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A STUDY ON THE INTERACTIONS OF SOME SYNTHETIC AND NATURAL DYES OF DIFFERENT CHARGE TYPES WITH SURFACTANTS AND POLYMERS

A thesis submitted in part fulfillment of the requirements for the degree of

Doctor of Philosophy

By

BORNALI BORUAH

Registration No. 011 of 2011

Department of Chemical Sciences
School of Science
Tezpur University, Tezpur
Assam, India

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Dedicated to.....

My parents and Grandparents

ABSTRACT

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This thesis describes a study of the nature of the physico-chemical interactions of aqueous dyes with surfactants and polymers by spectroscopic and thermodynamic means. This thesis has been arranged in four major chapters, *viz.*, Introduction, Experimental, Results and Discussion and Conclusions; which have been briefly described here.

Chapter I: Introduction

Surfactants are amphiphilic molecules characterized by a hydrophilic head group and a hydrophobic hydrocarbon chain. The fundamental property of surfactants is to form organised structures like micelle or reverse micelle in aqueous and nonaqueous solutions. Surfactants, due to their ability to form self-aggregates and modify interfacial properties, find applications in many industrial processes such as detergency, emulsification, flocculation, enhanced oil recovery and in biological membrane studies. In aqueous polymer-surfactant systems, the solubilization powers as well as the viscosity of aqueous solutions of polymer-bound micelles are higher than that of the separate surfactant and polymer solution. The modification of the properties of both of the polymers and surfactants in the systems is utilised in paints and coatings, adhesives, cosmetics, emulsification, etc., and in many biological analysis. The solvatochromic shift of aqueous dyes in presence of the surfactant and polymer, both individually and in combination has been found to be useful in many ways.

The interactive forces which facilitates the dye binding to surfactants and to both polymers and surfactants together are not yet clearly understood, which may be due to limited choice of dye-polymer-surfactant systems in the reported studies. Therefore, an attempt has been made to understand the interactive forces operative in these systems explicitly. A study of the acid-base equilibrium of two synthetic dyes of different charge types, the dimerization of another synthetic dye and the physicochemical behaviour of a natural dye in different surfactants and in polymer-surfactant systems has been presented in the thesis. The different polymers and surfactants were varied without a tremendous change in structures. Finally, an attempt has been made to quantitatively depict the interactions in the chosen dye-polymer-surfactant systems.

ABSTRACT

Chapter II: Experimental:

This chapter consists of the description of the materials and the methods adopted in the studies. The sources and purification of the chemicals, the preparation of experimental solutions, recording of electronic absorption spectra, fluorescence spectra, surface tension, and pH and determination of the thermodynamic parameters have been described in this chapter.

The UV-visible spectra were recorded on a Shimadzu UV-2550 UV-vis double beam spectrophotometer with matched pair of cells of 1 cm path length using thermostated cell holder. The fluorescence spectra were taken using a Hitachi F-2500 fluorescence spectrophotometer with the excitation and emission slit widths set at 5 nm. The surface tensions were determined using a K9ET (Kruss GmbH) tensiometer. Temperatures were maintained with Thermo Haake K10. The pHs were determined by using an Orion Multi Parameter Kit. Temperatures were maintained within ±0.1 K in all the experiments. The detailed descriptions of the instruments along with the methods are included in this chapter.

Chapter III: Results and Discussions

This chapter describes the experimental results and their analysis and interpretation. For systematic organization, this chapter has been divided into three major sections. The first section (III.A) deals with the study of the acid-base equilibrium of two synthetic dyes of different charge types with surfactants and polymers. The second section (III.B) deals with the study of monomer-dimer equilibrium of a dye in aqueous polymer-surfactant medium. In the third section (III.C), the interactions of a natural dye, curcumin with surfactants of various charge types have been studied in absence and presence of polymers.

Chapter III.A: Acid-base equilibrium of dyes in aqueous polymer-surfactant medium

Chapter III.A.1: Acid-base equilibrium of phenol red in aqueous polymer-surfactant medium

This section contains the results of the spectrophotometric investigation of the acid-base equilibrium of phenol red (PR), a sulphonephthalein dye, in aqueous media containing water soluble nonionic polymers, *viz.*, polyvinyl alcohol (PVA) and polyethylene glycols(PEG) in the presence of sodium dodecyl sulphate (SDS), an anionic surfactant. A partition equilibrium method was utilized to determine the equilibrium

constant of partition of the PR between micellar pseudophase and aqueous phase and the CAC of SDS in buffered aqueous systems containing the polymers.

The association of PR with SDS increases in presence of PVA and PEG in a well-buffered medium. In case of PEG, it was observed that the association increases with the increase in molecular weight of the polymer indicating a major role of hydrophobic interaction in such dye and polymer-surfactant systems. The pH-dependent association constants, K_{ass} of PR with SDS-PVA, and SDS-PEG systems have been determined which are found to decrease in the order PVA > PEG 600 > PEG400 > PEG 200. In case of organic Tris buffer system there is partition of the buffer components between the aqueous phase and micellar pseudophase which shields the polar head group region of the SDS micelles bound to PVA and PEG. As a result the association of PR with SDS-PVA and SDS-PEG systems is greater in Tris buffered medium than in inorganic phosphate buffered medium of the same pH. From the thermodynamic studies it has been found that interactions of the sulphonaphthalein dye with the aqueous SDS-PVA and SDS-PEG systems are endothermic and entropy driven.

Chapter III.A.2: Acid-base equilibrium of neutral red in aqueous polymer-surfactant medium

This section deals with the studies of the interactions of an aqueous phenazinium dye, *viz.*, neutral red (NR) with nonionic Tween surfactants in the presence of some nonionic polymers, *viz.*, PVA, PEG-200, PEG-400 and PEG-600. The equilibrium constants of the interaction of the dye with the micelles in the absence and in the presence of the polymers have been determined by the partition equilibrium method based on UV-VIS spectroscopy. The distribution of the two forms of the dye between the bulk water and the micelles have been computed from the equilibrium constants by an iterative method using a FORTRAN program.

It has been observed that both the electrically neutral base and the cationic conjugate acid forms of the dye are significantly associated with nonionic micelles bound to non-ionic polymers in the experimental pH range, although the base form binds preferentially over the acid form. The CAC of the surfactants in the presence of the polymers increases in the order: PVA < PEG-600 < PEG-400 < PEG-200, which indicates that the surfactant-polymer aggregation decreases with decreasing molecular weight of the polymer. The thermodynamic parameters of the binding of the dye with the micelles in

presence of the polymers have been evaluated, and the values indicate the dye binding to be entropy driven. The apparent pK_as of the dye have been predicted from the concentrations of the acid and base forms of the free and bound dye so obtained as well as determined directly by a standard spectrophotometric method. The predicted pK_as agreed well with the experimental results indicating predictability of the acid-base behavior of the dye in aqueous surfactant-polymer systems by the present method. The apparent pK_a of the dye decreases in the aqueous non-ionic surfactant-polymer due to a preferential binding of the neutral base form of the dye to the non-ionic micelles in presence of the polymers.

Chapter III.B: The monomer-dimer equilibrium of methylene blue in aqueous polymer-surfactant medium

The results of the monomer-dimer process of methylene blue (MB) in an aqueous solution of the anionic surfactant, SDS and a nonionic polymer, PVA are described in this section. A spectroscopic method has been used to determine the effective dimerisation constant of methylene blue ($^{eff}K_D$) in presence of the surfactant and the polymer, individually and together, in buffered aqueous solutions of low ionic strength. For determination of $^{eff}K_D$ a series of solution at progressively increasing concentration of the dye, were prepared in water with a fixed concentration of SDS and a fixed concentration of PVA for each set of experiments. The intensity of absorbance of the monomer band was measured as a function of dye concentration in water and for the other systems.

The value of ($^{eff}K_D$) was found to decrease in the order: H_2O > PVA-SDS > SDS > PVA. The monomer-dimer process of the dye is influenced by hydrophobic interactions. The hydrophobic interaction between the dye molecules is greater in micellar medium than that in water or in aqueous PVA-SDS system. Thermodynamic studies reveal that, aggregation of methylene blue in the polymer-surfactant system is exothermic with a large negative ΔH^0 and a negative ΔS^0 values. The presence of SDS facilitates dimerisation of methylene blue below its critical aggregation concentration (CAC) but the dye dissolves in the monomeric form in the hydrophobic PVA-SDS complex above the CAC.

