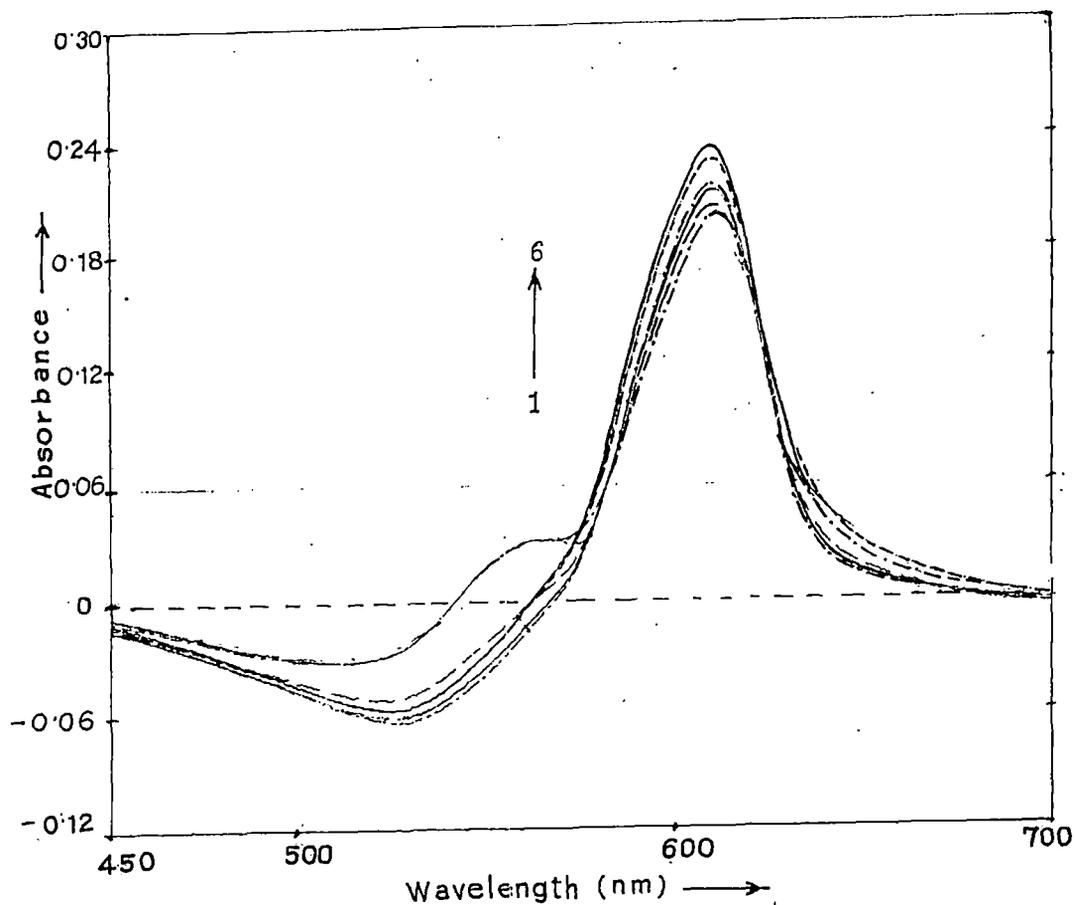


Fig. 47 (c) The difference Spectra of Crysyl violet Acetate and SDS against CVA in water at 50°C . Concentration of CVA $4 \times 10^{-5} \text{ mol. dm}^{-3}$ and concentration of SDS ($10^{-2} \text{ mol. dm}^{-3}$): (1) 0.40 (2) 0.60 (3) 1.00 (4) 1.50 (5) 2.00 (6) 3.00. The broken line represents the set of curves when the concentration of SDS is below $5 \times 10^{-4} \text{ mol. dm}^{-3}$.

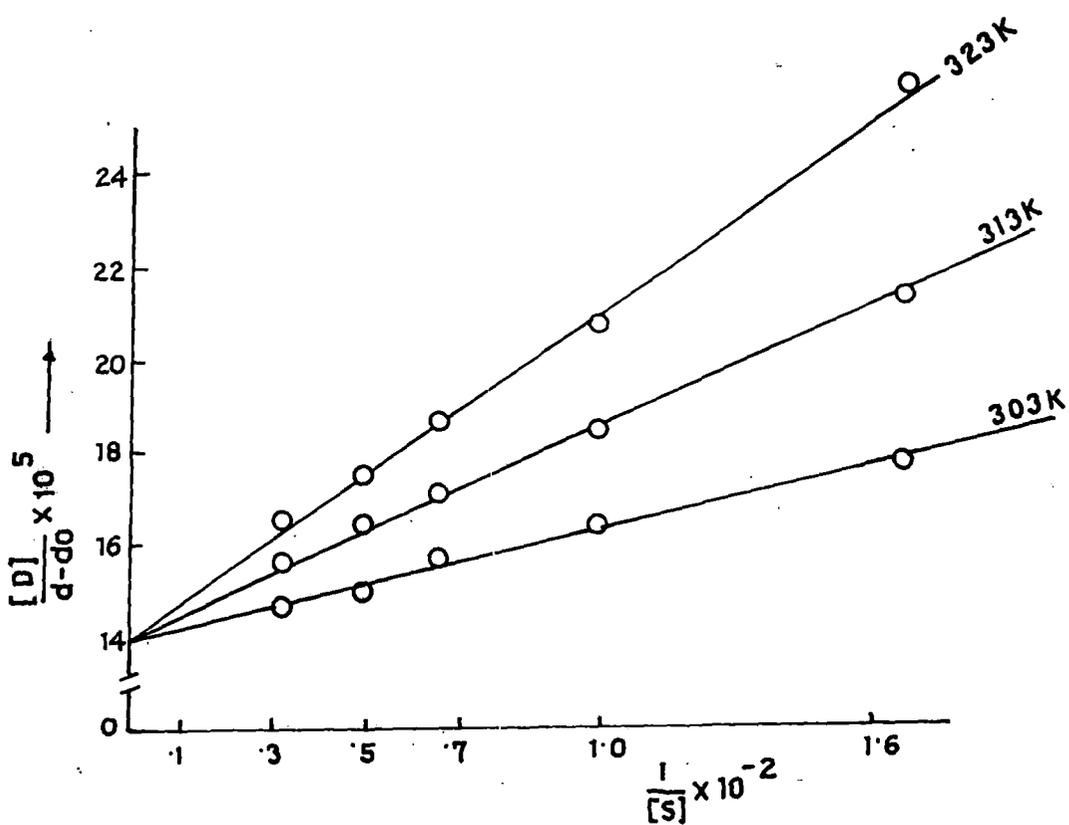


Fig. 48. Spectral determination of equilibrium constant and molar extinction co-efficient of CVA - SDS complex in water at 303K, 313K, 323K using eqn (31). These plots were made by least squares method with standard deviation of 5%.

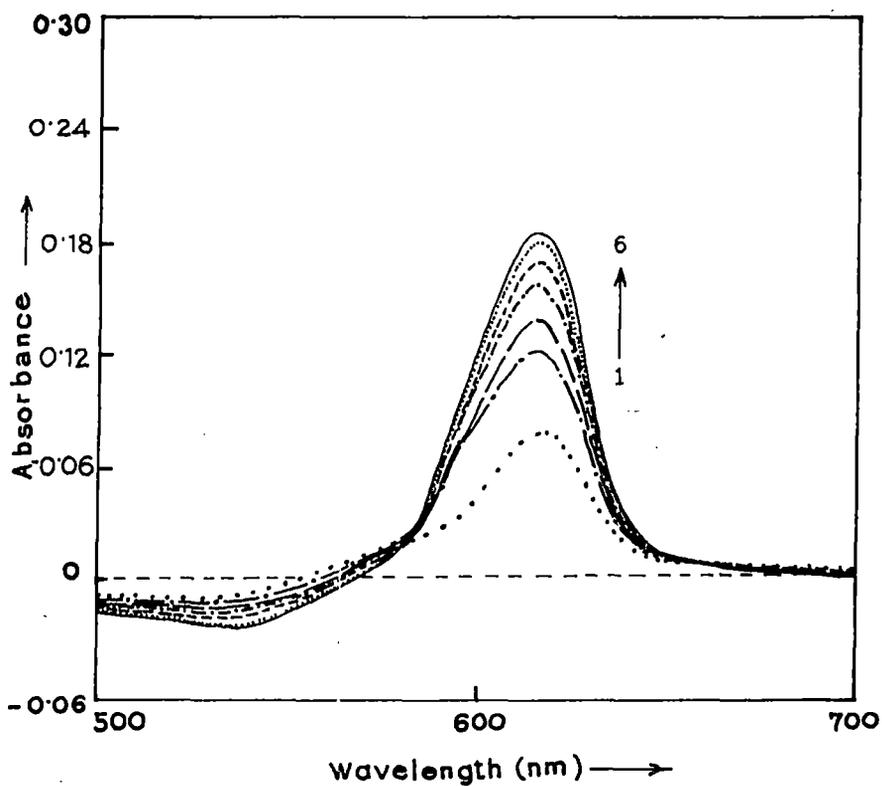


Fig.49 (a) The difference Spectra Cresyl Violet Acetate (CVA) and Triton X-100 against CVA in water at 40°C. Concentration of CVA 2×10^{-5} mol. dm^{-3} and concentration of Triton X-100 (10^{-2} mol. dm^{-3}) : (1) 0.20 (2) 0.30 (3) 0.50 (4) 1.50 (5) 4.00 (6) 6.00. The broken line represents the set of curves when the concentration of Triton X - 100 is below 2.5×10^{-4} mol. dm^{-3} .

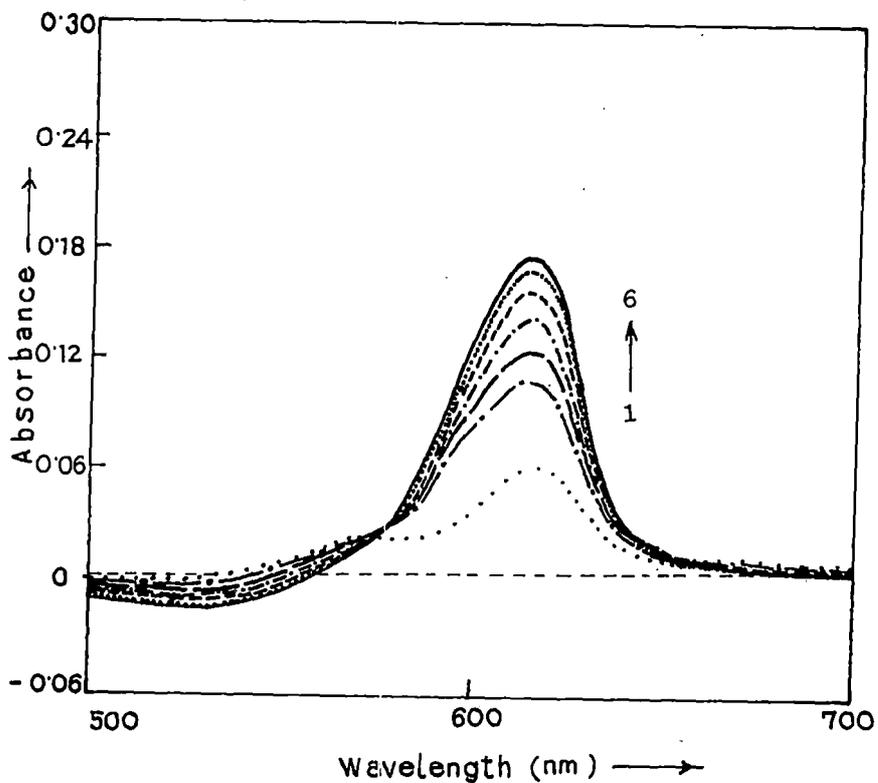


Fig.49(b). The difference Spectra Cresyl Violet Acetate (CVA) and Triton X-100 against CVA in water at 50°C . Concentration of CVA $2 \times 10^{-5} \text{ mol. dm}^{-3}$ and concentration of Triton X-100 ($10^{-2} \text{ mol. dm}^{-2}$) : (1) 0.20 (2) 0.30 (3) 0.50 (4) 1.50 (5) 4.00 (6) 6.00. The broken line represents the set of curves when the concentration of Triton X-100 is below $2.5 \times 10^{-4} \text{ mol. dm}^{-3}$.

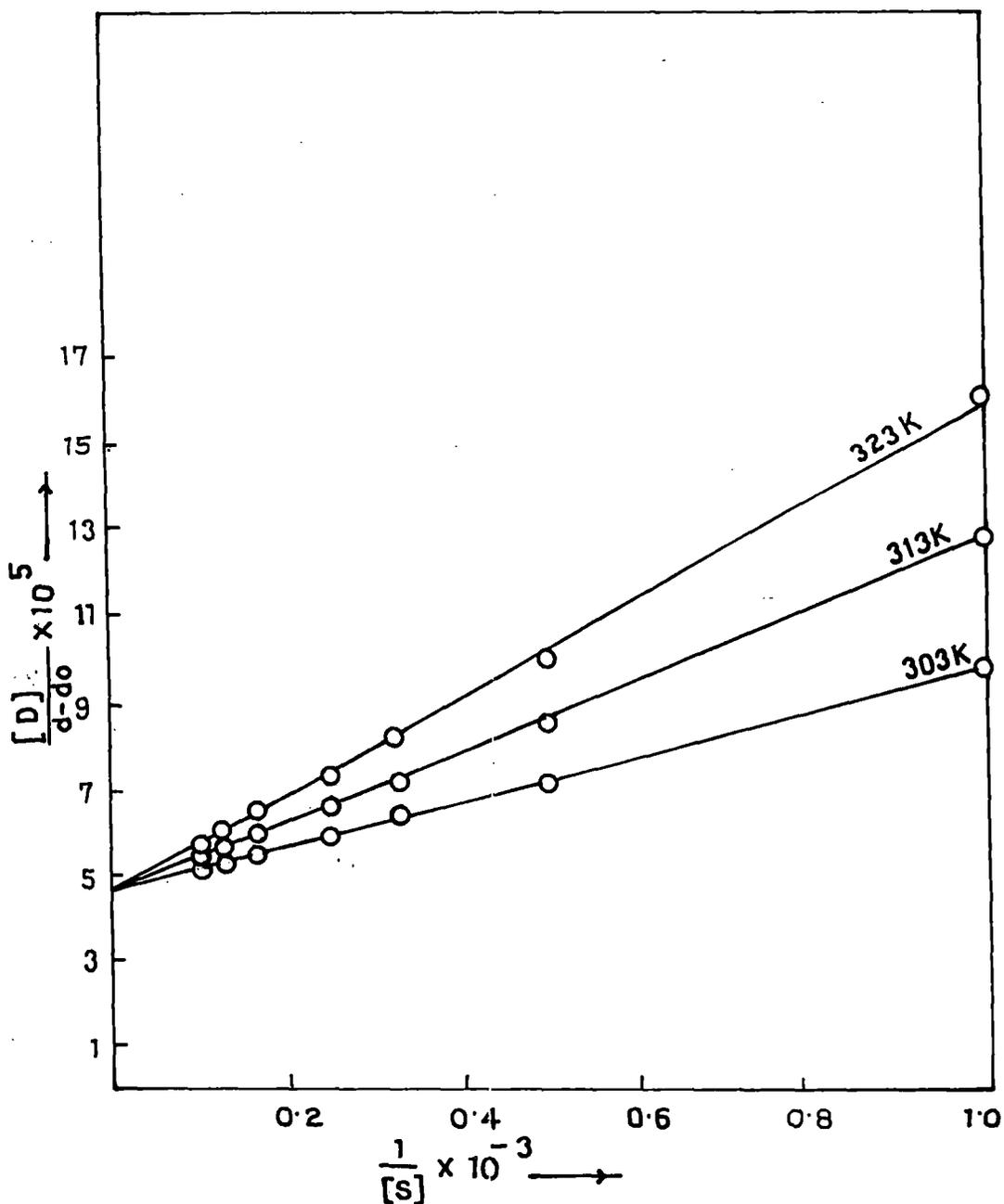
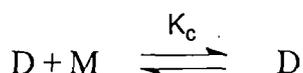


Fig. 50. Spectral determination of equilibrium constant and molar extinction co-efficient of CVA - Triton X - 100 complex in water at 303K, 313K, 323K using eqn. (31) These plots were made by least squares method with standard deviation of 5%.

surfactant micelles passes through a isobestic point (575nm) supporting the formation of a 1:1 dye-micellar complex above the cmc. The spectral properties are shown in Table 19. Dye-surfactant charge transfer complex formation can be assumed to follow the equilibrium



Where D, M, DM and K_c represent the dye, micelle, dye-micelle complex and the complexation constant respectively.