ABSTRACT

Chapter III.C: Interaction of curcumin with surfactants and polymers in aqueous medium

Chapter III.C.1: With submicellar surfactants in absence and presence of polymers

The results of the studies of the interactions of a biologically important molecule curcumin in aqueous surfactant solutions with both cationic, *viz.*, hexadecyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium bromide (TTAB) and dodecyltrimethylammonium bromide (DTAB), and anionic surfactants, *viz.*, SDS, SDBS, SDSN in submicellar concentration ranges of the surfactants both individually and in combination with a nonionic polymer, PVA are presented in this section.

The electronic spectra of curcumin-ionic surfactant systems at submicellar concentrations in acidic and neutral media indicate the formation of micelles by dye-surfactant complexes similar to that by the dye-surfactant ion-pair, formed between oppositely charged dye and surfactants systems. The fluorescence spectral behaviour of curcumin in presence of the cationic surfactants is consistent with the formation of micelles by the dye-surfactant complexes.

In submicellar anionic surfactant medium also interesting striking spectral behaviour has been observed which may be attributed to a complex formation between the diketo curcumin with the surfactants. The apparently unusual interaction possibly takes place through ion-dipole, van der Waals and/or H-bonding interactions of the diketo moiety with the surfactant head groups. The presence of the polymer suppresses the formation of the dye-surfactant complex.

Chapter III.C.2: With micellar surfactants in presence of PVA

The results of the interaction of curcumin with micellized surfactants of various charge types, *viz.*, anionic (SDS), cationic (CTAB) and nonionic (Tween-80), in presence of a polymer, *viz.*, PVA in neutral pH condition are also included in this section. The binding constants of curcumin with surfactant in presence of polymer have been estimated from the changes in absorption intensity and the fluorescence intensity of curcumin as a function of the concentration of surfactants using an established method.

The binding constant increased in the order PVA-SDS < PVA-CTAB < PVA-TW80 indicating the strongest binding of curcumin with non-ionic surfactant micelles. The presence of the polymer significantly enhances the binding of the surfactant micelles to the lipophilic curcumin molecule. The interaction has been suggested to be mainly

hydrophobic which may also involve ion-dipole, dipole-dipole, H-bonding and van der Waals interactions. Observed large values of partition constant of curcumin between surfactant-polymer domains and water again indicate that curcumin exists predominantly in the polymer bound micelles.

Chapter III.C.3: Interaction of curcumin with chitosan in presence of surfactants

In this section the results of a study of the binding of aqueous curcumin with chitosan in presence of CTAB and Tween-80 by monitoring the changes in the absorption and the fluorescence spectra at physiological pH (pH 7.40) condition are included. The binding constants and the distribution of curcumin in the interior of chitosan have been evaluated by fluorescence quenching method. The binding constant increased in the presence of surfactants in the order: chitosan < chitosan-CTAB < chitosan-Tween-80 indicating the strongest binding of curcumin with chitosan in presence of the nonionic surfactant. It has been inferred from the observed fluorescence quenching by hydrophobic and hydrophilic quenchers that, in the chitosan solution, curcumin is distributed between the hydrophobic interior and the polar cationic centres of chitosan at the experimental pH. The stability provided to curcumin by chitosan alone and in presence of CTAB and Tween-80 has been studied by investigating the kinetics of degradation of curcumin by means of spectrophotometry. Chitosan suppresses the hydrolytic degradation of curcumin efficiently and the effect is more pronounced in presence of the surfactants. Thermodynamic quantities of the interactions suggest that the binding process is driven by both enthalpy and entropy. It has been seen that addition of chitosan further increases the stability provided by the surfactants to aqueous curcumin

Chapter IV: Conclusion

The summary of the conclusions drawn from the present study on the interactions in the chosen aqueous dyes-surfactant-polymer systems is as follows:

- The partition equilibrium method can be used to study predict the acid-base behaviour of phenol red and neutral red aqueous polymer-surfactant systems.
- The CAC of the surfactants, in presence of a dye, decreases with increasing molecular weight of the nonionic polymers and increasing chain length of the Tween series of surfactants.
- In the mixed polymer-surfactant systems the surfactant and the polymer cooperatively facilitate the aggregation of methylene blue.

ABSTRACT

- Curcumin forms dye-surfactant complexes through ion-dipole / H-bonding / van der Waals interactions in acidic and neutral aqueous submicellar anionic surfactant solutions.
- Presence of a nonionic polymer suppresses the submicellar dye-surfactant complex formation.
- Curcumin is stabilized more by the micellar surfactants in presence of polymers than that in the absence of the polymers. The stabilization by Tween 80 is greater than that by CTAB and SDS.
- The stability of aqueous curcumin can be further improved over the stabilization by surfactants by adding chitosan to the surfactant solutions.

List of Abbreviations and Symbols

AR	Analytical reagent
CAC	Critical aggregation concentration
CAS	Chemical Abstract Service
CI	Color Index
CMC	Critical Micelle Concentration
CMC*	CMC in aqueous surfactant solution
CMC_{IP}	CMC of aqueous surfactant solution in presence of dye
CTAB	Cetyltrimethylammonium bromide or Hexadecyltrimethylammonium bromide
DSIP	Dye surfactant ion-pair
DTAB	Dodecyltrimethylammoniumbromide or Lauryltrimethylammonium bromide
LR	Laboratory reagent
MB	Methylene blue
NR	Neutral red or (3-amino-7-dimethylamino-2-methyl phenazine hydrochloride)
PEG	Polyethylene glycol
pKa	Negative logarithm of acid dissociation constant
PR	Phenol red or phenolsulfonephthalein
PVA	Polyvinyl alcohol
SDBS	Sodium dodecylbenzenesulphonate
SDS	Sodium dodecylsulphate
SDSN	Sodium dodecylsulphonate, or 1-dodecanesulfonic acid sodium salt
TTAB	Tetradecyltrimethylammonium bromide
TW20	Polyoxyethylene(20) sorbitan monolaurate
TW40	Polyoxyethylene(20) sorbitan monopalmitate
TW60	Polyoxyethylene(20) sorbitan monostearate
TW80	Polyoxyethylene(20) sorbitan monooleate

List of Tables

Table		Page No.
Table I.A(1)	*Examples of some common surfactants*	1
Table I.A(2)	*The CMC's of some common surfactants at 298K in water*	3
Table I.A(3)	*Some dye-surfactant systems studied in submicellar surfactant region*	8
Table I.A(4)	*Some dye-surfactant systems studied in micellized surfactants*	10
Table II.A(1)	*Detail description of the dyes used in the study*	52
Table II.A(2)	*Detail description of the surfactant used in the study*	56
Table II.A(3)	*Detail description of the polymers used in the study*	58
Table II.B(1)	*Preparation of experimental solutions for the determination of equilibrium constant for an aqueous dye-surfactant-polymer system at a fixed pH*	60
Table III.A(1)	*The CAC's of SDS in the buffered solutions (0.1 M TRIS + 0.1M HCl), pH dependent association constants*, K_{ass} and the pH independent equilibrium constants, K_s of PR with the surfactant in the polymer-surfactants systems at 298 (± 0.1) K.*	75
Table III.A(2)	*The thermodynamic parameters of the interaction of PR with SDS in PVA-SDS, PEG 200-SDS, PEG 400-SDS, PEG 600- SDS systems, at pH 7.70 (Tris buffer)*	76
Table III.A(3a)	*The pH dependent association constant, K_{ass} and pH independent equilibrium constant, K_s of NR with TW80 in presence of 1.25% (v/v) PEG 200, PEG 400, PEG 600 and 1.25% (w/v) PVA at 298 (±0.1)K*	84
Table III.A(3b)	*The pH dependent association constant, K_{ass} and pH independent equilibrium constant, K_s of NR with TW60 in presence of 1.25% (v/v) PEG 200, PEG 400, PEG 600 and 1.25% (w/v) PVA PVA at 298*	85