For a 1:1 complex, the equilibrium constant K_c and molar extinction coefficient (ϵ) have been determined using the Ketelaar's equation (Benesi-Hildebrand equation in the modified form) at three different temperatures (303K, 313K, 323K). The plot of $[CVA]_0 / d - d_0$ against $1 / [SDS]_0$ at three different temperatures were found to be linear in all cases confirming 1:1 complex formation (fig. 50). The extent of CVA - Triton X - 100 interaction in the aqueous medium (K_c) and ϵ_c are calculated from the slope and intercept of the above plot. The thermodynamic quantities of the complexes are shown in Table 20. The exothermic process exhibits a negative entropy change and the release of heat leads to a stable organized state.

The thermodynamic and spectrophotometric properties of these complexes suggest that CVA forms a strong charge - transfer (CT) or electron donor - acceptor (FDA) complex with Triton X - 100 (above cmc).

Aqueous CVA - Tween 80 System (above cmc)

A remarkable change in the absorption spectra of CVA was noticed when the Tween 80 concentration was above the cmc. However, at Tween 80 concentration below cmc no significant change in the spectra was observed. The difference spectra of CVA ($5 \times 10^{-5}M$) and Tween 80 ($1.1 \times 10^{-3}M$ to $8.0 \times 10^{-3}M$)

³M) are shown in the figs. 51a, 51b and 51c. The spectra showed shifted absorption band to a longer wave length, i.e. at 615nm with one isobestic point at 580nm (λ_{\max} for CVA is 585 nm). The spectral properties are shown in Table 19. The presence of sharp isobestic point and spectral shift are attributed to 1:1 molecular complex formation between CVA and Tween 80. The equilibrium constant (K_c) as well as molar extinction co-efficient (ϵ_c) of the CVA - Tween 80 interaction were evaluated using the Ketelaar's equation (Benesi - Hildebrand equation). In this case the complex absorbs at a wavelength where the surfactant is completely transparent. The plots of $[D]_0/d_0$ against $[S]_0^{-1}$ (symbols have their usual meanings) were found to be a linear in all cases confirming 1:1 complex formation. A representative plot is shown in fig. 52 for the CVA- Tween 80 system at three different temperatures (293K, 303K, 313K). From the slopes and the intercepts, K_c and ϵ_c of the CVA-Tween 80 complex were calculated in aqueous medium.

The thermodynamic parameters were calculated from the temperature dependence of the equilibrium constants by the usual method. The results are presented in the Table 20.

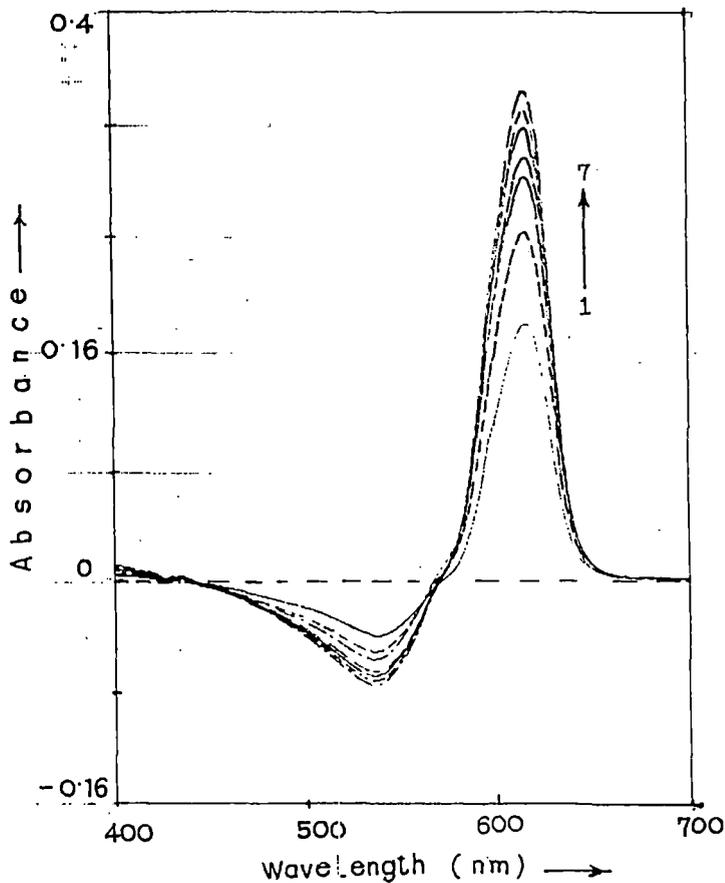


Fig. 51(a) The difference Spectra of CVA and Tween-80 against CVA in water at 20°C. Concentration of CVA 5×10^{-5} mol. dm^{-3} and Concentration of Tween-80 (10^{-3} mol. dm^{-3}) : (1) 1.10 (2) 2.20 (3) 3.20 (4) 4.40 (5) 5.50 (6) 6.60 (7) 8.80. The broken line represents the set of curves when the Concentration of Tween-80 is below 1.0×10^{-5} mol. dm^{-3} .

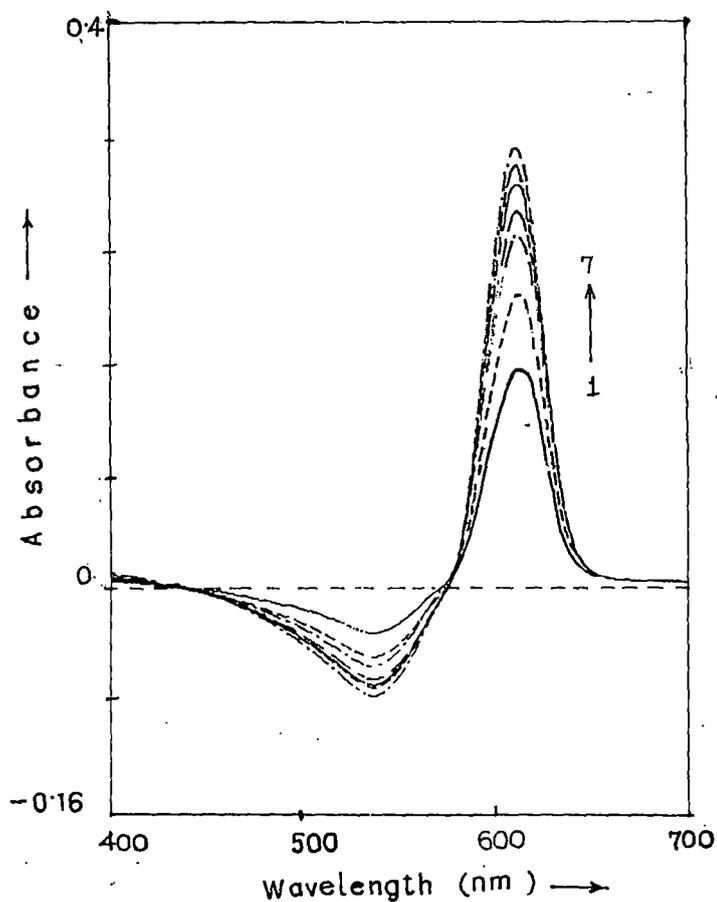


Fig. 51 (b). The difference Spectra of CVA and Tween-80 against CVA in water at 30°C. Concentration of CVA 5×10^{-5} mol. dm^{-3} and Concentration of Tween-80 (10^{-3} mol. dm^{-3}) : (1) 1.10 (2) 2.20 (3) 3.20 (4) 4.40 (5) 5.50 (6) 6.60 (7) 8.80. The broken line represents the set of curves when the Concentration of Tween-80 is below 1.0×10^{-5} mol. dm^{-3} .

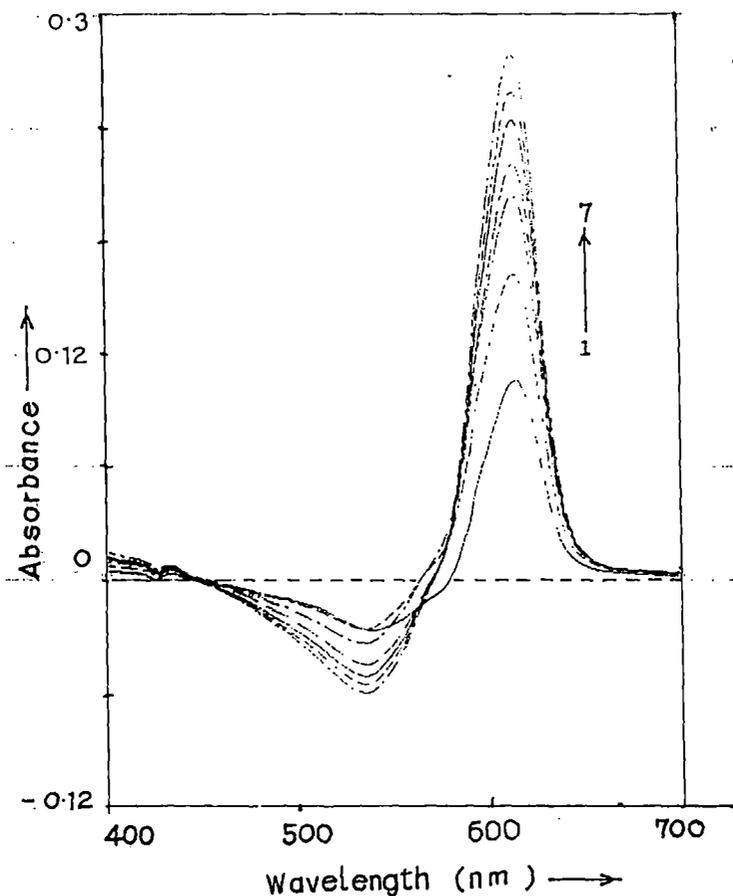


Fig. 51(c). The difference Spectra of CVA and Tween-80 against CVA in water at 40°C . Concentration of CVA $5 \times 10^{-5} \text{ Mol. dm}^{-3}$ and Concentration of Tween-80 ($10^{-3} \text{ mol. dm}^{-3}$) : (1) 1.10 (2) 2.20 (3) 3.20 (4) 4.40 (5) 5.50 (6) 6.60 (7) 8.80. The broken line represents the set of curves when the Concentration of Tween-80 is below $1.0 \times 10^{-5} \text{ mol. dm}^{-3}$.

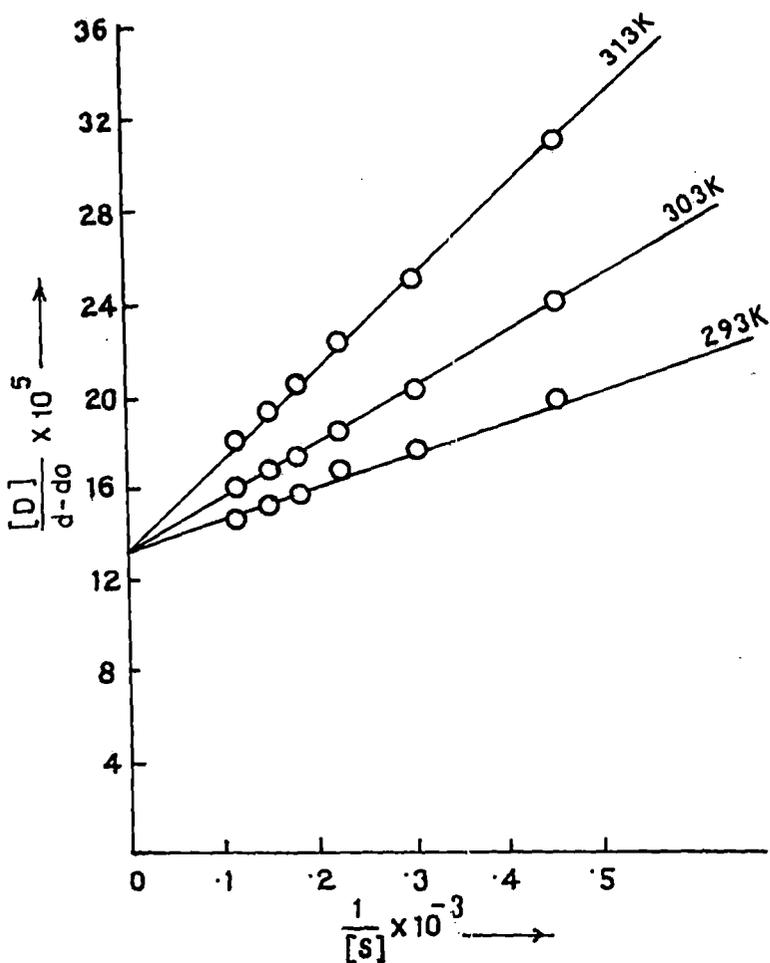


Fig. 52. Spectral determination of equilibrium constant and molar extinction co-efficient of CVA - Tween-80 complex in water at 293K, 303K, and 313K using eqn. (31). These plots were made by least squares method with standard deviation of 5%.

Table-19 : Spectral properties of oxazine dyes and their complexes with an anionic and non ionic surfactants in super micellar concentration ranges.

Dye	Surfactant	Temperature(K)	λ_{\max} of the dye (± 1) nm	ϵ_{\max} of the dye (± 50)m ² M ⁻¹	λ_{\max} of the complex(± 2)nm	λ_{iso} of the complex(± 1)nm
	SDS	303	585	2400	610	625
CVA	Triton X-100	303	585	2100	615	575
	Tween-80	293	585	2100	615	580

Table -20: Equilibrium Constants and other thermodynamic parameters of the super micellar interaction products of oxazine dyes with Anionic and non-ionic surfactants.