	(±0.1)K	
Table III.A(3c)	*The pH dependent association constant, K_{ass} and pH independent equilibrium constant, K_s of NR with TW40 in presence of 1.25%(v/v) PEG 200, PEG 400, PEG 600 and 1.25% (w/v) PVA at 298 (±0.1)K*	86
Table III.A(3d)	*The pH dependent association constant, K_{ass} and pH independent equilibrium constant, K_s of NR with TW40 in presence of 1.25% (v/v) PEG 200, PEG 400, PEG 600 and 1.25% (w/v) PVA PVA at 298 (±0.1)K*	87
Table III.A(4)	*The thermodynamic parameters of the interaction of NR with Tweens-PVA and Tweens-PEGs systems, at pH 7.00 (phosphate buffer)*	92
Table III.A(5)	*The $pK_{a,app}$ values of NR in nonionic Tween surfactant -polymer systems at 298 (±0.1) K. [S]= $1x10^{-3}$ mol dm^{-3}*	93
Table III.B(1)	*Spectral properties of MB*	102
Table III.B(2)	*Effective dimerization constants of MB at 298 (±0.1) K*	102
Table III.B(3)	*Thermodynamic parameters for monomer-dimer process of MB at 298 (±0.1) K*	104
Table III.C(1)	*The association constant, K_c of curcumin with cationic surfactants at 298 (±0.1) K*	114
Table III.C(2)	*The association constant, K_c of curcumin with anionic surfactants at 298 (±0.1) K*	121
Table III.C(3)	*The binding constant, K_s, partition coefficient, K_x of curcumin in surfactant-polymer systems at pH 7.00 and 298 (±0.1) K*	132
Table III.C(4)	*Rate of degradation of curcumin in aqueous buffer (pH 7.40) and in chitosan-surfactant systems, yield of suppression of degradation by chitosan, and the curcumin-chitosan association constants*	143

List of Figures

Figure		Page No
Fig. I.A.1	*Schematic representation of (a) a surfactant monomer, (b) spherical micelle, (c) reverse micelle and (d) vesicle*	2
Fig. I.A.2	*Changes of some physical properties of aqueous surfactant solution (in arbitrary scale) with concentration of the surfactant*	3
Fig. I.A.3	*A two dimensional representation of the regions of a spherical micelle: ∿∿ -hydrocarbon chain, O-head group, X-counterion*	4
Fig. I.A.4	*The schematic picture of some surfactant micelles: (a) spherical, (b) oblate, (c) cylindrical and (d) lamellar*	4
Fig. I.A.5	*A schematic representation of the various interactions of ionic dyes with surfactants of various charge types as a function of the surfactant concentration*	14
Fig. II.A.1	*Structural formulae of the dyes studied*	52
Fig. II.A.2	*Structural formulae of the surfactants studied*	56
Fig. II.A.3	*Plot of surface tension (mN/m) as a function of the logarithm of SDS concentrations at 298 (±0.1) K for determination of CMC of SDS*	57
Fig. II.A.4	*Structural formulae of the polymers studied*	58
Fig. III.A.1	*UV-visible absorption spectra of PR (3.50x 10^{-5} mol dm^{-3}) at various concentrations of SDS in presence of 5% PVA at pH 7.70 (phosphate buffer) at 298 (±0.1) K: [SDS] / 10^{-3} M = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5) 10.0 and (6) 12.0*	68
Fig. III.A.2	*UV-visible absorption spectra of PR (3.5 x10^{-5} mol dm^{-3}) at pH of 7 70 (Tris buffer) in aqueous solution of various concentrations of SDS in presence of 5% PEG 200 at 298 (±0.1) K: [SDS] / 10^{-3} M = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5) 10.0 and (6) 12.0*	68
Fig. III.A.3	*Linear plots of $\{(d_o-d) / (d-d_m)\}$ vs. $[S_o]$ for PR-SDS system in presence of different polymers (5%) at a pH of 7.70 and 298 (±0.1) K*	73
Fig. III.A.4	*van't-Hoff plot for the interaction of PR with SDS in presence of*	76

	different non-ionic polymers at pH 7.70 (Tris buffer)	
Fig. III.A.5	*UV-visible absorption spectra of NR (5.0x 10^{-5} mol dm^{-3}) in presence of various concentrations of TW80 at pH 6.80 and temperature 298 (±0.1) K: [TW80]/(10^{-4} mol dm^{-3}) = (1) 0.00, (2) 0.40, (3) 0.80, (4) 1.20, (5)1.60 and (6) 2.00*	79
Fig. III.A.6	*UV-visible absorption spectra of NR (5.0x10^{-5} mol dm^{-3}) in presence of various concentrations of PVA (w/v %) at pH 6.80 and temperature 298 (±0.1) K: PVA/ w/v % = (1) 0.00, (2) 0.45, (3) 0.60, (4) 1.20, (5)0.75 and (6) 1.25*	79
Fig. III.A.7	*UV-visible absorption spectra of NR In presence of various concentrations of TW80 in presence of fixed concentration of 1.25% (w/v) PVA at pH 6.80 and temperature 298 (±0.1) K: [TW80] /(10^{-4} mol dm^{-3}) = (1) 0.00, (2) 0.30, (3) 0.60, (4) 0.90, (5) 1.20 and (6)1.50*	80
Fig. III.A.8	*Plots of {(d_o-d) / (d-d_m)} vs. surfactant concentration [S_o] for NR-Tween systems in presence of PVA (1.25%) at pH 7.00 and 298 (±0.1) K*	90
Fig. III.A.9	*The van't-Hoff plots for the interaction of NR with TW80 in the presence of different nonionic polymers at pH 7.00*	90
Fig. III.A.10	*The $pK_{a,app}$ of NR in aqueous solutions of TW20, TW40, TW60 and TW80 in presence of PVA (1.25%) at pH 7.00 and 298 (±0.1) K. The solid lines are predicted by the present method. The symbols indicate experimental $pK_{a,app}$.*	94
Fig. III.B.1	*UV-visible absorption spectra of MB (5x10^{-5} mol dm^{-3}) at pH 7.00 and 298 (±01) K: 1 (in water), 2 (in presence of 1.0 % PVA), 3{in presence of SDS (2 0x10^{-3} mol dm^{-3} and PVA (1.0 %)}, 4{in presence of SDS (1x10^{-1} mol dm^{-3})}and 5{ in presence of SDS (1.6x10^{-2} mol dm^{-3})}.*	96
Fig. III.B.2	*UV-visible absorption spectra of MB (5x10^{-5} mol dm^{-3}) at pH 7.00 in presence of various concentration of SDS at 298K (±01): [SDS] / 10^{-3} mol dm^{-3} = 1(2.0), 2(4.0), 3(6.0), 4(8.0), 5(10.0), 6(12.0) and 7(14.0).*	96

Fig. III.B.3	*Spectra of MB (5x 10^{-5} M) at pH 7.00 in presence of various concentration of PVA at 298 (±0.1) K: [PVA] = 1(0.1%), 2(0.2%), 3(0.3%), 4(0.4%), 5(0.5%), 6(0.6%) and 7(0.7%).*	97
Fig. III.B.4	*Spectra of MB (5x 10^{-5} mol dm^{-3}) at pH 7.00 in aqueous solution of varying concentration of SDS in presence of 5.0 % PVA (M.W. 14000) at 298(±01) K: [SDS] / 10^{-3}M = 1 (0.0), 2 (2.0), 3(4.0), 4(6.0), 5(8.8) and 6(12.0)*	97
Fig. III.B.5	*van't Hoff plot for monomer-dimer process of MB at pH 7.00 (phosphate buffer)*	104
Fig. III.C.1	*UV-Visible spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) at various pH of the medium at 298 (±0.1) K*	106
Fig. III.C.2	*UV-visible spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in presence of various concentrations of CTAB at pH 7.00 and temperature 298(±0.1) K: [CTAB] / (10^{-5} mol dm^{-3}) = {**(a):** (1) 0.00, (2) 1.0, (3) 2.0, (4) 4.0 and (5) 6.0; **(b):** (6) 8.0, (7) 12.0, (8)14.0, (9)16.0 and (10) 18.0; **(c):** (11) 20.0, (12) 22.0, (13) 24.0, (14) 26.0, (15) 28.0, (16) 30.0, (17) 40.0, (18) 50.0 and (19) 60.0*	108
Fig. III.C.3	*UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in presence of various concentrations of TTAB at pH 7.00 and temperature 298K (±0.1): [TTAB]/ (10^{-4} mol dm^{-3}){**(a):** (1) 0.0, (2)1.0, (3) 2.0, (4) 3.0, (6) 6.0, (7) 9.0 and (8) 12.0; **(b):** (9)15.0, (10)18.0, (11) 21.0, (12) 24.0, (13) 27.0, (14) 30.0 and (15) 40.0}*	109
Fig. III.C.4	*UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in presence of various concentrations of DTAB at pH 7.00 and temperature 298(±0 1) K· [DTAB]/ (10^{-4} mol dm^{-3}) = (1) 0.00, (2) 1.0, (3) 2.0, (4) 4.0, (5) 8.0, (6)12.0, (7)16.0, (8) 20.0 and (9) 24.0*	109
Fig. III.C.5	*Fluorescence spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in presence of various concentrations of CTAB at pH 7.00 and temperature 298 (±0.1) K: [CTAB]/ (10^{-5} mol dm^{-3}) = (1) 0.00, (2) 2.0, (3) 4.0, (4) 8.0, (5) 10.0, (6)14.0, and (7)18.0*	111
Fig. III.C.6	*UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in*	112