Dye	Surfactant	pH	Temperature (K)	Shifting of λ_{max}	$K_c (M^{-1})$	$-\Delta G$ kJM^{-1}	$-\Delta H$ kJM^{-1}	$-\Delta S$ $JM^{-1}K^{-1}$
CVA	SDS	5.60	303	585 nm to 610nm	616.0	16.18	41.57	84.60
			313		308.0	14.91		
			323		196.0	14.17		
CVA	Triton X-100	4.70	303	585 nm to 615nm	940.0	17.25	35.63	60.37
			313		611.0	16.69		
			323		427.3	16.27		
CVA	Tween-80	5.60	293	585nm to 615nm	900.0	16.56	45.35	96.66
			303		561.0	15.94		
			313		330.0	15.09		

4.3.3 Interaction of Cresyl fast violet (CFV) in aqueous solution with SDS, Triton X – 100 and Tween 80.

Aqueous CFV – SDS System (below cmc)

The visible absorption spectra of cresyl fast violet, CFV (2.0×10^{-5} M) in aqueous media in absence and presence of SDS are shown in fig 53. The concentration of SDS in the study of interaction of CFV with SDS are varied from 0.5×10^{-5} M to 2×10^{-5} M. The spectral behaviour of CFV – SDS system are similar to those of CVA in SDS. The $\lambda_{\text{isobestic}}$ and λ_{max} were found to be 622 nm and 585 nm respectively. The spectral properties are shown in Table 21. For a fixed concentration of CFV (2.0×10^{-5} M) the absorbance at 585 nm decreases with the increase in concentration of SDS. The absorbance on the higher wavelength (around 640nm) side of the CFV band increases with the increase in concentration of SDS. This is attributed to the protonation of dye under the present condition. Moreover, a new shoulder appears at 525nm. The opposite charge on the dye and the surfactant is the primary requirement for this interaction. Therefore, it can be suggested that as the oppositely charged ions, viz, CFV^+ and SDS^- come closer to each other due to electrostatic attraction, the hydrophobic nature of the large organic ions and the hydrogen-bonded water structure enforce them to form closely associated ion pairs, $\text{CFV}^+ \text{SDS}^-$. The equilibrium constant values are obtained by using the Ketelaar's equation [eqn. 31].

The plots of $[\text{CFV}]_0 / (d-d_0)$ Vs $1/[\text{SDS}]_0$ at various temperatures yielded straight lines in a wide range of concentration of SDS (Fig 54). The true equilibrium constant values and the thermodynamic parameters are given in Table 22 at pH 5.25. The high values of the ΔH° and ΔS° can be attributed to the formation of ionic hydrogen bonds during molecular interaction.¹²² The positive entropy change suggests that the free dye and surfactant ions are more ordered

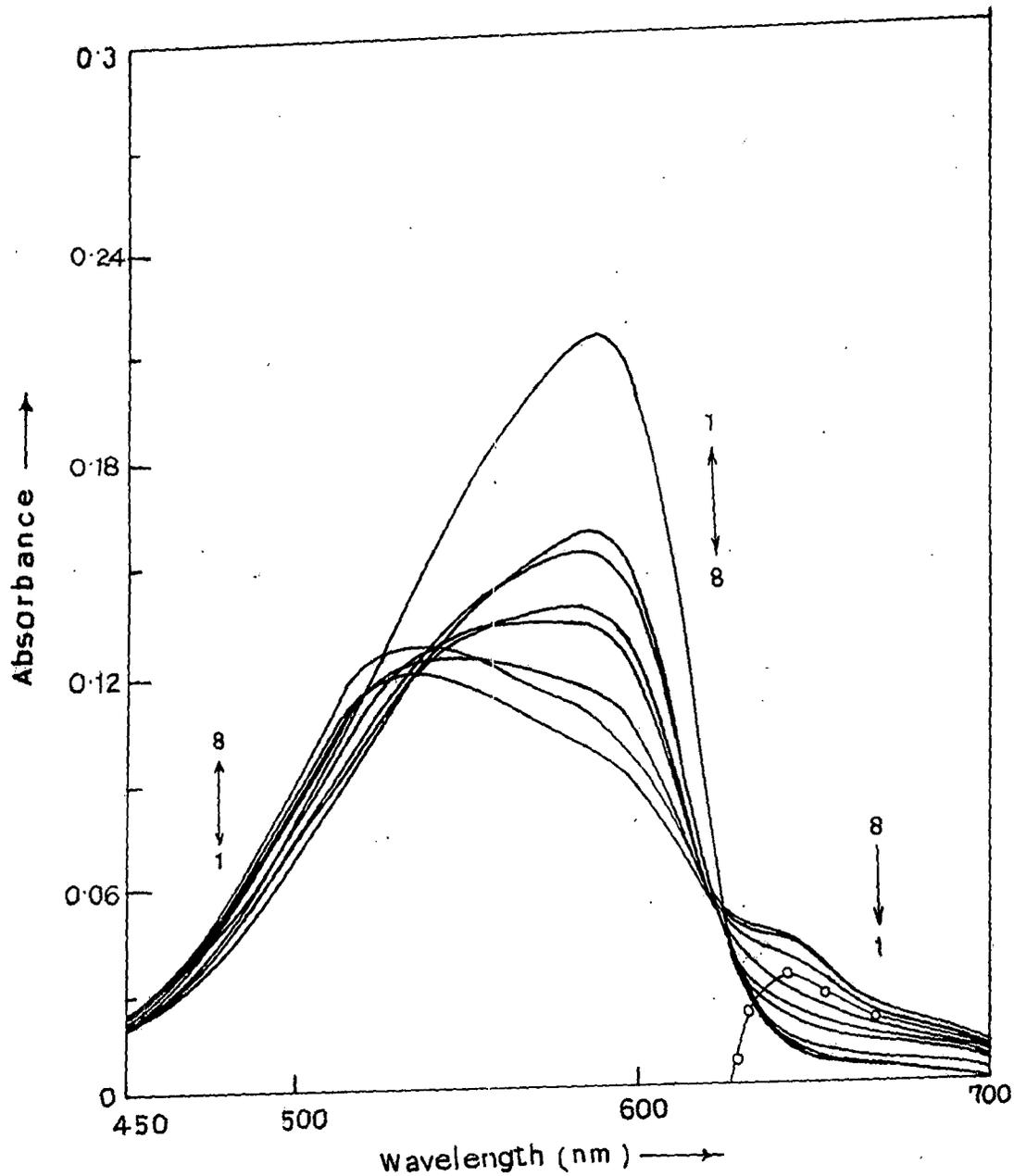


Fig. 53. Effect of variation in concentration of SDS on the spectra of CFV at 30°C $[\text{CFV}] = 2 \times 10^{-5} \text{ M}$ $[\text{SDS}] \times 10^5 \text{ M} =$ (1) 0.00 (2) 0.50 (3) 0.80 (4) 1.00 (5) 1.20 (6) 1.50 (7) 1.80 (8) 2.00; $\circ-\circ-\circ$, difference spectra of (8) and (1).

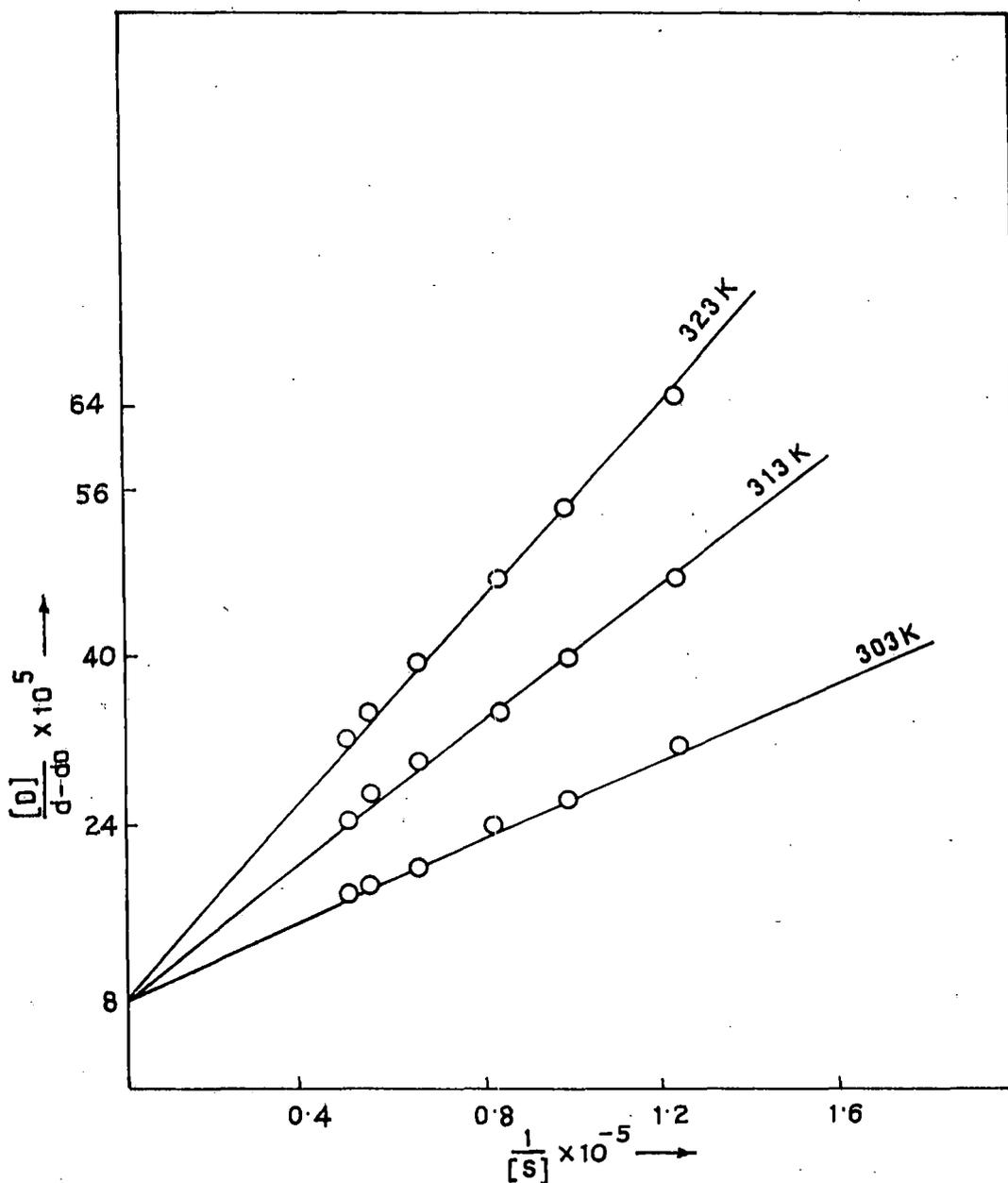


Fig. 54. Spectral determination of Equilibrium constant and molar extinction coefficient of CFV - SDS Complex in water at 303K, 313K, 323K using Eqn. (31). These plots were made by least square method with standard deviation of 5%.

Table - 21 : Spectral properties of oxazine dyes and their protonated ions pairs (complexes) with SDS in sub micellar concentration ranges at different temperatures.

Dye	Temperature (K)	λ_{\max} of the dye (± 1) nm	ϵ_{\max} of the dye (± 50) m^2M^{-1}	λ_{iso} of the complex (± 1) nm	ϵ_{iso} (± 100) m^2M^{-1}	λ_{\max} of the complex (± 2) nm	ϵ_{\max} of complex (± 100) m^2M^{-1}
CFV	303	585	1080	622	270	640	240
	313	585	1020	622	210	640	150
	323	585	990	622	90	640	60

Table –22: Equilibrium constants and the other Thermodynamic parameters of the sub micellar interaction product of oxazine dye with an anionic surfactant.

Dye	Surfactant	PH	Temperature (K)	K_c (M^{-1})	$K/C = K_c/[H^+]$ (M^{-2})	$-\Delta G$ kJM^{-1}	$-\Delta H$ kJM^{-1}	ΔS $JM^{-1}K^{-1}$
CFV	SDS	5.25	303	44.44×10^3	7.90×10^9	57.44		
			313	24.61×10^3	4.38×10^9	57.80	38.60	61.80
			323	16.66×10^3	2.96×10^9	58.58		

than the protonated ion pair in water due to the tendency of water to retain its ordered structure. Positive entropy changes in case of hydrophobic interactions have been reported.^{123,124}

Aqueous CFV – SDS System (above cmc)

In the presence of SDS above its cmc, the absorption spectrum of CFV shows interesting changes. A new band at 615 nm appears with increasing intensity as the SDS concentration increases (fig 55). A sharp isobestic point at 565nm indicates existence of an equilibrium between CFV (4.0×10^{-5} M) and SDS (concentration vary from 4×10^{-3} M to 3×10^{-2} M) via incorporation of dye molecules into the SDS micelles. The spectral properties are shown in Table 23. The equilibrium constants at three different temperatures (303K, 313K and 323K) of the CFV – SDS complex were evaluated by using the Ketelaar's equation (Benesi Hildebrand equation in the modified form) (Eqn 31). The plot of $[\text{CFV}]_0/d-d_0$ against $1/[\text{SDS}]_0$ was found to be linear in all cases confirming 1:1 complex formation (Fig. 56). The thermodynamic parameters were calculated from the temperature dependence of the equilibrium constant by the usual method. (Table 24)

Aqueous CFV – Triton X 100 system (above cmc)

As has already been mentioned that the visible absorption spectra of CFV (2.0×10^{-5} M) in aqueous solution exhibit an absorption maximum at 585nm at 303K. In the presence of Triton X 100, above its cmc a change occurs, the spectral band shifts from 585nm to 615nm with increasing intensity as the Triton X 100 concentration increases due to incorporation of dye into the surfactant micelles (fig. 57). Concentration of Triton X 100, a nonionic surfactant, was varied from 2.0×10^{-3} M to 1.5×10^{-2} M. As was the case of other dyes also, no change in the spectra of CFV was observed if the surfactant present in the mixture at a concentration below its cmc. The spectral properties are shown in

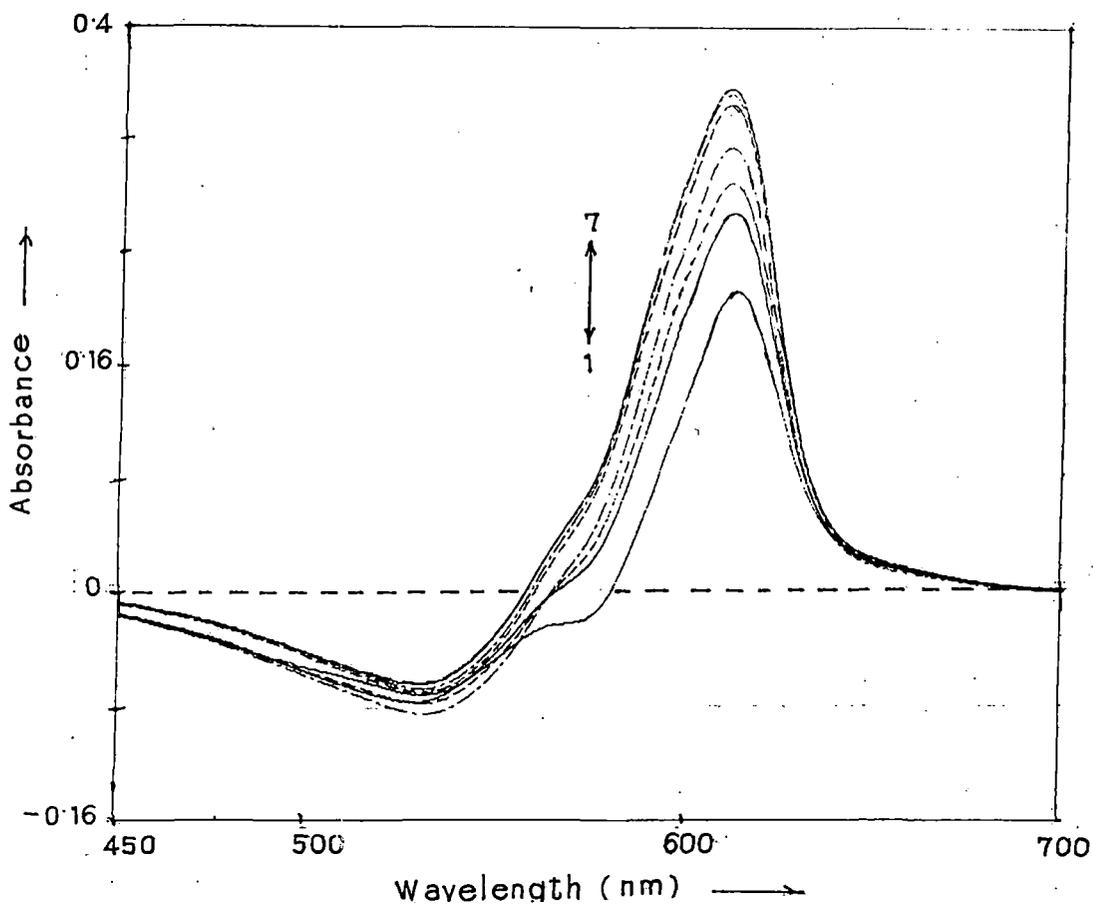


Fig.55. The difference Spectra Creyls Fast Violet (CFV) and SDS against CFV in water at 30°C. The concentration of CFV $4 \times 10^{-5} \text{ mol. dm}^{-3}$ and concentration of SDS ($10^{-2} \text{ mol. dm}^{-3}$) : (1) 0.40 (2) 0.50 (3) 0.60 (4) 1.00 (5) 1.50 (6) 2.00 (7) 3.00. The broken line represents the set of curves when the concentration of SDS is below $5 \times 10^{-4} \text{ mol. dm}^{-3}$.

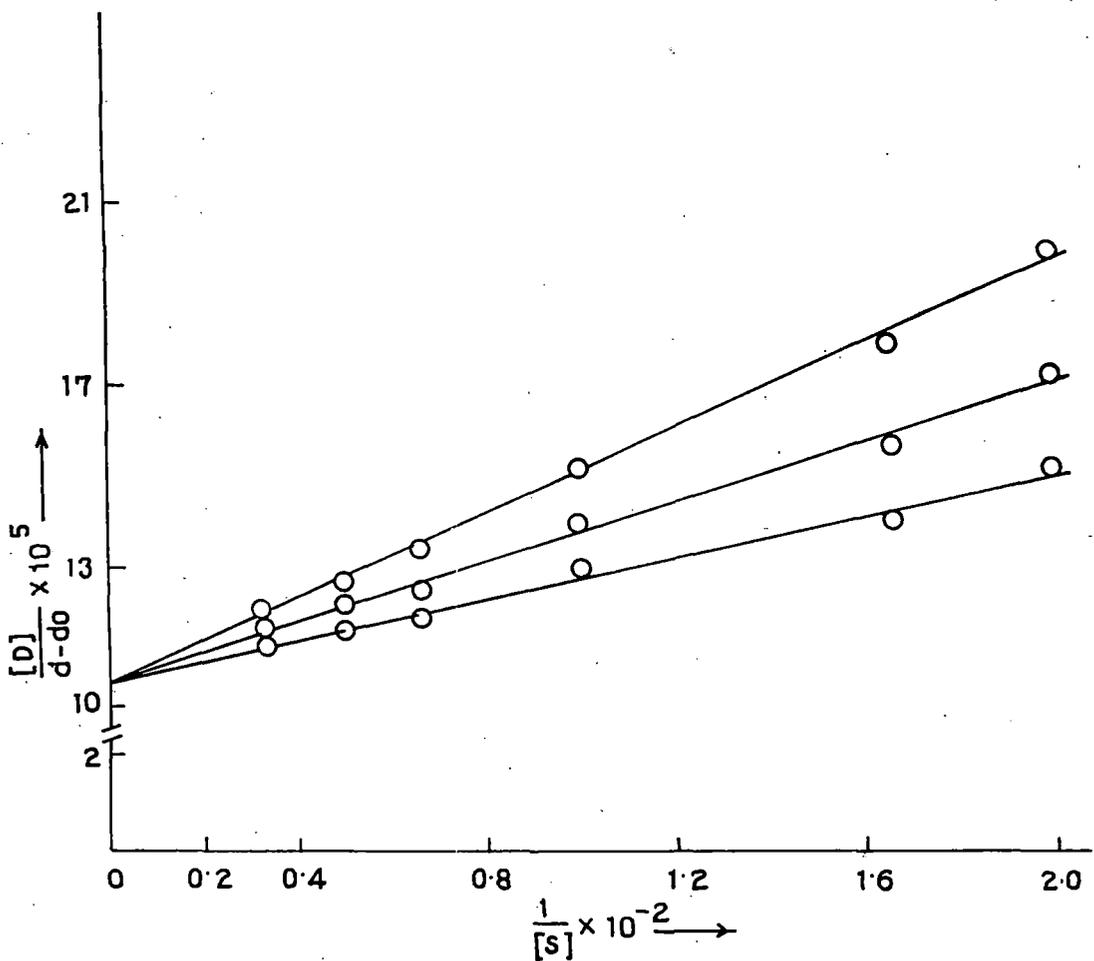


Fig. 56. Spectral determination of equilibrium constant and molar extinction co-efficient of CFV - SDS complex in water at 303K, 313K, 323K using eqn (31). These plots were made by least squares method with standard deviation of 5%.

Table 23. The spectrum of the CFV- Triton X 100 complex formed via charge transfer process passes through a isobestic point at 590 nm, supporting the formation of a 1:1 dye-micellar complex. For a 1:1 complex, the equilibrium constant K_c and molar extinction co-efficient ϵ_c can be determined by using the Ketelaar's equation (Benesi – Hildebrand equation in the modified form) (eqn. 31). The plot of $[CFV]_0/d-d_0$ against $1/[S]_0$ at three different temperatures were found to be linear confirming 1:1 complex formation. The binding constant of CFV – Triton X-100 complex in the aqueous medium K_c and the extinction coefficients were calculated from the slopes and intercept of the above plots (fig.58).The thermodynamic quantities of the complexes were obtained from K_c values at three different temperatures and are given in Table 24.

Aqueous CFV – Tween 80 System (above cmc)

The visible absorption spectra of CFV (2.0×10^{-5} M) in aqueous solution exhibits an absorption maximum at 585nm. In the presence of Tween 80 above its cmc a change occurs in the spectrum. A new band at 620nm appears and intensity increases as the Tween 80 concentration increases (figs. 59a, 59b, 59c) but decreases as the temperature increases. However, no effect of Tween 80 was observed at a concentration below its cmc. The experimental concentration of Tween 80 was varied from 1.0×10^{-3} M to 8.0×10^{-3} M at temperatures of 293K, 303K and 313K. The spectral properties are shown in Table 23. The charge transfer spectra via incorporation of the dye into the surfactant micelles passes through a isobestic point, at 585nm, supporting the view of the formation of a dye micellar complex again. The equilibrium constant K_c , and molar extinction coefficient ϵ_c are determined by using the Ketelaar's equation (Benesi-Hildebrand equation in the modified form) (eqn. 31) at three different temperatures (293K, 303K, 313K) as before. The Plots of $[D]_0/d-d_0$ against $1/[S]_0$ were found to be linear in all cases, confirming 1:1 complex formation, where $[D]_0$ and $[S]_0$ represents the concentration of CFV and the surfactant ,

Tween-80 respectively. A representative plot at three different temperatures (293K, 303K, 313K) is shown in fig 60. From the slope and the intercepts, K_c and ϵ_c of the CFV-Tween 80 complex in aqueous medium were calculated. The thermodynamic parameters and K_c values are presented in the Table 24.

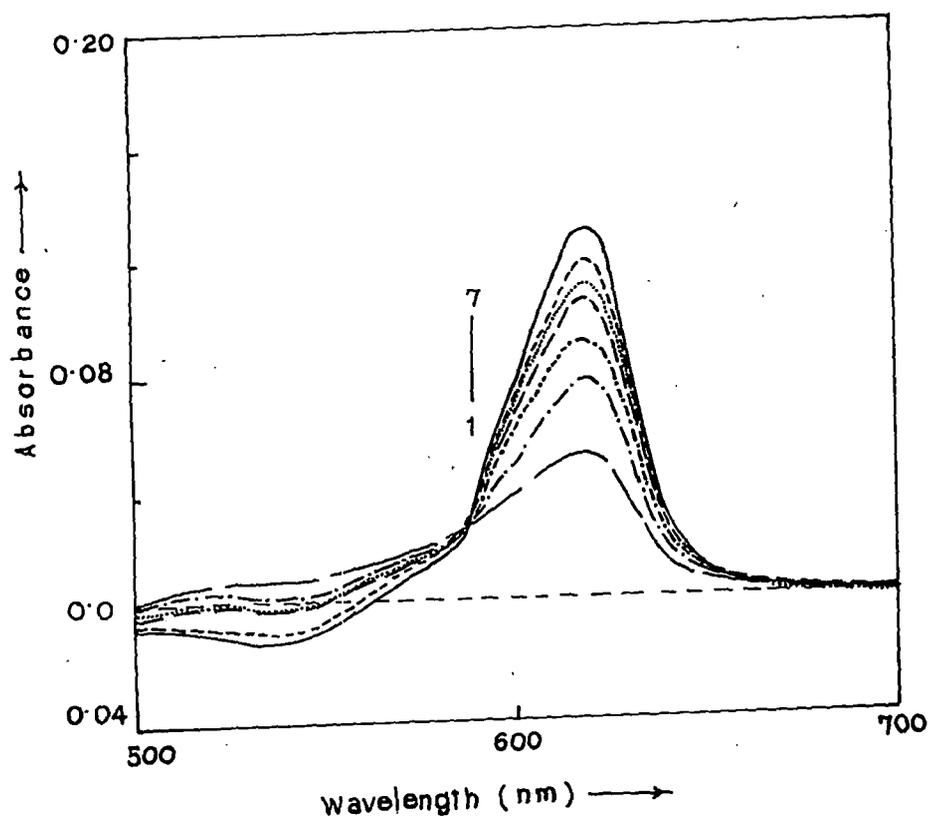


Fig. 57. The difference Spectra of Cresyl Fast Violet (CFV) and Triton X -100 against CFV in water at 30°C. Concentration of CFV 10^{-5} mol. dm^{-3} and Concentration of Triton X - 100 (10^{-3} mol. dm^{-3}) : (1) 2.00 (2) 3.00 (3) 4.00 (4) 6.00 (5) 8.00 (6) 10.00 (7) 15.00. The broken line represents the set of curves when the Concentration of Triton X - 100 is below 2.5×10^{-4} mol. dm^{-3} .

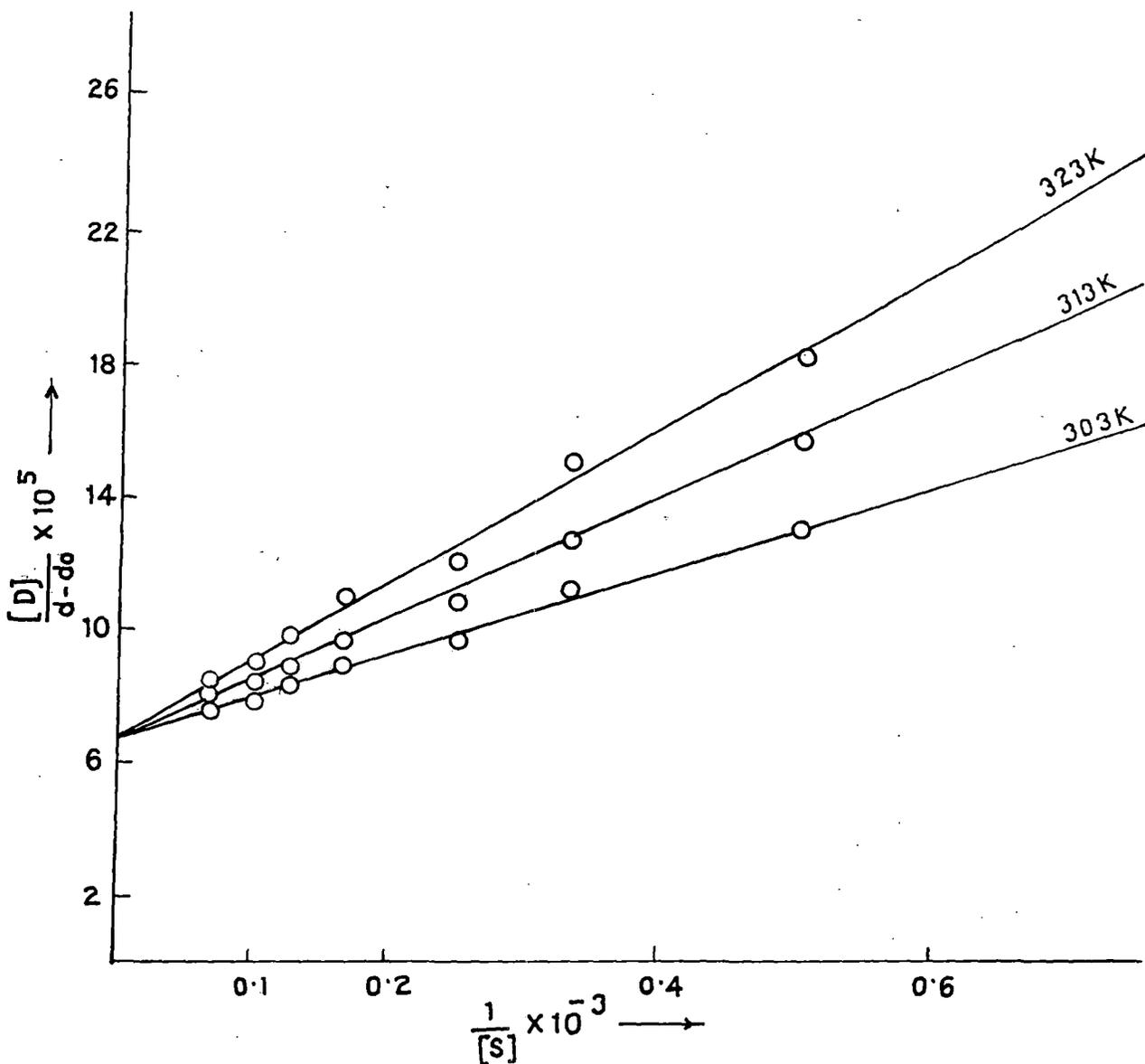


Fig. 58. Spectral determination of equilibrium constant and molar extinction co-efficient of CFV - Triton X - 100 complex in water at 303K, 313K, 323K using eqn.(31) These plots were made by least squares method with standard deviation of 5%.

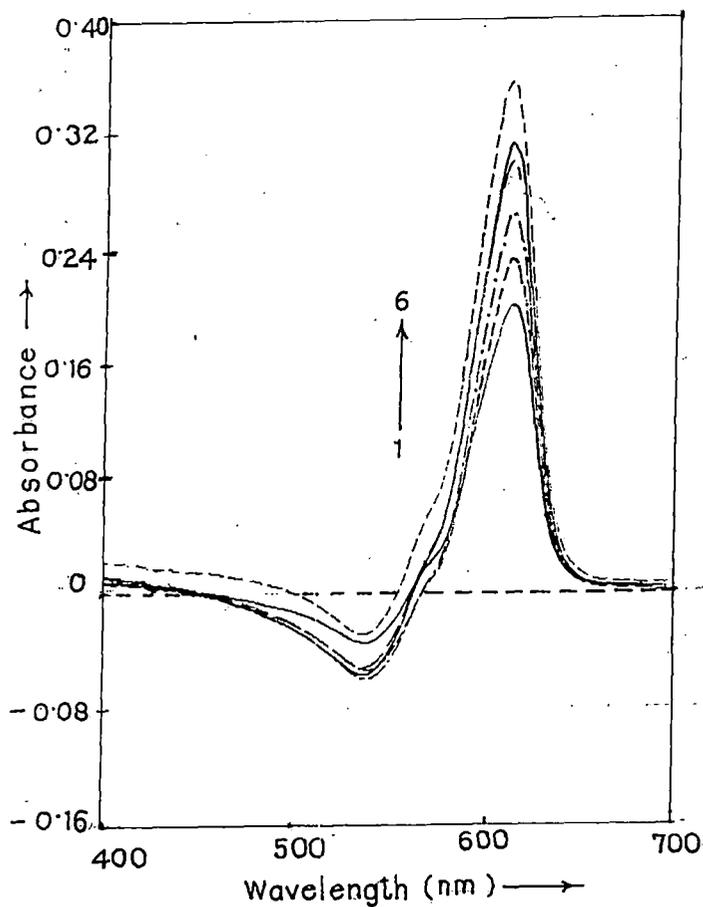


Fig. 59 (a) The difference Spectra of CFV and Tween-80 against CFV in water at 20°C. Concentration of CFV 1×10^{-5} mol. dm^{-3} and Concentration of Tween-80 (10^{-3} mol. dm^{-3}) : (1) 1.00 (2) 2.00 (3) 3.00 (4) 4.00 (5) 5.00 (6) 8.00. The broken line represents the set of curves when the Concentration of Tween-80 is below 1×10^{-5} mol. dm^{-3} .