	various concentrations of CTAB in presence of 1% (w/v) PVA at pH 7.00 and temperature 298 (±0.1) K: [CTAB]/ (10^{-5} mol dm^{-3}) = (1) 0.00, (2) 2.0, (3) 4.0, (4) 6.0, (5) 9.0 and (6)12.0	
Fig. III.C.7	*Fluorescence spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of CTAB in presence of 1% (w/v) PVA at pH 7.00 and temperature 298 (±0.1) K: [CTAB]/ (10^{-5} mol dm^{-3}) = (1) 0.00, (2) 2.0, (3) 4.0, (4) 6.0, (5) 9.0 and (6)12.0*	112
Fig. III.C.8	*UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of SDS at pH 7.00 and temperature 298 (±0.1) K: [SDS] /10^{-4} mol dm^{-3} {**(a):** (1) 0.0 (2) 5.0 (3) 8.0 (4) 10.0 (5) 14.0 and (6) 18.0; **(b):** (7) 20.0 (8) 30.0 (9) 40.0 (10) 60.0 and (11) 80.0}*	116
Fig. III.C.9	*UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in presence of various concentrations of SDSN at pH 7.00 and temperature 298 (±0.1) K: [SDSN]/ (10^{-4} mol dm^{-3}) {**(a):** (0) 0.00, (1) 3.0, (2) 4.0, (3) 6.0, (4) 8.0 and (5) 10.0; **(b):** (6) 12.0, (7) 15.0, (8) 18.0, (9) 20.0 and (10) 30.0}*	116
Fig. III.C.10	*UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in presence of various concentrations of SDBS at pH 7.00 and temperature 298 (±0.1) K: [SDBS]/ (10^{-5} mol dm^{-3}) {**(a):** (0) 0.00, (1) 3, (2) 6, (3) 8 and (4) 10; **(b):** (5) 11.0, (6) 12.0, (7) 15.0 and (8) 20.0}*	117
Fig. III.C.11	*Fluorescence spectra of curcumin (2.5x10^{-5} mol dm^{-3}) in presence of various concentrations of SDS at pH 7.00 and temperature 298 (±0.1) K: [SDS]/ (10^{-4} mol dm^{-3}) {**(a):** (1) 0.0 (2) 5.0 (3) 8.0 (4) 10.0 (5) 14.0 and (6) 18.0; **(b):** (7) 20.0 (8) 30.0 (9) 40.0 (10) 60.0 and (11) 80.0*	118
Fig. III.C.12	*UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of SDS in presence of 1% (w/v) PVA at pH 7.00 and temperature 298(±0.1) K: [SDS] /10^{-4} mol dm^{-3} = (1) 0.0, (2) 5.0, (3) 8.0, (4) 12.0, (5) 16.0 and (6) 20.0*	120
Fig. III.C.13	*Fluorescence spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various*	120

	concentrations of SDS in presence of 1% (w/v) PVA at pH 7.00 and temperature 298(±0.1) K: [SDS] /10^{-4} mol dm^{-3} = (1) 0.0, (2) 5.0, (3) 8.0, (4) 12.0, (5) 16.0 and (6) 20.0	
Fig. III.C.14	*UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of SDS at pH 7.00 and temperature 298 (±0.1) K: [SDS] /10^{-3} moldm^{-3} = (1) 0.0, (2) 5.0, (3) 8.0, (4) 10.0, (5)14.0 and (6) 18.0*	123
Fig. III.C.15	*Fluorescence spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of SDS at pH 7.00 and temperature 298 (±0.1) K: [SDS] /10^{-3} mol dm^{-3} = (1) 0.0, (2) 5.0, (3) 8.0, (4) 10.0, (5)14.0 and (6) 18.0*	123
Fig. III.C.16	*UV-visible spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of SDS in presence of 1.0% (w/v) PVA at pH 7.00 and temperature 298 (±0.1) K: [SDS]/10^{-3} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)10.0 and (6) 12.0*	124
Fig. III.C.17	*Fluorescence spectra of curcumin (2.5x10^{-5} mol dm^{-3}) in various concentrations of SDS in presence of 1.0% (w/v) PVA at pH 7.00 and temperature 298 (±0.1) K: [SDS]/10^{-3} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)10.0 and (6) 12.0*	124
Fig. III.C.18	*UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of CTAB at pH 7.00 and temperature 298 (±0.1) K: [CTAB]/ 10^{-4} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 16.0*	126
Fig. III.C.19	*Fluorescence spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of CTAB at pH 7.00 and temperature 298 (±0.1) K: [CTAB] /10^{-4} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 16.0*	126
Fig. III.C.20	*UV-visible spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of CTAB in presence of 1.0% (w/v) PVA at pH 7.00 and temperature 298 (±0.1) K: [CTAB] /10^{-4} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 16.0*	127
Fig. III.C.21	*Fluorescence spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various*	127

	concentrations of CTAB in presence of 1.0% (w/v) PVA at pH 7.00 and temperature 298 (±0.1) K: [CTAB]/ 10^{-4} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 16.0	
Fig. III.C.22	*UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of TW80 at pH 7.00 and temperature 298 (±0.1) K: [TW80] / 10^{-4} moldm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 16.0*	129
Fig. III.C.23	*Fluorescence spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of TW80 at pH 7.00 and temperature 298 (±0.1) K: [TW80]/ 10^{-4} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 16.0*	129
Fig. III.C.24	*UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of TW80 in presence of 1% (w/v) PVA at pH 7.00 and temperature 298 (±0.1) K: [TW80] /10^{-4} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 16.0*	130
Fig. III.C.25	*Fluorescence spectra of curcumin (2.5 x10^{-5} M) in various concentrations of TW80 in presence of 1% (w/v) PVA at pH 7.00 and temperature 298K (±0.1): [TW80] / 10^{-4} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 16.0*	130
Fig. III.C.26	*UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in presence of various concentrations of chitosan at pH 7.40 and 298 (±0.1) K: [chitosan] / 10^{-6} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 14.0*	134
Fig. III.C.27	*Fluorescence spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in presence of various concentrations of chitosan at pH 7.40 and 298 (±0.1) K: [chitosan] / 10^{-6} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 14.0*	134
Fig. III.C.28	*Absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) at various concentrations of chitosan in presence of 1.5x 10^{-3} mol dm^{-3} of CTAB at pH 7.40 and 298 (±0.1) K: [chitosan] / 10^{-6} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 14.0*	136
Fig. III.C.29	*Fluorescence spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) at various*	136

	concentrations of chitosan in presence of 1.5x 10^{-3} mol dm^{-3} of CTAB at pH 7.40 and 298(±0.1) K: [chitosan] / 10^{-6} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 14.0	
Fig. III.C.30	*UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) at various concentrations of chitosan in presence of 1.0x 10^{-3} mol dm^{-3} of TW80 at pH 7.40 and 298 (±0.1) K: [chitosan] / 10^{-6} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 14.0*	138
Fig. III.C.31	*Fluorescence spectra of curcumin (2.5x 10^{-5} M) at various concentrations of chitosan in presence of 1.0x 10^{-3} mol dm^{-3} of TW80 at pH 7.40 and 298 (±0.1) K: [chitosan] / 10^{-6} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 14.0*	138
Fig. III.C.32	*The van't- Hoff plot for the interaction of curcumin with chitosan at pH 7.40.*	141
Fig. III.C.33	*UV-vis absorption spectra of curcumin (2.5x 10^{-5} M mol dm^{-3}) in (a) pH 7.40 (phosphate buffer), (b) 1.0x 10^{-5} mol dm^{-3} chitosan alone, (c) 1.0x 10^{-5} mol dm^{-3} chitosan in presence of 1.5x 10^{-3} mol dm^{-3} CTAB, (d) 1.0x 10^{-5} mol dm^{-3} chitosan in presence of 1.0x 10^{-3} mol dm^{-3} TW80. The rate of degradation is determined from the initial slope of the best-fit linear curve*	144
Scheme III.A(1)	*The various equilibria and the species involved in the PR-micelle-polymer systems investigated*	69
Scheme III.A(2)	*A schematic representation of the various equilibria and the species involved in NR-nonionic micelle-polymer systems investigated*	81
Scheme III.C(1)	*The chemical structure of products obtained from the degradation of curcumin in phosphate buffer at pH 7 20*	142

Declaration

I hereby declare that the thesis entitled "***A Study on the Interactions of some Synthetic and Natural Dyes of Different Charge Types with Surfactants and Polymers***" being submitted to the Department of Chemical Sciences, Tezpur University, is a record of original research work carried out by me. Any text, figures, results or designs that are not of own devising are appropriately referenced in order to give credit to the original author(s). All sources of assistance have been assigned due acknowledgement. I also declare that neither this work as a whole nor a part of it has been submitted to any other university or institute for any other degree, diploma or award.

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Date: 16/07/12

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(A Central University Established by an Act of Parliament)
NAPAAM, TEZPUR-784028
DISTRICT :: SONITPUR :: ASSAM :: INDIA

Ph: 03712-267004
03712-267005
Fax: 03712-267006
03712-267005

I certify that the thesis entitled "***A Study on the Interactions of some Synthetic and Natural Dyes of Different Charge Types with Surfactants and Polymers***" submitted to the Tezpur University in the Department of Chemical Sciences under the School of Science, in partial fulfillment for the award of the degree of Doctor of Philosophy in Science is a record of research work carried out by Ms. Bornali Boruah under my supervision and guidance.

All help received by her from various sources have been duly acknowledged.

No part of this thesis has been submitted elsewhere for award of any other degree.

Place: Tezpur University
Date: 16/7/2012

(Dr. Robin Kumar Dutta)
Professor
Department of Chemical Sciences
School of Science

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Table of Contents

Contents **Page No**

Chapter-I Introduction

I.A Surfactants and Micelles 1

I.A.1 Surfactants 1

I.A.2 Micellization and CMC 2

I.A.3 Micellar features 4

I.A.4 Surfactant assemblies other than micelles 5

I.A.5 Applications of surfactants 5

I.A.6 Solubilization by micelles 6

I.A.7 Micellar catalysis 6

I.B Dye-surfactant interactions 7

I.B.1 Dye-surfactant interactions in submicellar surfactants 7

I.B.2 Interaction of dyes with micellized surfactants 9

I.B.3 Acid-base equilibria of dyes in aqueous micellar medium 13

I.C Polymer-surfactant interactions 18

I.D Interaction of dyes with surfactants in presence of polymers 22

I.E Curcumin-surfactant interactions 24

I.E.1 Curcumin 24

I.E.2 Interaction of curcumin with surfactants 25

I.F Lacuna and rational 26

I.G Aim and objectives 28

References 30

Chapter-II Experimental

II.A Materials 51

II.A.1 Dyes 51

II.A.2 Surfactants 53

II.A.3 Polymers 57

II.A.4 Buffer components 59

II.B Preparations of solutions 59

II.B.1 Preparation of experimental solutions in buffer medium 59

II.C Experimental measurements 61

II.D Methods 61

II.D.1 Calculation of the apparent acid dissociation constant of NR 62

in nonionic surfactant micelles in presence of nonionic polymers
References 65
Chapter-III Results and discussion
III.A Acid-base equilibrium of dyes in aqueous polymer-surfactant medium 66
III.A.1 Acid-base equilibrium of phenol red in aqueous polymer-surfactant medium
III.A.1(i) Acid-base equilibrium of phenol red in polymer -anionic micellar medium 66
a. Spectral behaviour 66
b. Determination of equilibrium constants and other thermodynamic parameters 69
III.A.2 Acid-base equilibrium of neutral red in aqueous polymer-surfactant medium 77
III.A.2(i) Acid-base equilibrium of neutral red in polymer -nonionic micellar medium 77
a. Spectral behaviour 77
b. Determination of equilibrium constants and other thermodynamic parameters 81
III.B Monomer-dimer equlibrium of methylene blue in aqueous polymer-surfactant medium 95
III.B.2 Monomer-dimer equilibrium of methylene blue in polymer-anionic micellar medium 95
a. Spectral behaviour 95
b. Determination of effective dimerization constant ($^{eff}K_D$) and other thermodynamic parameters 99
III.C Interaction of curcumin with surfactants and polymers in aqueous medium 105
III.C.1 Interaction of curcumin with submicellar surfactants in absence and presence of polymers 105
III.C.1(i) Interaction of curcumin with submicellar cationic surfactants in absence and in presence of polymer 107
a. Spectral behaviour 107
b. Determination of binding constants 113
III.C.1(ii) Interactions of curcumin with submicellar anionic 115

surfactants in absence and presence of polymer
a. Spectral behaviour 115
b. Determination of binding constants 121
III.C.2 Interaction of curcumin with micellar surfactants in presence of PVA 122
a. Spectral behaviour in SDS-PVA system 122
b. Spectral behaviour in CTAB-PVA system 125
c. Spectral behaviour in TW80-PVA system 128
d. Determination of binding constants 128
III.C.3 Interaction of curcumin with chitosan in presence of surfactants 133
a. Spectral behaviour 133
b. Determination of binding constants 139
c. Kinetic study 141
References 145
Chapter-IV Conclusion
IV.A.1 Acid-base equilibrium of phenol red in aqueous polymer-surfactant medium 148
IV.A.2 Acid-base equilibrium of neutral red in aqueous polymer-surfactant medium 148
IV.B Monomer-dimer equlibrium of methylene blue in aqueous polymer-surfactant medium 149
IV.C.1 Interaction of curcumin with submicellar surfactants in absence and in presence of polymers 150
IV.C.2 Interaction of curcumin with surfactants in presence of PVA 150
IV.C.3 Interaction of curcumin with chitosan in presence of surfactants 151
List of publications 152

CHAPTER-I

I: Introduction

This thesis describes a spectroscopic and thermodynamic study of the interactions of some aqueous dyes with some surfactants and polymer-surfactant systems. The background of the work including the nature of surfactants, the nature of dye-surfactant interactions and the nature of polymer-surfactant interactions together with the motivation and the strategy of the work has been presented in this chapter.

I.A: *Surfactants and micelles*

I.A.1: *Surfactants*

The word 'surfactant' is the abbreviation for the surface active agents, which literally means active at surfaces and interfaces.[1,2] Surfactants are amphiphilic in nature with a hydrophilic charged head group and a long hydrophobic hydrocarbon tail. The head group of a typical surfactant molecule may consist of an ionic or a highly polar nonionic group and the hydrocarbon chain consists of 7-20 carbon atoms.[1]

Surfactants have been broadly classified into two groups, *viz.*, naturally occurring surfactants and synthetic surfactants. The typical examples of naturally occurring surfactants are lipids and the bile salts. Depending upon the nature of the hydrophilic head group synthetic surfactants are primarily classified into four sub groups: (i) anionic, (ii) cationic, (iii) nonionic and (iv) zwitterionic. Some common examples of synthetic surfactants of various types are illustrated in the **Table I.A(1)**.

Table I.A(1): Examples of some common surfactants.

Class	Examples	Structures
Anionic	Sodium dodecyl sulphate	$CH_3(CH_2)_{11}SO_4^-Na^+$
Cationic	Cetyl trimethylammonium bromide	$CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$
Nonionic	Polyoxyethylene octyl phenyl ether	$C_{14}H_{22}O(C_2H_4O)_n$ (n = 9-10)
Zwitterionic	Dodecyl betaine	$C_{16}H_{33}NO_2$

Apart from the above class of surfactants a new group of surfactants known as 'gemini surfactant' have been identified. Gemini surfactants differ from the traditional surfactants in that they contain two hydrophilic groups and two (sometimes three) hydrophobic groups.[3]

I.A.2: ***Micellization and CMC***

Surfactants in solutions have a tendency to adsorb at the interfaces. On increasing the surfactant concentration in aqueous solution, as the concentration exceeds a certain value, the surfactant molecules aggregate to form a nearly spherical shape called micelles (**Fig. I.A.1**). This critical concentration, characteristic of a surfactant is called its critical micelle concentration. While, in nonpolar medium, the aggregates are oriented in such a way that the polar head groups of the surfactants shielded from the solvent by the hydrocarbon tails. These aggregates have been termed as "reverse micelles". Amphiphiles with short alkyl influence the hydrogen-bonding structure of water and are termed as hydrotropes.[4] The earliest works on micelle were by J. McBain[5] and Hartley. [6] The solubilization power and other properties exhibited by the micelles are very useful in various fields of science and technology and have been the subject of excellent reviews and reports.[1,7-21] The IUPAC definition of CMC is, "There is a relatively small range of concentration separating the limit below which virtually no micelles are detected and the limit above which virtually all additional surfactants form micelles. Many properties of the surfactant solution, if plotted against concentration, appear to change at a different rate above and below this range".[22] The temperature at which the concentration of the surfactant reaches the CMC is defined as the Krafft point or Krafft temperature.[23]