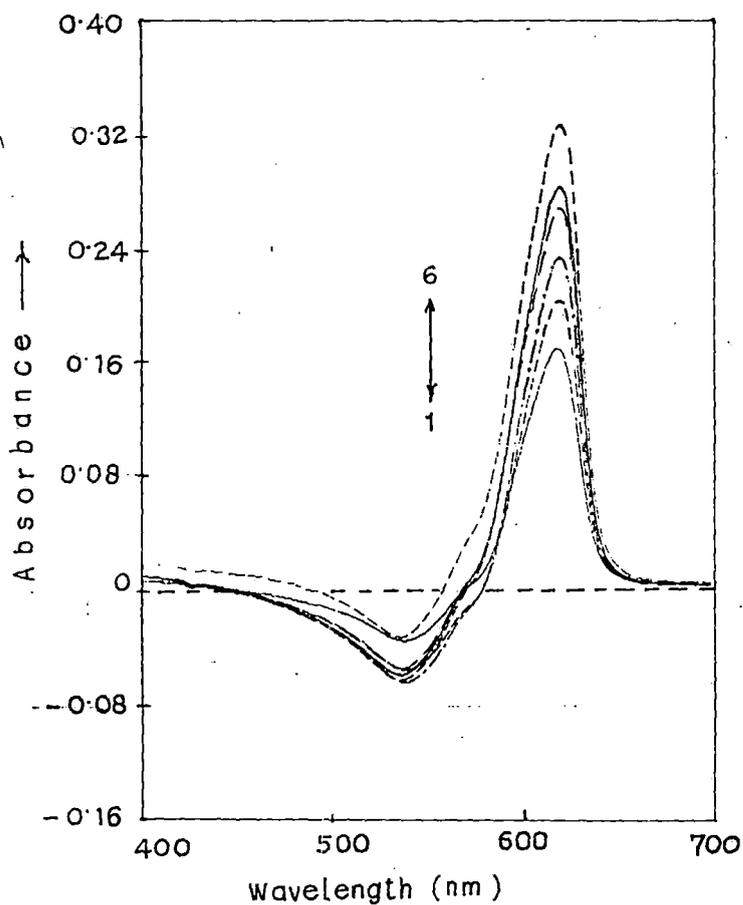


Fig. 59.(b). The difference Spectra of CFV and Tween-80 against CFV in water at 30°C. Concentration of CFV 1×10^{-5} mol. dm^{-3} and Concentration of Tween-80 (10^{-3} mol. dm^{-3}): (1) 1.00 (2) 2.00 (3) 3.00 (4) 4.00 (5) 5.00 (6) 8.00. The broken line represents the set of curves when the Concentration of Tween-80 is below 1×10^{-5} mol. dm^{-3} .

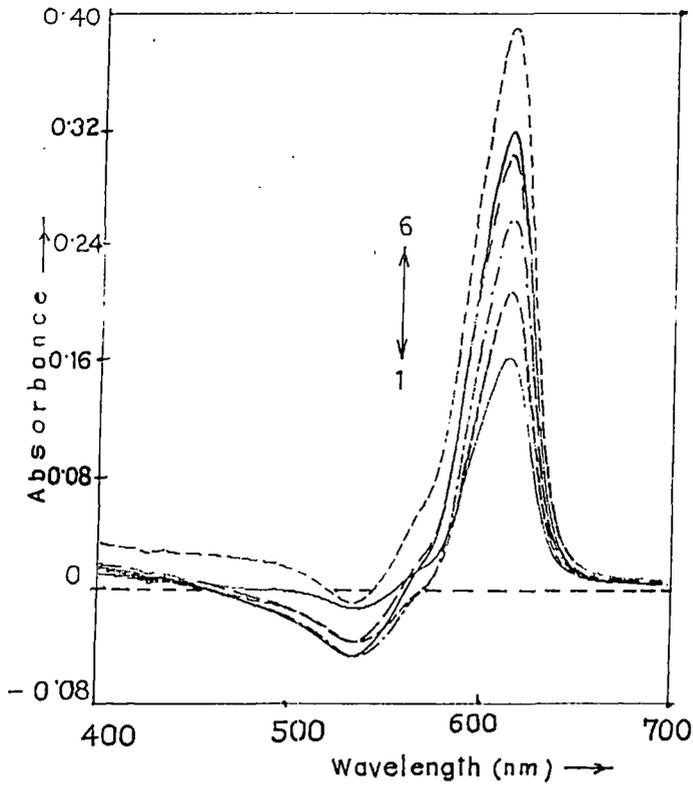


Fig. 59(c). The difference Spectra of CFV and Tween-80 against CFV in water at 40°C. Concentration of CFV 1×10^{-5} mol. dm^{-3} and Concentration of Tween-80 (10^{-3} mol. dm^{-3}) : (1) 1.00 (2) 2.00 (3) 3.00 (4) 4.00 (5) 5.00 (6) 8.00. The broken line represents the set of curves when the Concentration of Tween-80 is below 1×10^{-5} mol. dm^{-3} .

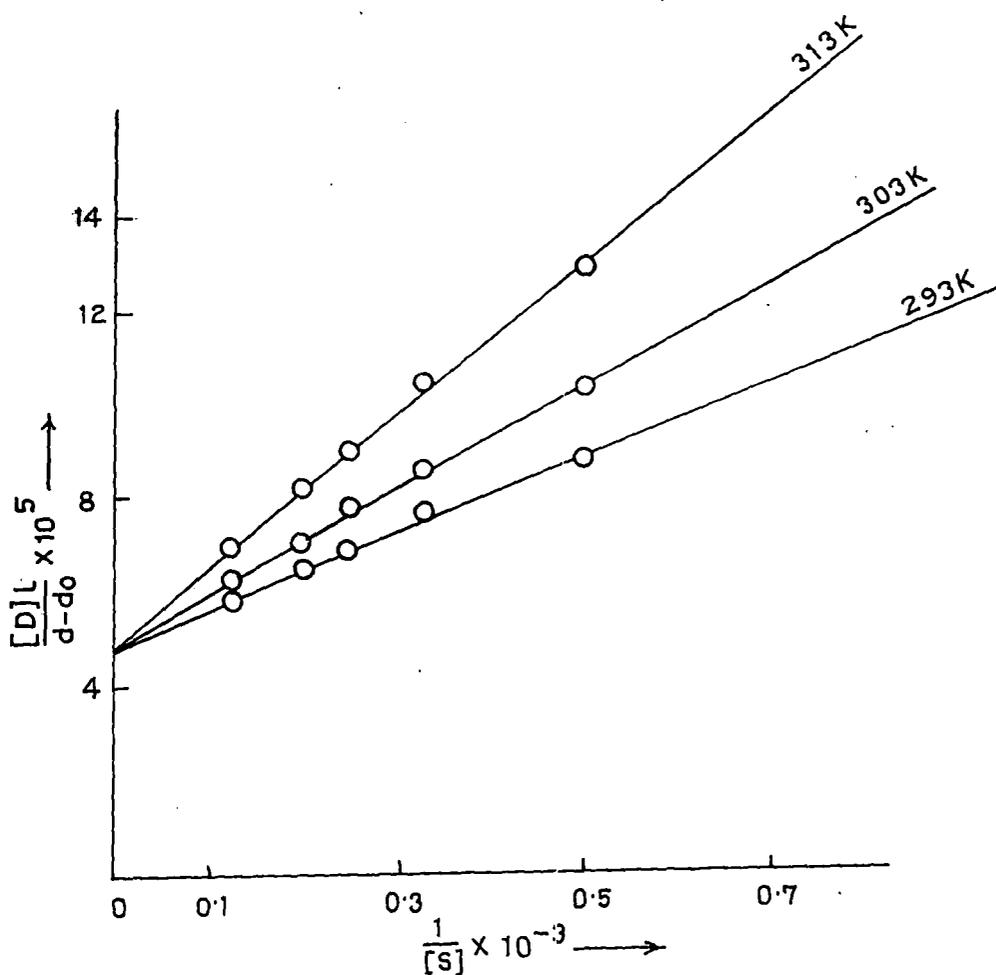


Fig. 60 . Spectral determination of equilibrium constant and molar extinction co-efficient of CFV - Tween-80 complex in water at 293K, 303K and 313K using eqn. (31). These plots were made by least squares method with standard deviation of 5%.

Table-23: Spectral properties of oxazine dyes and their complexes with an anionic and non ionic surfactants in super micellar concentration ranges.

Dye	Surfactant	Temperature(K)	λ_{\max} of the dye (± 1) nm	ϵ_{\max} of the dye (± 50) m^2M^{-1}	λ_{\max} of the complex(± 2)nm	λ_{iso} of the complex (± 1)nm
	SDS	303	585	1080	615	645
CFV	Triton X-100	303	585	490	615	590
	Tween-80	293	585	990	620	585

Table – 24: Equilibrium Constants and other thermodynamic parameters of the super micellar interaction products of oxazine dyes with Anionic and non-ionic surfactants.

Dye	Surfactant	pH	Temperature (K)	Shifting of λ_{\max}	$K_c (M^{-1})$	$-\Delta G$ kJM^{-1}	$-\Delta H$ kJM^{-1}	$-\Delta S$ $JM^{-1}K^{-1}$
CFV	SDS	5.50	303	585 nm to 610nm	462.0	15.45	41.57	85.33
			313		324.5	15.04		
			323		190.9	14.10		
CFV	Triton X-100	5.00	303	585 nm to 615nm	578.0	16.02	33.26	56.52
			313		374.0	15.42		
			323		294.6	15.27		
CFV	Tween-80	5.68	293	585 nm to 615nm	685.0	15.90	29.69	47.49
			303		432.0	15.28		
			313		240.0	14.72		

4.3.4 Interaction of Brilliant Cresyl Blue (BCB) in aqueous solution with SDS, Triton X – 100 and Tween – 80.

Aqueous BCB – SDS System (below cmc)

The visible absorption spectra of BCB ($2.0 \times 10^{-5}M$) in aqueous media without SDS and with SDS (below cmc) are shown in fig. 61. As the concentration of SDS increases from $0.6 \times 10^{-5}M$ to $4.0 \times 10^{-5}M$, which is far below its cmc, the intensity of BCB spectrum decreases. The spectral behaviour of BCB – SDS are similar to those of CVA – SDS system. The spectral properties are shown in Table 25. The isobestic point and the λ_{max} are found to be 670nm and 625nm respectively. For a fixed concentration of BCB ($2.0 \times 10^{-5}M$), the absorbance at 625nm is decreased with the increase in concentration of SDS. The absorbance on the higher wavelength side of the BCB band is quite pronounced and increases with the increase in concentration of SDS. This is attributed to the protonation of dye molecule in presence of SDS. Inspection of the differences in absorbances of the BCB bands in the presence and absence of SDS reveals that the difference passes through a maximum near 700 nm. On increasing the concentration of SDS (from $0.6 \times 10^{-5}M$ to $4.0 \times 10^{-5}M$) for a fixed concentration of BCB ($2.0 \times 10^{-6}M$), a series of spectra is obtained, which pass through a sharp isobestic point at 670nm. This modification in spectral feature is attributed to the ion pair formation between the positively charged dye molecule and negatively charged surfactant SDS. Using Katelaar's equation (equation no 31) we obtain the equilibrium constant K_c by plotting $[BCB]_0 / d - d_0$ as a function of $1 / [SDS]_0$ for various temperatures (fig. 62). The plots are straight lines indicating 1:1 type of complex. The true equilibrium constant, K'_c and the thermodynamic parameters are evaluated at pH 5.25 and listed in Table 26.

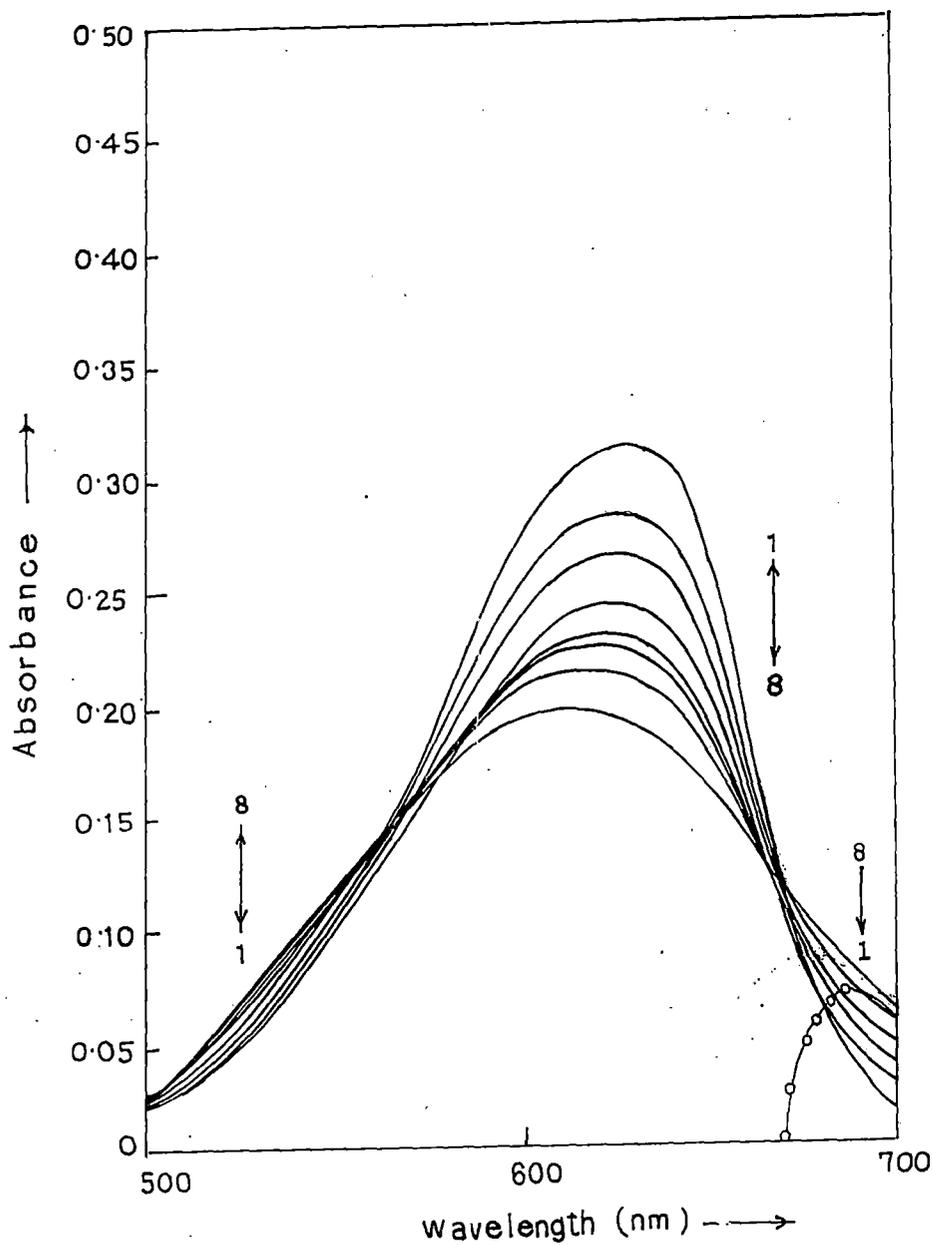


Fig. 61. Effect of variation in concentration of SLS on the spectra of BCB at 30°C ; $[BCB] = 2 \times 10^{-5} M$; $[SDS] \times 10^5 M = (1) 0.00 (2) 0.60 (3) 1.00 (4) 1.50 (5) 2.00 (6) 2.50 (7) 3.00 (8) 4.00$; o o o, difference spectra of ⑧ and ① .