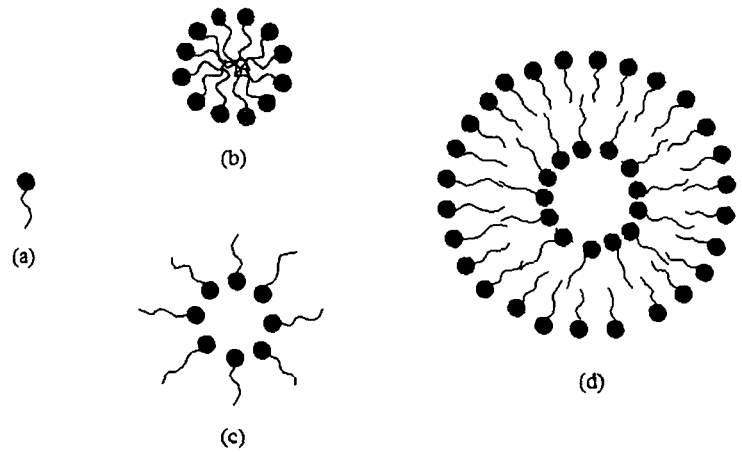

Fig. I.A.1: Schematic representation of (a) a surfactant monomer, (b) spherical micelle, (c) reverse micelle and (d) vesicle.

The CMC can be determined by plotting the various physical properties against the concentrations of surfactants which is illustrated by Preston's classic graph[1,5,24-37] (**Fig. I.A.2**). The CMC's of some common surfactants at 298 K in aqueous medium are shown

in **Table I.A(2)**.[38-40] The CMC of surfactants depend on a number of factors: (a) the length and structure of hydrocarbon chain, (b) the nature of the head group, (c) the presence of additives, (d) the temperature, etc.[10,41-43]

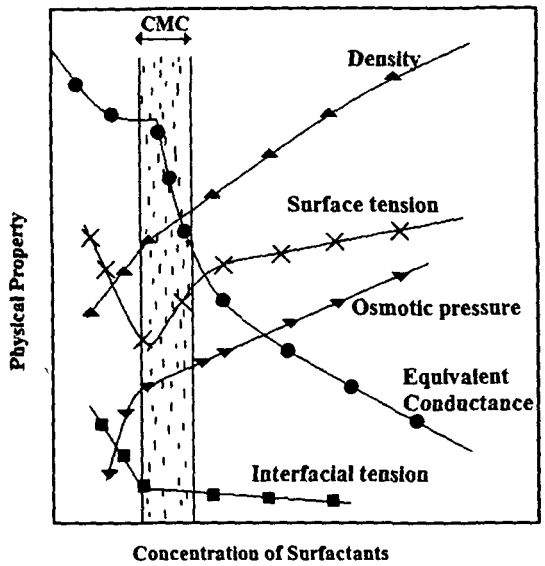

Fig. I.A.2: Changes of some physical properties of aqueous surfactant solution (in arbitrary scale) with concentration of the surfactant.

Table I.A(2): The CMC's of some common surfactants at 298K in water.[38-40]

Surfactant	CMC/ (mol dm^{-3})
Sodium Dodecyl Sulphate (SDS)	8.0×10^{-3}
Sodium Dodecyl Benzene Sulphonate (SDBS)	1.2×10^{-3}
Cetyl trimethylammonium bromide (CTAB)	9.2×10^{-4}
Tetradecyl trimethylammonium bromide (TTAB)	3.6×10^{-3}
Dodecyl trimethylammonium bromide (DTAB)	16.0×10^{-3}
Polyoxyethylene(20) sorbitan monolaurate (Tween-20)	5.0×10^{-5}
Polyoxyethylene(20) sorbitan monopalmitate (Tween-40)	2.3×10^{-5}
Polyoxyethylene(20) sorbitan monostearate (Tween-60)	2.1×10^{-5}
Polyoxyethylene(20) sorbitan monooleate (Tween-80)	1.0×10^{-5}
Iso-octylphenoxy-polyethoxy-ethanol (Triton X-100)	3.0×10^{-5}

I.A.3: *Micellar features*

Each micelle consists of a definite number of monomer molecules, termed as aggregation number (N), usually ranging from 10 to 150, which determines its general size

and shape.[44,45] The sizes of the micelles normally cover the range of 1-10 nm.[21] Ionic micelle forms an electrical double layer, in which the Stern layer encompasses the interfacial region containing the head groups and extends to about one half of the counterions associated with the micelle and water.[11,46] In case of nonionic micelles, the hydrated polyoxyethylene chains comprise the outer region.[47] A schematic representation of a spherical micelle with illustration of its different regions is shown in **Fig. I.A.3**. The micelle can assume different shapes depending on the nature of the surfactant and its concentration.[48-54] Some of the principal morphological structures are shown in **Fig. I.A.4**.

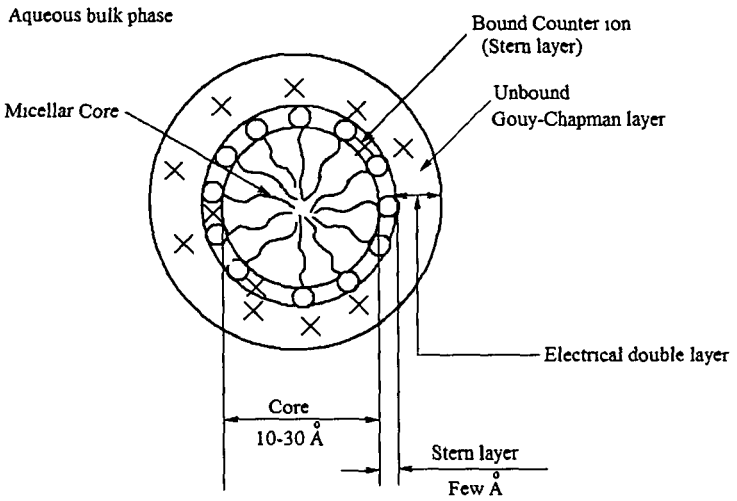

Fig. I.A.3: A two dimensional representation of the regions of a spherical micelle: ∿∿ -hydrocarbon chain, O-head group, X-counterion.

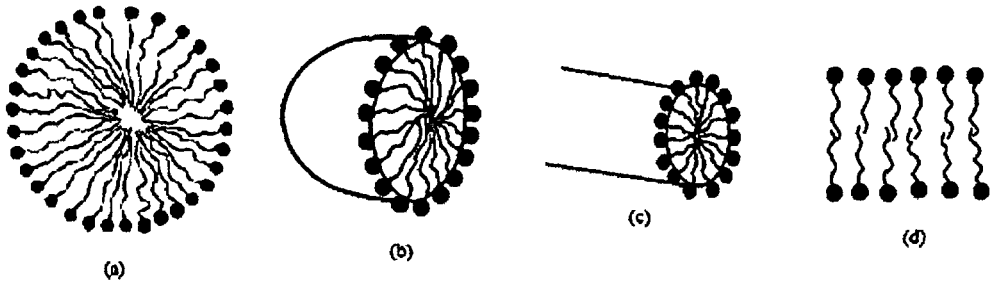

Fig. I.A.4: The schematic picture of some surfactant micelles: (a) spherical, (b) oblate, (c) cylindrical and (d) lamellar.

Israelachvili, *et al.* established a relationship between the shape of the surfactant monomer and the aggregate morphology on the basis of packing parameter approach.[55] Some researchers criticised this packing parameter approach for predicting the aggregate

pattern.[56,57] Dobes *et al.* identified a new parameter, micellar proportion, for expressing the time spent by the analyte in the micellar phase.[58]

The micellization is governed by the hydrophobic interaction between the alkyl chains and the polar repulsion between the head groups.[59-61] The formation of micelles in aqueous surfactant solutions occurs primarily as a result of an increase in entropy of the resultant solution,[6] negative values are rarely observed.[62,63] The thermodynamic analysis of micelle formation process has been treated using a mass action model and phase separation model,[64] where the standard free energy of micellization ΔG^{o}_{mic} is described by Eq. I.A(1),

$$\Delta G^{o}_{mic} = -RT\ln\chi_{cmc} \qquad \text{I.A(1)}$$

where, χ_{cmc} is the surfactant mole fraction at CMC.

I.A.5: *Surfactant assemblies other than micelles*

Surfactant may self assemble to form a variety of aggregates including the microemulsions and biological membranes apart from the micelles and reverse micelles. Microemulsions are thermodynamically stable, macroscopically homogeneous dispersions of water-in-oil (W/O) or oil in water (O/W).[65,66] O/W microemulsions can be formed by dispersing oil in an aqueous surfactant solution and adding a short chain alcohol or amine as a co-surfactant. On the other hand, when water droplets are dispersed in oil the W/O microemulsion is formed.[67,68] Sometimes a cosurfactant, generally an alcohol of intermediate chain length, is required for microemulsion formation.[18,69] Biological membranes are made up of phospholipid bilayers. There are two layers of phosphate "heads" with fatty acid "tails" in the biological membranes.[10,18]

I.A.6: *Applications of surfactants*

Surfactants play an important role in many aspects of our day to day life ranging from the formulation of industrial products to biological applications.[2,18,70-100] Apart from the household detergency,[18,70,71] surfactants are used in the production and processing of foods,[72-74] agrochemicals,[75-77] pharmaceuticals,[78-80] petroleum,[2,81-83] mineral ores,[81,83] fuel additives and lubricants,[84-86] paints,[85,86] coatings and adhesives,[85,87,88] in removing hazardous materials from industrial waste water.[89,90]

I.A.7: *Solubilization by micelles*

Solubilization into aqueous media is of practical importance in many industrial processes such as detergency,[18,70,71] emulsion polymerization,[101] micellar catalysis,[10] oil recovery,[81-83], drug delivery, [102,103] etc. The extent of solubilization of the solubilizate depends on the structure of the surfactant molecule, concentration of the surfactant, molecular properties of the solubilised species, temperature and added electrolytes.[104-109] The sites on solubilization in the micelles have been determined by various methods including X-ray diffraction,[110,111] UV-visible spectroscopy[112] and NMR spectroscopy.[113,114]

There is a linear relationship between the free energy of solubilization with the number of carbon atoms of the solubilizate as well as with the number of carbon atoms in the hydrocarbon chain of the surfactants.[115,116] A number of experimental techniques have been used to study the solubilization equilibrium, ion-ion, ion-dipole, dipole-dipole as well as hydrophobic interactions of solubilizate with surfactant micelles, such as vapour pressure measurements,[117] maximum solubility,[118] calorimetry,[42] semi-equilibrium dialysis,[119-121] etc. Additives considerably affect the solubilization process.[122-127] In presence of a polymer the surfactant aggregates are formed which solubilise the solubilizate at concentrations below the normal CMC of the surfactant.[128-133]

I.A.8: *Micellar catalysis*

The presence of micelles markedly alter the reaction rates and equilibria of many organic reactions.[10,134,135] The micellar catalysis can be explained in terms of the differences in the reactivity of the substrate in the micellar phase and in bulk medium and the degree and nature of the micelle-substrate binding, which is analogous to the enzyme-substrate binding in *Michaelies-Menton kinetics*.[119-121,136-140] Kinetic considerations are most frequently based on the so-called pseudophase model. [137,141,142] The acceleration of the rate of reactions by micelles is often interpreted as solvent effects.[143] A number of reactions are carried out in micellar medium; some examples are: electrophilic and nucleophilic reactions,[144,145] electrochemical reactions,[146] redox reactions,[140,147] hydrolysis,[139,158,150] electron transfer reactions,[150,151] proton transfer reactions,[152] electron donor-acceptor equilibria,[153] etc. Many micelle catalysed reactions are *p*H dependent.[154,155] Micellar catalysis has also been successfully explained in terms of an electrostatic model.[156] Micellar catalyzed acid dissociation reactions are known to shift acid-base

equilibrium of indicator dyes in micellar medium.[157] The dye-surfactant interactions also involve micellar catalysis.[158]

I.B: *Dye-surfactant interactions*

Dye-surfactant interactions are important in textile industry as well as chemical research, such as biochemistry, analytical chemistry, environmental chemistry and photosensitization.[159-174] Therefore, the investigation of dye-surfactant interaction mechanism and its effect on fabrics dyeing has been the subject of many previous works.[175-177] In order to understand the chemical equilibria, mechanisms and kinetics of micelle-sensitized color and fluorescence reactions the knowledge on the property of micelle-solubilized dye is very important.

Spectral variations of dyes induced by surfactants are also been used to measure the CMC of amphiphiles and surface property of micelles.[33-39,178-182] The studies on the dye-surfactant interactions have been reviewed by Diaz Garcia and Sanz-Medel[158] and Barni *et al.*[183] There are some other reviews on dye-surfactant interactions by Love *et al.*[157] Hinze,[7] Kert and Simoncic,[159] Oakes and Dixon,[184] which deals with its industrial and analytical applications. Surfactants, both in micellized and premicellized form, affect the spectral characteristics of dyes leading to a shift in wavelength of maximum absorption or emission and sometimes the appearance of new bands and consequent disappearance of the original ones.[160] Such solvatochromism is observed in all types of dyes, both synthetic, e.g., azo,[6,115,180,182,185-212] azine,[39,174,213-226] cyanine,[228-239] acridine,[155,240-247] triphenylmethane,[39,134,180,245-257] arylmethane,[258] anthraquinone[258,259] etc. and natural, e.g. curcumin.[97-100]

I.B.1: *Dye-surfactant interactions in submicellar surfactants*

If a surfactant is added to a solution of a dye at submicellar concentrations, specific molecular interactions occur between the dye and the surfactant, which primarily occurs with surfactants that are oppositely charged to the dye.[182] In the presence of a dye, the formation of premicellar aggregates at concentrations below the CMC of some surfactants is a well known phenomenon.[213,260] Molecular complexes having specific and characteristic physicochemical features may be formed at concentrations below the CMC of the surfactant.[158] The characteristic changes occur in the absorption spectra of the dye can be attributed to self-assembly of dye-surfactant complex,[238] formation of dye-

surfactant salt,[158] ion-pair,[261,262] dye-rich induced micelles,[263] induced self-assembly of dyes,[161] change in microenvironment of the dye[264] and formation of charge transfer complex.[213]

Some of the systems studied on the interactions of dyes with surfactants in submicellar concentration ranges of the surfactants are listed in the **Table I.A(3)**.

Table I.A(3): Some dye-surfactant systems studied in submicellar surfactant region.

Systems	**Nature of interaction (observations and conclusions)**
Azo dyes-cationic surfactant	Complex formation,[187,206,265-268] Induced dye aggregation[195,203,204] Metachromism,[190] Ion pair formation[190,202,212,269-271]
Azo dyes-anionic and cationic surfactants	Complex formation[272]
Azo dyes-cationic and cationic gemini surfactants	Ion pair formation[273]
Acridine orange-anionic surfactant	Electrostatic-hydrophobic interaction,[153,274] Induced dye aggregation[275]
Alizarin red S-cationic surfactant	Soluble dye-surfactant complex[276,277]
Arylazonapthol dyes-anionic, cationic nonionic and zwitterionic surfactants	No interaction in nonionic or anionic, Complex with cationic or zwitterionic[172-177]
Basic yellow 2-anionic surfactants	Ion pair formation[278]
Congo red-cationic surfactant	Poorly soluble complex formation[115]
Cyanine dyes-cationic surfactant	Induced dye aggregation[230]
Cyanine dyes-anionic surfactant	Induced dye aggregation,[279,280] Metachromism[233]
Esters of azonaphtholsulphonate-cationic surfactant	Induced dye aggregation[193,194]
8-Hydroxyquinoline-5-sulphonic acid-cationic surfactant	Metachromism[281]
Iodaniline dyes-cationic and anionic surfactants	Complex formation[282]
Indigo carmine and amaranth-cationic	Complex formation[283]

surfactant	
Multicharged anionic planar dyes-cationic surfactant	Complex formation [284]
Metal-chrome azurol S-cationic surfactant	Complex formation [254]
Phenoxazine dyes-anionic surfactant	Ion pair formation [223, 285, 286]
Phenazine dyes-anionic surfactant	Induced dye aggregation [287,288], Ion pair formation [220,261,289-291]
Phenazine dyes-anionic and cationic surfactants	Complex formation [272]
Phenazine dyes-anionic, cationic, nonionic and zwitterionic surfactants	Complex formation [292]
1-Phenylazo-4-naphthol dye-cationic surfactant	Induced dye aggregation [198]
Picric acid-cationic surfactant	Ion pair formation [269]
Pinacyanol chloride-cationic surfactant	Induced dimerization of dye [293]
Pinacyanol-anionic surfactant	Insoluble dye-surfactant salt [39]
Rhodamine 6G-cationic surfactant	Salt formation and Induced dye aggregation [294, 295]
Sulfonephthalein dyes-cationic surfactant	Salt and ion pair formation [245,262,296,297] Turbidity [249], Metachromism [281]
Thiazole orange-anionic surfactant	Induced dye aggregation [239]
Triphenyl methane dye-anionic surfactant	Complex formation, [276, 277] Induced dye aggregation, [298] Ion pair formation [299-301]
Triphenyl methane dyes-cationic surfactant	Ion pair formation [302]
Xanthene dyes-anionic and cationic surfactants	Induced dye aggregation [174,303]
Xanthene dyes-anionic surfactant	Ion pair formation [300]