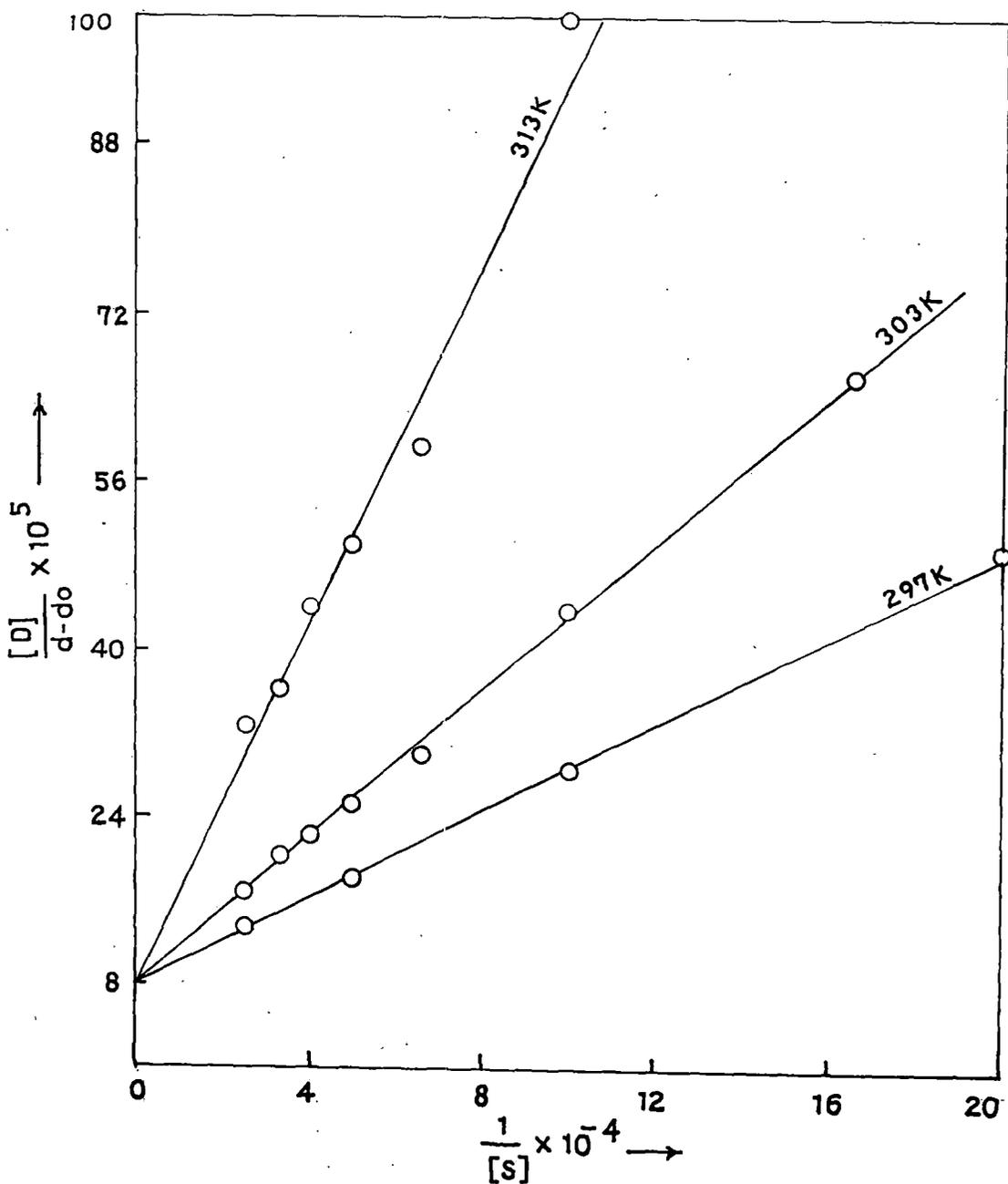


Fig. 62 . Spectral determination of Equilibrium constant and molar extinction coefficient of BCB - SDS Complex in water at 297K, 303K, 313K using Eqn (31). These plots were made by least squares method with standard deviation of 5%.

Table-25: Spectral properties of Oxazine dyes and their protonated ions pairs (complexes) with SDS in sub micellar concentration ranges at different temperatures.

Dye	Temperature (K)	λ_{\max} of the dye (± 1) nm	ϵ_{\max} of the dye (± 50) m^2M^{-1}	λ_{iso} of the complex (± 1) nm	$\epsilon_{\text{iso}}(\pm 100)\text{m}^2\text{M}^{-1}$	λ_{\max} of the complex (± 2) nm	ϵ_{\max} of complex (± 100) m^2M^{-1}
BCB	297	625	1570	670	600	700	400
	303	625	1400	670	550	700	250
	313	625	1300	670	450	700	175

Table –26: Equilibrium constants and the other Thermodynamic parameters of the submicellar interaction product of Oxazine dye with an anionic surfactant.

Dye	Surfactant	pH	Temperature (K)	K_c (M^{-1})	$K^{\prime}C = K_c/[H^+]$ (M^{-2})	$-\Delta G$ kJM^{-1}	$-\Delta H$ kJM^{-1}	ΔS $JM^{-1}K^{-1}$
BCB	SDS	5.25	297	40.00×10^3	6.95×10^9	55.96		
			303	22.00×10^3	3.82×10^9	55.58	51.96	12.18
			313	10.33×10^3	1.795×10^9	55.45		

Aqueous BCB – SDS System (above cmc)

The visible absorption spectra of BCB, (2.0×10^{-5} mol dm⁻³) in aqueous solution exhibits an absorption maximum at 625 nm. In the presence of SDS above its cmc spectacular change occurs. The intensity of the band at 625nm gradually diminishes with the appearance of a new band at 635 nm. Intensity of the new band increases as the concentration of SDS increases. (Fig.63). One sharp isobestic point at 670nm indicates the presence of dynamic equilibrium between BCB and SDS. The micelled dye gives the red shifted λ_{max} . In this experiment, the conc. of SDS varied from 4.0×10^{-3} M to 3.0×10^{-2} M. The spectral properties are shown in Table 27. The equilibrium constant (K_c) as well as molar extinction coefficient, ϵ_c , of the BCB – surfactant complex were evaluated using the modified Benesi-Hildebrand equation as before. The plots of $[D]_0/d - d_0$ against $1/[S]_0$ was found to be linear in all cases confirming 1:1 complex formation. The extent of BCB-SDS interaction in the aqueous medium (K_c) and ϵ_c were calculated from the slope and intercept respectively. A representative plot is shown in fig 64. The thermodynamic parameters were calculated from the temperature dependence of the equilibrium by the usual method. The results are presented in the Table 28.

Aqueous BCB – Triton X-100 System (above cmc)

The non ionic surfactant Triton X – 100 does not affect the spectra of BCB below its cmc value indicating the absence of any molecular interaction between surfactant and the dye under this condition. As has been already mentioned, the visible absorption spectra of BCB (2.0×10^{-5} M) in aqueous solution exhibits an absorption maximum at 625 nm at 303K. In the presence of Triton X – 100 above its cmc a spectacular change occurs. The band at 625nm diminished completely and instead, a new peak appears at 642nm. Therefore, apparently the main band of the spectrum has been shifted. Moreover, the intensity of the new band increases steadily with surfactant concentration (fig

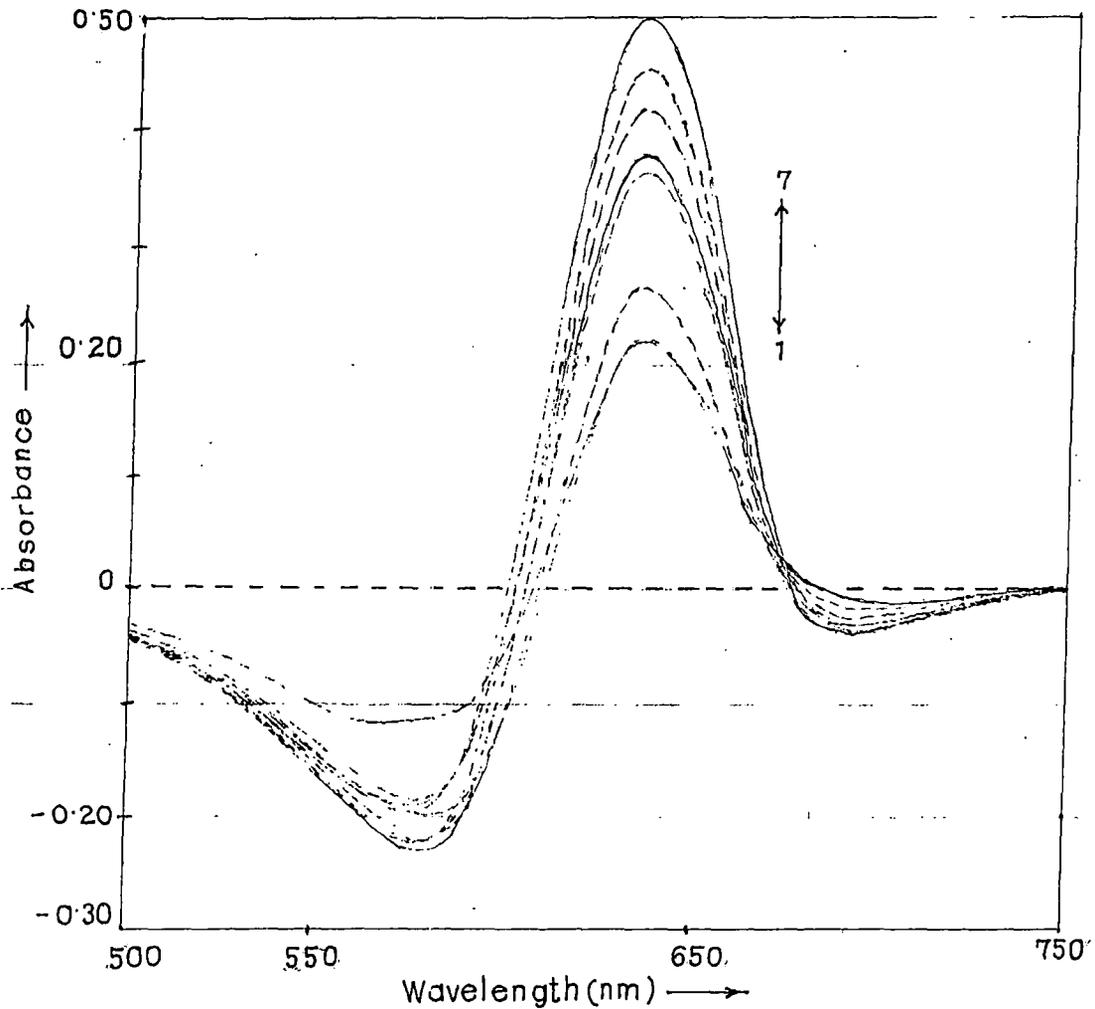


Fig. 63. The difference Spectra of Brilliant Creys Blue (BCB) and SDS against BCB in water at 30°C. The concentration of BCB $8 \times 10^{-5} \text{ mol. dm}^{-3}$ and concentration of SDS ($10^{-2} \text{ mol. dm}^{-3}$) : (1) 0.40 (2) 0.50 (3) 0.60 (4) 1.00 (5) 1.50 (6) 2.00 (7) 3.00. The broken line represents the set of curves when the concentration of SDS is below $5 \times 10^{-4} \text{ mol. dm}^{-3}$.

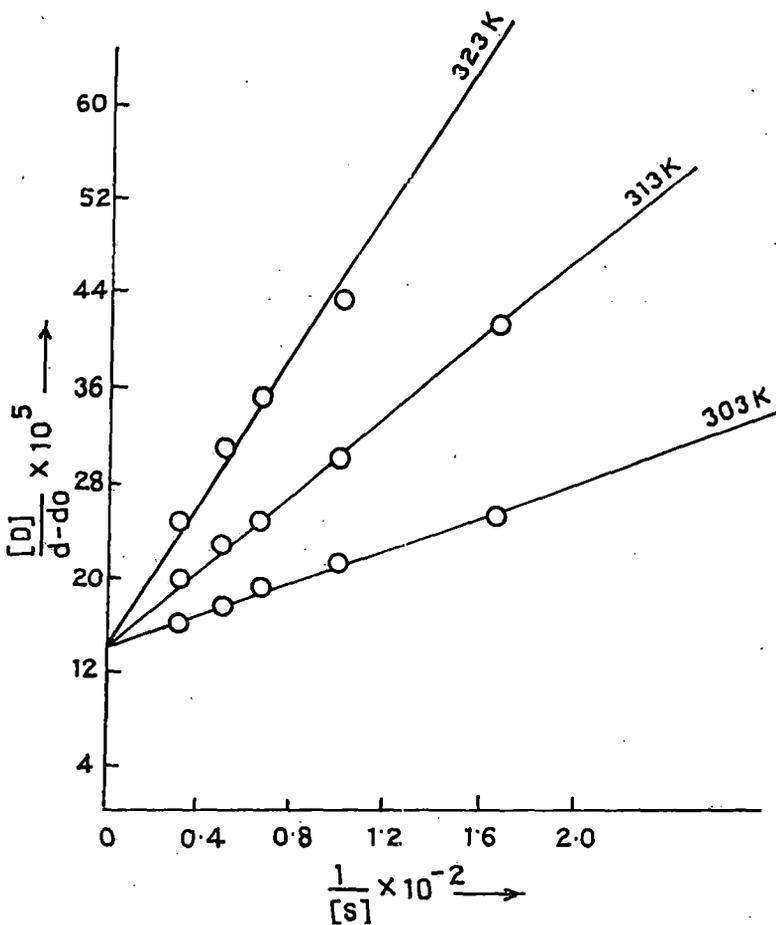
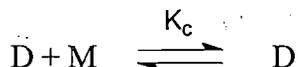


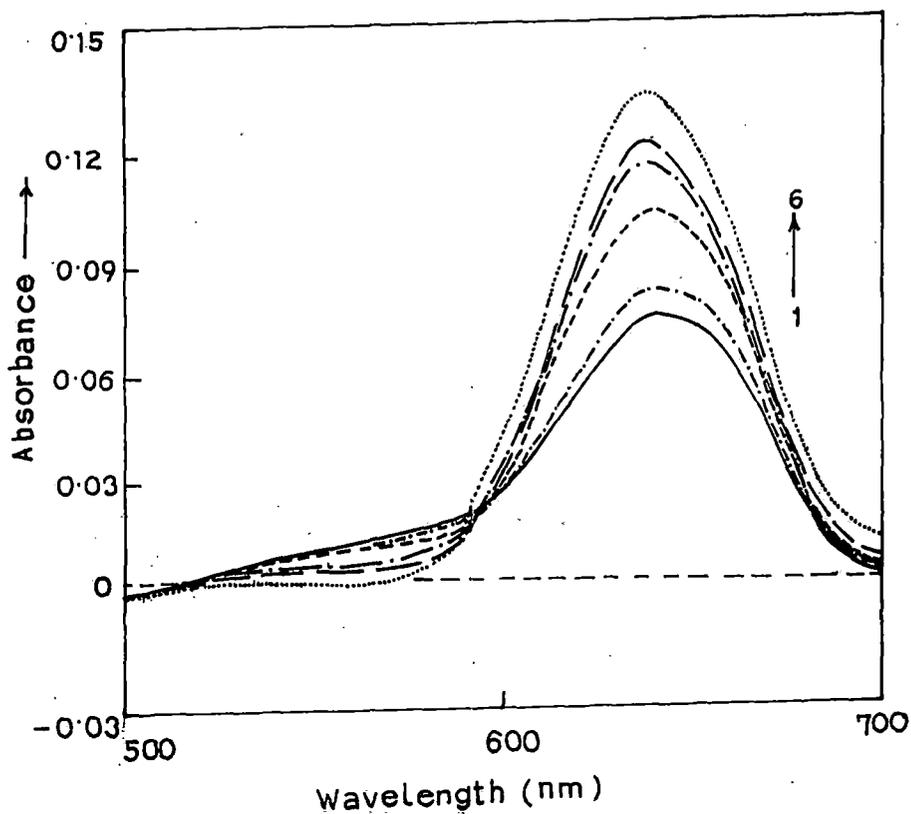
Fig. 64 . Spectral determination of equilibrium constant and molar extinction coefficient of BCB - SDS complex in water at 303K, 313K, 323K using equn (31). These plots were made by least squares method with standard deviation of 5%.

65). The spectrum of the dye due to the interaction with Triton X – 100 micelles passes through a isobestic point (590 nm) supporting the view of the formation of a dye- micellar complex above the cmc. The spectral properties are given in Table 27. Dye-surfactant complex formation can be assumed to follow the equilibrium :



where D, M, DM and K_c represent the dye, micelle, dye-micelle complex and the complexation constant respectively. For a 1:1 complex, the equilibrium constant K_c , and molar extinction co-efficient ϵ_c can be determined using the Benesi-Hildebrand Equation in the modified form at different temperatures. The observation is attributed to the formation of charge transfer or electron donor-acceptor complexes of BCB with Triton X-100 micelles. The equation 31 is valid when $[S] \gg [D]$ and the complex absorbs at a wave length where the surfactant is completely transparent. The plot of $[D]_0 / d - d_0$ against $1/[S]_0$ at three different temperatures were found to be linear confirming 1:1 complex formation (fig. 66). The extent of BCB – Triton X – 100 interaction in the aqueous medium i.e. equilibrium constant K_c and ϵ_c were calculated from the slope and intercept respectively. The thermodynamic quantities of the complexes were obtained (Table 28) from K_c values at different temperatures. The exothermic process exhibits a negative entropy and the release of heat leads to a stable or organized state.

The thermodynamic and spectrophotometric properties of these complexes suggest the formation of a strong charge – transfer (CT) or electron donor acceptor (EDA) complex with Triton X-100.



55 . The difference Spectra of Brilliant Cresyl Blue (BCB) and Triton X-100 against BCB in water at 30°C. Concentration of BCB $2 \times 10^{-5} \text{ mol. dm}^{-3}$ and concentration of Triton X - 100 ($10^{-2} \text{ mol. dm}^{-3}$) : (1) 0.20 (2) 0.30 (3) 0.50 (4) 1.50 (5) 4.00 (6) 6.00. The broken line represents the set of curves when the concentration of Triton X - 100 is below $2.5 \times 10^{-4} \text{ mol. dm}^{-3}$,

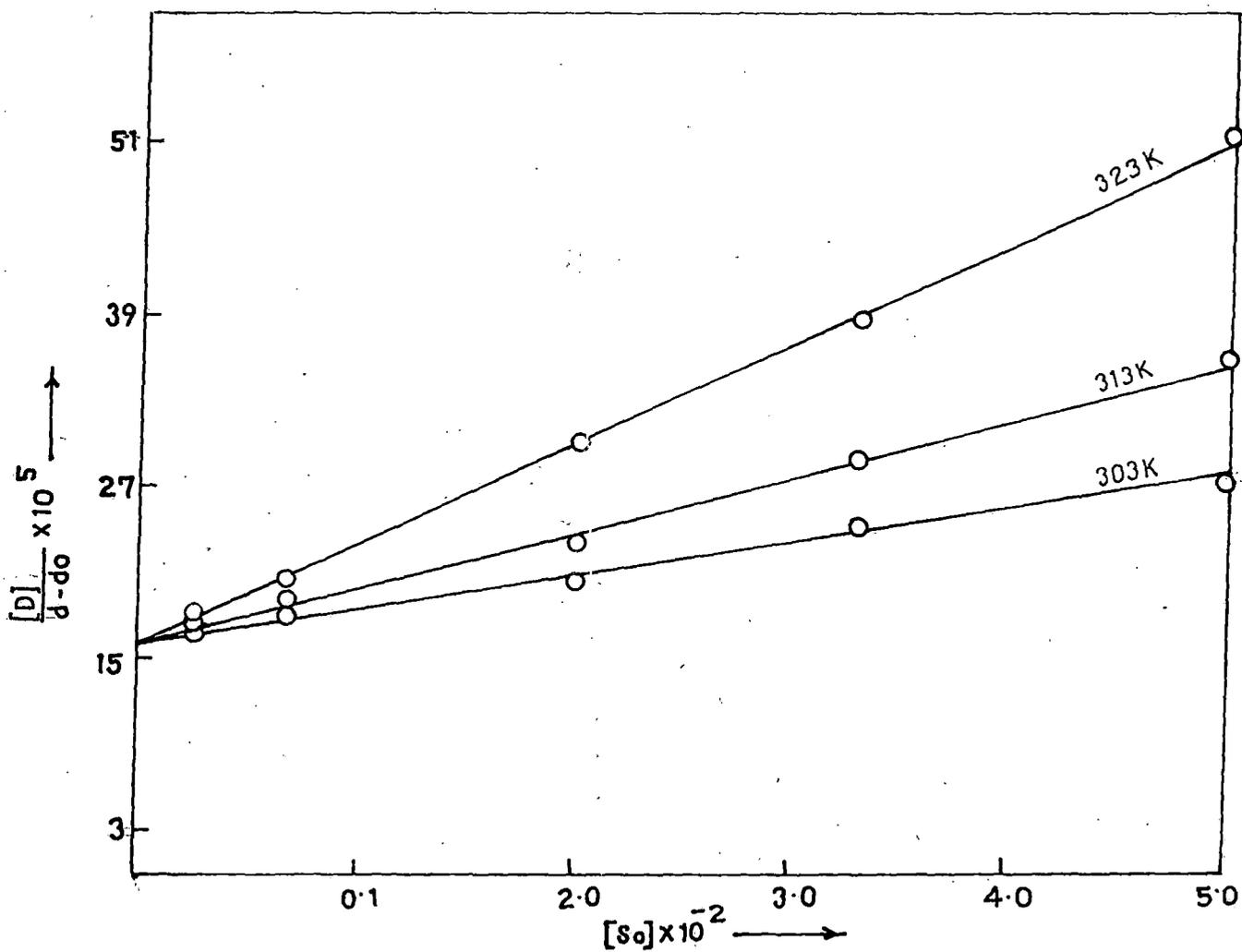


Fig. 66. Spectral determination of equilibrium constant and molar extinction co-efficient of BCB - Triton X - 100 complex in water at 303K, 313K, 323K using eqn. (31). These plots were made by least squares method with standard deviation of 5%.

Aqueous BCB – Tween 80 System (above cmc)

The visible absorption spectra of BCB ($2.0 \times 10^{-5}M$) in absence and in presence to different concentrations of Tween 80 at supermicellar concentrations are shown in figs. 67a and 67b. A remarkable change in the spectra was noticed in the presence of super micellar concentration of Tween-80. The difference spectra shows shifted absorption band at longer wave length, 638 nm, with two isobestic point at 600 nm and 710nm. Concentration of Tween 80 ranged from $2.0 \times 10^{-4}M$ to $3.0 \times 10^{-3}M$ in the experiment. Presence of sharp isobestic points and spectral shift are attributed to the 1:1 molecular complex formation between BCB and the surfactants. The spectral properties are given in Table 27. This complex is a charge transfer complex or electron donor acceptor complex formed between surfactant micelles and the dye. The equilibrium constant (K_c), as well as molar extinction coefficient (ϵ_c) of the BCB – Tween – 80 complex were evaluated using the Ketelaar's equation (Benesi-Hildebrand equation in the modified form). [equation no 31]

The plots of $[D]_0 / d-d_0$ against $1/[S]_0$ were found to be linear in all cases, confirming 1:1 complex formation again. A representative plot is shown in fig.68 for the BCB – Tween 80 complex at three different temperatures (293K, 303K, 313K). From the slopes and the intercepts, K_c and ϵ_c of the BCB-surfactant interaction in aqueous medium were calculated. The thermodynamic parameters were calculated from the temperature dependence of the equilibrium by the usual method. The results are presented in the Table 28 which are consistent with the formation of 1:1 molecular complexes between BCB and Tween 80 in aqueous solution.

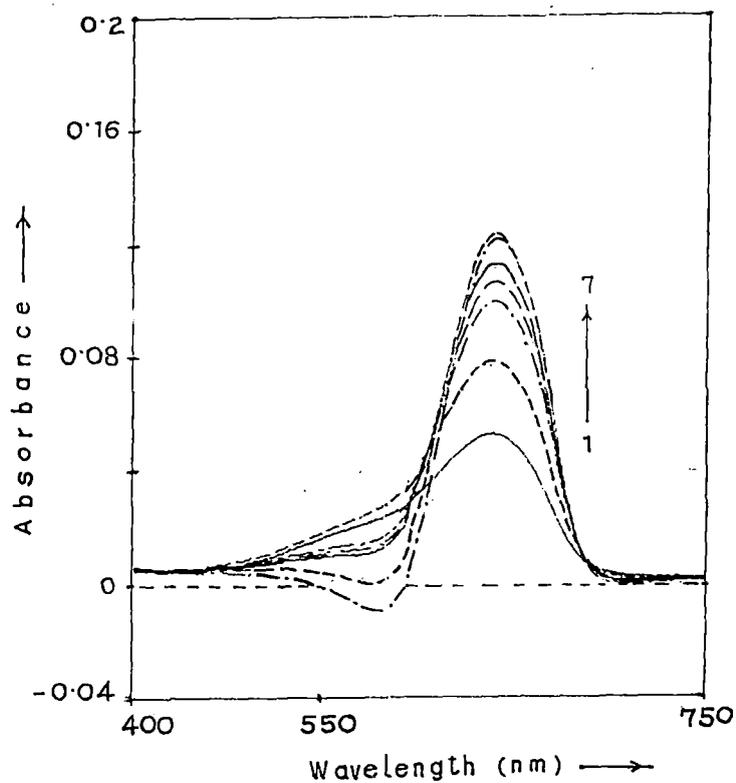


Fig. 67(a) The difference Spectra of BCB and Tween-80 against BCB in water at 20°C. Concentration of BCB (2×10^{-5} mol. dm^{-3}) : (1) 0.20 (2) 0.40 (3) 0.80 (4) 1.00 (5) 1.20 (6) 2.00 (7) 3.00. The broken line represents the set of curves when the Concentration of Tween-80 is below 1×10^{-5} mol. dm^{-3} .

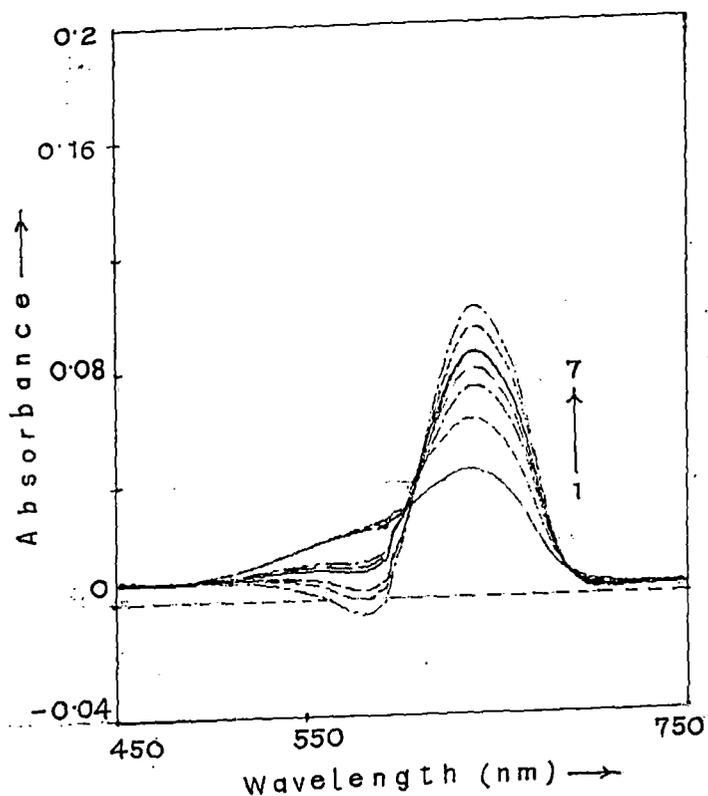


Fig. 67(b)..The difference Spectra of BCB and Tween-80 against BCB in water at 30°C . Concentration of BCB ($2 \times 10^{-5} \text{ mol. dm}^{-3}$) : (1) 0.20 (2) 0.40 (3) 0.80 (4) 1.00 (5) 1.20 (6) 2.00 (7) 3.00. The broken line represents the set of curves when the Concentration of Tween-80 is below $1 \times 10^{-5} \text{ mol. dm}^{-3}$.

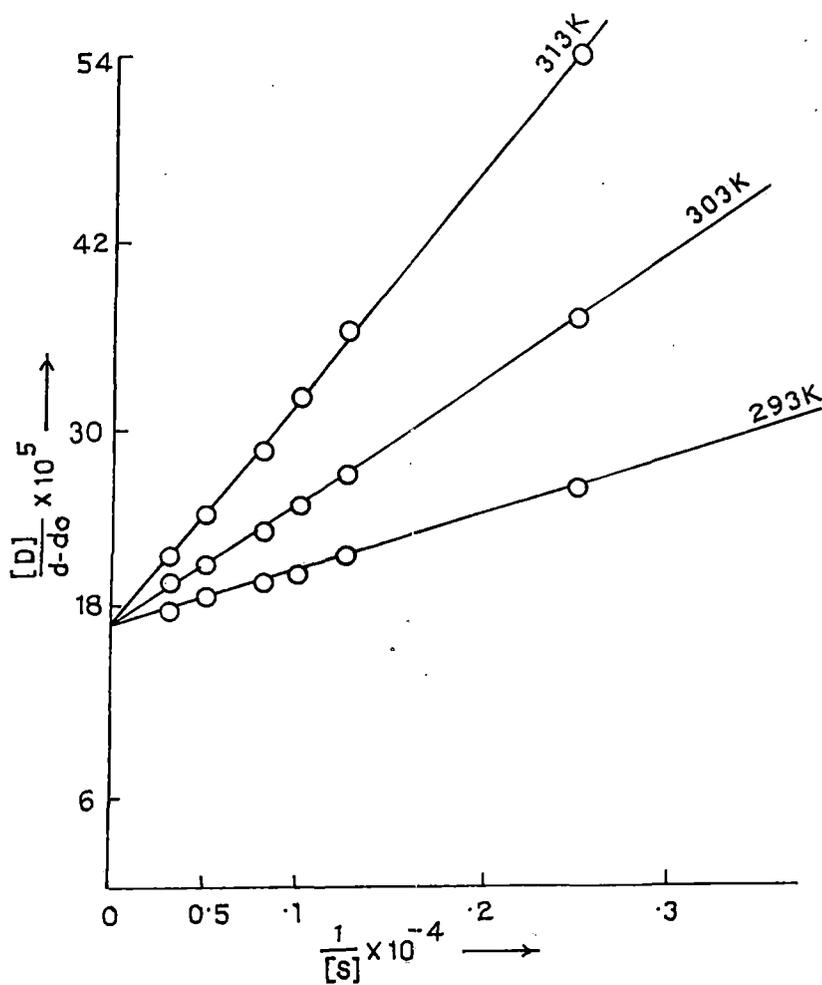


Fig. 68. Spectral determination of equilibrium constant and molar extinction co-efficient of BCB - Tween-80 complex in water at 293K, 303K and 313K using eqn. (31). These plots were made by least squares method with standard deviation of 5%.

Table-27: Spectral properties of oxazine dyes and their complexes with an anionic and non ionic surfactants in super micellar concentration ranges.

Dye	Surfactant	Temperature(K)	λ_{\max} of the dye (± 1) nm	ϵ_{\max} of the dye (± 50) m^2M^{-1}	λ_{\max} of the complex(± 2)nm	λ_{iso} of the complex(± 1)nm
	SDS	303	625	1300	635	670
BCB	Triton X-100	303	625	1300	642	590
	Tween-80	293	625	1300	638	600nm and 710nm

Table -28: Equilibrium Constants and other thermodynamic parameters of the super micellar interaction products of oxazine dyes with Anionic and non-ionic surfactants.

Dye	Surfactant	pH	Temperature (K)	Shifting of λ_{\max}	$K_c (M^{-1})$	$-\Delta G$ kJM^{-1}	$-\Delta H$ kJM^{-1}	$-\Delta S$ $JM^{-1}K^{-1}$
BCB	SDS	5.40	303	622 nm to 635nm	194.44	13.27	60.97	157.73
			313		82.35	11.48		
			323		42.00	10.04		
BCB	Triton X-100	4.20	303	622 nm to 642nm	720.0	16.57	49.88	109.41
			313		432.0	15.79		
			323		226.8	14.55		
BCB	Tween-80	5.60	293	622 nm to 642nm	821.67	16.35	51.96	121.32
			303		425.00	15.25		
			313		231.82	14.17		

General Discussion

The visible absorption spectra of oxazine dyes (viz., BCB, CVA, CFV and NBA) in absence and in the presence of varying concentration of SDS (much below the cmc) in aqueous solution at temperatures 303K, 313K and 323K are studied. The color change observed in many dyes on the addition of very small amount of oppositely charged surfactant has been attributed to ion pair formation⁶³, dye-surfactant salt formation⁵, the formation of dye dimers or higher aggregates⁹, and micelle and mixed micelle formation etc.^{46,65} However, Lewis⁷³ had pointed out that the ion pair formation, a phenomenon in itself does not alter the spectral absorption of the associated ions. Moreover, in the case of cationic dyes, like Phenazinium, Thiazinium and Oxazines, the dimerisations are known to cause hypsochromic shifts in the spectra.^{74,75} Therefore the band at longer wave length, is not due to dimer species of the dye. The formation of mixed micelle or dye-rich induced micelle, which is expected to provide a relatively less polar environment to the chromophore, should lead to a hypsochromic shift; whereas in the present case a bathochromic shift has been observed. Diaz-Garcia et al⁴⁹ citing works of various researchers, have pointed out how the studies and basic knowledge (available so far) on micellar interactions may be contradictory and insufficient to permit a clear choice between different possible interpretations of dye-surfactant interactions.

We did not observe any interaction between oxazine dyes and Cetyltrimethylammonium bromide (CTAB, a cationic surfactant) at a wide range of concentration and with Triton X-100, or Tween 80 (both are nonionic surfactants) in the sub-micellar concentration range. This indicates that the opposite charge on the dye and the surfactant is the primary requirement for this interaction in the submicellar concentration region. Therefore, it can be suggested that as the oppositely charged ions, (e.g., NBA⁺ and SDS⁻) come closer to each other due to electrostatic attraction, the hydrophobic nature of the

large organic ions and hydrogen-bonded water structure enforce them to form closely associated ion pairs, ($\text{NBA}^+ \text{SDS}^-$). This water-structure enforce ion pair poorly soluble (compared to the free ions) in water due to hydrophobicity and that is what has been observed in some of the present systems under certain concentration conditions.

However, it is clear that some more changes, in addition to the ion pair formation, has to occur to the chromophore to affect the large shift of the absorption band. We have seen that the dye absorption band remained unperturbed even on lowering pH of the aqueous dye solution upto 4.0, while a new peak appears at 640nm due to protonation of CVA near pH 2.0. For the entire experimental submicellar concentration range of SDS, the pH's of the aqueous SDS solutions were between 4.75 to 5.25. However, it can be said taking the example of CVA, that the higher wave length band at 650 nm in submicellar SDS, may be due to the protonated CVA, viz. HCVA^{2+} caused by a strong acidic environment exhibited by monomeric SDS^- bound to CVA^+ in the hydrophobic ion pair of $\text{CVA}^+ \text{SDS}^-$. If protonation is a part of the interaction, the interaction should be favoured by lower pH. Unfortunately, we could not study the effect of pH as SDS is hydrolysed in acidic medium (which is quite appreciable at the low experimental concentrations of SDS) and is precipitated out.⁷⁰ Moreover use of buffer is avoided because it may affect the dye-surfactant interaction as a result of the interaction of the buffer constituents with the dye or the surfactant.³³ The behaviour of other Oxazine dyes is similar to that of CVA in SDS as above.

The protonation can be explained in terms of the Hamaker constant⁷⁶. The Hamaker constant H_{123} for the dispersion/hydrophobic interaction between the species, viz. CVA^+ , 1, and SDS^- , 2, in water, 3, can be represented as

$$H_{123} = H_{12} - (H_{13} + H_{23} - H_{33}) \quad (37)$$

Water tries to retain its ordered structure and due to the hydrophobic repulsion between CVA^+ and water, and SDS^- and water, the terms H_{13} and H_{23} are very low compared to H_{33} and this makes the Hamaker constant very high. The value of H_{123} becomes so high that it is enough to induce protonation of the dye. The protonation stabilizes the ion paired system as the ionic hydrogen bonds are stronger than hydrogen bonds between neutral molecules by about an order¹²². After protonation due to the stronger interaction of the ammonium ion of the protonated dye (viz. HCVA^{2+}) with water, the ion pair is more stabilized. The addition of Na_2SO_4 to Oxazine dye in water does not affect the spectra of dye as there is no hydrophobic ion pairing and hence no hydrophobic force induced protonation taking place.

The plots of $[\text{Dye}]/d - d_0$ Vs $1/[\text{SDS}]_0$ at various temperatures yielded straight lines in wide range of the concentration of SDS. Deviations from the straight lines were observed towards higher concentrations of SDS, which was due to the disappearance of the protonated ion pairs as a result of solubilization of the dye by mixed micelle or micelle formation.⁶⁵ The true equilibrium constant and the Thermodynamic parameters are comparable to those reported by Dutta and Bhat.⁷⁰ The high values of the ΔH° and ΔS° can be attributed to the formation of ionic hydrogen bonds involving the resulting ammonium ions. The positive entropy change suggests that the free dye and surfactant ions are more ordered than the protonated ion pair in water due to the tendency of water to retain its ordered structure. It may be mentioned that similar observations i.e., positive entropy changes in case of hydrophobic interactions, have been reported earlier^{123,124}. Cationic Oxazine dye did not show any interaction with CTAB, a cationic surfactant, even above the cmc. This again supports the fact that hydrophobic ion pair formation and hence the opposite charges on the dye and the surfactant are the primary requisites for the hydrophobic force induced protonation.

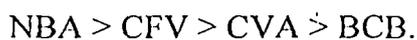
The difference spectra for all the dyes in presence of surfactant micelles give well defined bands which are assigned to the dye molecules entrapped into the micelles. These spectra always show troughs near λ_{\max} value of the corresponding dyes in aqueous media. These troughs in the lower wave length region to that of micellised dye spectra correspond to depletion of dyes in the bulk aqueous medium due to migration of dye molecules from bulk water to the micellar phase. Experiments show that Oxazine dyes form stronger complexes with all non ionic surfactants compared to SDS. The nature of interaction of dye with the non ionic surfactants is therefore different from that with SDS. Since both of the non ionic surfactants viz., Triton X-100, and Tween 80 cannot even solubilize the dye in carbon tetrachloride solution, it is plausible that the hydrophilic part of the surfactants interacts with the dye in aqueous medium. A cationic dye can penetrate into the non ionic micelles to form a strong molecular complex at polar site on the oxygen of the hydroxyl group for having comparatively higher electron density. The molecular interaction between the Oxazines and non-ionic surfactants in aqueous medium is considered to be a charge transfer interaction. On the other hand, with the negatively charged micelles of SDS, the cationic dye are held in the stern layer of the micelle due to Coulombic interaction.

According to Mulliken's charge transfer (CT) theory,⁹⁶ the CT complex is represented by a resonance hybrid of a non ionic ground state structure (D....S) (here D represents Oxazine dye and S represents nonionic surfactant) and an ionic excited state structure ($D^- \dots S^+$). The excited or CT state is formed by the transfer of an electron from the non ionic surfactant, an electron donor to the dye, an electron acceptor on light absorption of suitable energy. In case of dye - SDS system, interaction is ionic in nature. The prominent interaction of Oxazine dyes with surfactants above their cmc in aqueous medium indicates that the surface formation in micelle is the necessary criterion for complex formation. The interfaces (micelle/water) catalyze the CT complex

formation due to adsorption of dye from solution and thus increase the concentration of CT complex. The data obtained from the spectral studies indicate that different surfactants yield dye-micelle complexes with different affinity which follow the order Tween 80 > Triton X 100 > SDS (Table 16, 20, 24, 28) Experimental results show that all Oxazine dyes form stronger complexes with all non-ionic surfactants compared to SDS, indicating that the nature of interaction in both cases are different. This is comparable with the interaction of phenazinium dye and Methyl Orange¹²⁵ with micelles of various charge types. It can be assumed that non-ionic micelles being composed of polyethylene oxide residues are more favourable for the location of a dye cation. The polar oxygen centers interact in a concerted manner through the orientation of the head groups of the surfactant molecules to offer a relatively large electron density for stronger complex formation. The molecular interactions between cationic dyes and non ionic surfactants in aqueous medium are thus considered to be charge transfer interactions which are comparable with that of starch-Iodine complex formation^{126,127}. The glucose units of the polymeric starch in the above complex causes induction through the polarity effect of oxygen centers with a specific conformational orientation. The increasing alkyl-hydrocarbon chain length of non-ionic surfactants enhancing the electron donor capacity of the molecule, due to an inductive effect, also supports the above trend of complex formation. The order of Kc (binding constant) may represent the trend of the effect produced by the surfactant micelles. It is difficult to examine the role of the hydrophobic effect on the tendency of formation of the molecular complex. Tweens possess identical head groups ($-(\text{CH}_2 - \text{CH}_2 - \text{O})_2$) but different non polar tails. It is reported that the larger the non polar tail in the tweens, the stronger the complex formation, indicating a direct correlation of complexation with hydrophobicity.⁹⁷ The experimental results provide an evidence of 1:1 molecular interaction between the cationic Oxazine dyes and Triton X-100 in aqueous solution . Since Triton X - 100 in carbon tetrachloride

solution can not even solubilize the dye, it is expected that the hydrophilic part of Triton X-100 interacts with the dye, whereas there is no hydrophobic interaction between the dyes and Triton X-100. In the neutral surfactant micelle of Triton X-100, a cationic Oxazine dye can penetrate the micelle to form a strong molecular complex at a polar site, the interactions may occur either at phenoxy group or at the poly oxyethylene chain. The positive centres of the dye molecules do not interact with the lone pair electron on the ether oxygen atom, but with the lone pair electron on the oxygen of the hydroxyl group for comparatively higher electron density of the surfactant.

From the Tables 14, 18, 22 and 26, it is seen that the equilibrium constant K'_c of CFV is the highest ($7.9 \times 10^9 \text{ dm}^3 \text{ M}^{-2}$) and that of NBA is the lowest ($1.4 \times 10^9 \text{ dm}^3 \text{ M}^{-2}$). The formation constants of Oxazine dyes with SDS in the sub-micellar concentration follows the order : CFV > BCB > CVA > NBA. The high values of ΔH° , ΔS° can be attributed to the formation of ionic hydrogen bonds involving the resulting ammonium ions¹²² as has been already mentioned. The positive entropy indicates that free dye and surfactant ions are more ordered than the protonated ion pair in water due to the tendency of water to retain its ordered structure^{123,124}. From the Tables 14, 18, 22 and 26, it can be observed that the positive entropy change for different dyes in the above interactions follow the order :



The extent of binding of Oxazines with SDS micelles in the super-micellar concentration ranges are less than that of charge transfer interaction with non-ionic surfactants. This is apparent from the equilibrium constant values listed in Tables 1, 20, 24 and 28. In charge transfer interactions; the cationic dyes act as electron acceptors and non ionic surfactants as donors. From the equilibrium constant values it is apparent that the electron donating ability of

Triton X - 100 is higher than that of Tween 80 and NBA form stronger charge transfer complex via $\pi - \pi$ interaction with Triton X - 100.

The electron accepting ability of the dyes is expected to decrease with an increasing number of substituting alkyl groups on the ring. It can be argued that the electron donating abilities of the non ionic surfactants towards the dye is increased with increasing alkyl hydrocarbon chain length. The presence of an aryl group in Triton X-100 result in an opposite effect compared to the Tweens. The results in the Tables 16, 20, 24 and 28 show that K_c values vary directly with the band shift $\Delta\nu$ and are indirectly proportional to cmc.^{128,129}

At a fixed concentration of the dye, where the aggregation is negligible, the nature of the spectrum of all dyes are affected in the presence of SDS where concentration of SDS is increased in the submicellar range. The absorbance starts decreasing with SDS concentration and the band disappears ultimately with the appearance of new absorption bands due to protonated ion pair formation. In the high concentration region of SDS, increase in the absorbance with a red shift is related to the formation of surfactant micelles in which the dye is incorporated. In the low surfactant concentration region, changes in the dye absorbance are attributed to the electrostatic interaction between oppositely charged molecules forming molecular complexes. The evidence that these interactions are due to oppositely charged molecules also comes from the fact that similarly charged dye surfactant systems have shown the absence of such spectral change.

As stated before, Oxazine dyes are present as ion pair in the submicellar region of the anionic surfactants and exhibit characteristic absorption bands. But as the surfactant concentration increases beyond the cmc, the absorbance of the bands progressively decrease with the appearance of the main dye absorption band with a shift of λ_{max} . This indicates that the dye-surfactant ion pair (complex) is unstable in the micellar region, where the surfactant molecules tend

to aggregate to form the micelles. However, the dye molecules is then entrapped inside the surfactant micelles forming a micellised dye-surfactant complex⁹⁸. The exothermic process exhibits a negative entropy change and the release of heat leads to a stable or organized state as has been mentioned already. It may be concluded that the nature of interactions of Oxazine dyes with different surfactants is different. Oxazine dye undergoes CT interaction with non ionic surfactants; ionic and hydrophobic interactions with negatively charged SDS, and no interaction with positively charged CTAB.

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