I.B.2: ***Interaction of dyes with micellized surfactants***

All type of surfactant micellar systems are known to dissolve insoluble dyes,[97-100] disintegrate dye aggregates into monomers or partition soluble dyes via incorporation into surfactant micelles.[174,203,275,279,288,303] Generally, hypsochromic and bathochromic shift of

the original dye bands are observed upon interaction of a dye with oppositely charged micelles.[39,187,304-308] Micelles affect not only the electronic structure of the dye but also the pK_a of indicators.[40,309] The nature of interactions of various types of dyes with micellized surfactants are listed in **Table I.A (4)**.

Table I.A(4): Some dye-surfactant systems studied in micellized surfactants.

Systems	Nature of interaction (observations and conclusions)
Acridines-anionic surfactant	Localization at the hydrophobic interior and hydrophilic interface of the micelle,[310] Association with micelles[311]
Acridines-anionic, cationic and nonionic surfactants	Association with micelles,[244] CT complex formation[312]
Alizarin red S-anionic, actionic and nonionic surfactants	Association with micelles[313]
8-Anilino-1-napthalenesulfonic acid ammonium salt-nonionic surfactants	Binding constants decreases with increasing number of ethylene oxide[314]
8-Anilino-1-napthalensulfonic acid ammonium salt-nonionic surfactant	Association with micelles[315, 316]
Arylazonaphthol dyes-nonionic surfactants	Solubilisation [173, 174]
Azo dyes-anionic surfactant	Molecular interaction with hydrophobic dyes,[317]CT interactions,[318] pK_a shift[309]
Azo dyes-cationic surfactant	Solvatochromism,[319] Electrostatic interactions,[320] Association with micelles[321]
Azo dyes-cationic surfactant	Induced tautomerism[322]
Azo dyes-anionic and cationic surfactants	Induced tautomerism,[323] Micelles alter enthalpy and entropy of ionization of dyes[324]
Azo dyes-cationic and cationic gemini surfactants	Association with micelles,[210] Solubilization[215]
Basic yellow 2-anionic surfactant	Association with micelles[278]
Basic yellow 25 and acid orange 7-cationic surfactant	Complex formation [325, 326]

Cyanine dyes-anionic and cationic surfactants	Hydrophobicity of the dyes increases,[227] Solvatochromism[327]
Cyanine dyes-anionic surfactant	Dye hydrophobicity plays the key role,[231-233,328] Solubilisation,[329] Aromatic part plays the key role [330,331]
Cyanine dyes-anionic, cationic and nonionic surfactants	Localisation at micelle-water interface,[332] De-aggregation of the dye[333, 334]
Cyanine dyes-nonionic surfactant	CT complex formation[335]
Disperse dyes of N-Alkyl and N-Carboxylic acid naphthalimides-cationic gemini surfactant	Solubilisation[336]
4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide-cationic surfactants	Complex formation[330]
2-(4-(Dimethylamino) styryl)-1-methylpyridinium iodide-anionic and cationic surfactants	Dye enters in different positions of the micelles[337]
2,6-Diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)-cationic and cationic gemini surfactants	Polarity dependent localisation of dye[338]
Light yellow-cationic surfactant	Solubilization[207]
Orange II, direct red 80, indigocarmine-cationic surfactant	Free micelles occur before the dyes become fully saturated with bound surfactant[320]
(2-P-toluinylnaphthalene-6-sulphonate) and (1-aminonaphthalene-8-sulphonate)-anionic surfactant	Molecular interaction[339, 340]
Phenazine dyes-anionic surfactant	Association with micelles[169]
Phenazine dyes-nonionic surfactant	CT complex formation[224,341]
Phenazine dyes-anionic, cationic and nonionic surfactants	Association with micelles,[220,342] CT complex formation[213,343]
Pyranine-nonionic surfactant	Modification of dye[344]
Pyrene-anionic surfactant	Partitioning into micelles[345]
Pyrene-cationic surfactant	Mixed micelle formation[346]
Pyridinium *N*-phenolate betaine dyes-	sphere → rod transition of micelles[347]

cationic surfactant	
Quinolinium betaine dyes-cationic surfactants	Hydrophobic dyes penetrate deeper into the micelle[348]
Riboflavin-nonionic surfactant	CT complex formation[224]
Rivanol-anionic, cationic and nonionic surfactants	Association with micelles[349]
Styryl pyridinium dyes-anionic surfactant	Combined electrostatic-hydrophobic interaction[350]
Sulfonephthalein dyes-anionic surfactant	Association with micelles[351]
Sulfonephthalein dyes-anionic, cationic and nonionic surfactants	Micellar catalysis[352]
Thiazine dyes-anionic surfactant	Association with micelles,[311] Mixed micelle formation,[353] Metachromism,[354] Micellar catalysis[355,356]
Thiazine dyes-nonionic surfactant	CT complex formation[218,357]
Thiazine dyes-anionic, cationic and nonionic surfactants	Molecular complex formation[358]
Triphenyl methane dyes-anionic surfactant	Micellar catalysis,[359] Mixed micelle formation[360]
Triphenyl methane dyes-nonionic surfactant	Association with micelles,[360,361] CT complex formation,[362] Micellar catalysis[316]
Triphenyl methane dyes-cationic surfactant	Mixed micelle formation,[363] Micellar catalysis[364-366]
Triphenyl methane dyes-anionic, cationic and nonionic surfactants	Micellar catalysis[354,367]
Triphenyl methane dyes-lecithin liposomes	Dye locate in the palisade of lecithin liposomes[368]
Xanthene dyes-nonionic surfactants	CT complex formation[224,369]
Xanthene dyes-anionic surfactants	Micellar catalysis[370] De-aggregation of the dye,[371] Association with micelles[372-374]
Xanthene dyes-anionic and cationic dyes	Association with micelles[375]
Xanthene dyes-cationic Gemini surfactants	Association with micelles[376]
Xanthene dye-anionic, cationic, and nonionic surfactants	Competition between electrostatic and hydrophobic forces,[377] De-aggregation,[378] CT complex formation[379]

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The interactions of surfactants of the dyes with other types of systems such as reverse micelles,[235,246,380-383] microemulsions,[137,384,385] polymers,[184,386-401] polymer membranes,[386,391,395,400,402,403] microcrystalline cellulose,[404] proteins,[277,405,406] lipid assemblies,[407,408] nucleic acids,[409] clay minerals,[410] etc. are similar to dye surfactant interactions. The similarities observed for these systems have been attributed to the presence of amphiphilic characters in the aggregates similar to that in the micelles.[188]

Among the various methods used for the study of dye-surfactant interactions in micellar medium, conductometric method,[266,267,271,273,411] Job's method,[412] principal component analytical method,[413] Stark effect spectroscopy,[414] Method of continuous variations,[415] potentiometric method,[205,319] electrical impedance spectroscopy (EIS),[416] along with conventional spectroscopic and thermodynamic methods are worth mentioned. The various interactions of ionic dyes with surfactants of various charge types as a function of the surfactant concentration may be summarized schematically as shown in the **Fig. I.A.5**.

I.B.3: ***Acid-base equilibrium of dyes in aqueous micellar medium***

The acid-base reactions are studied extensively as proton transfer reactions are all-pervading in chemistry.[417,418] The acid dissociation reaction in aqueous medium can be represented as,

$$A^{z} \overset{K_{a,w}}{\rightleftharpoons} B^{z-1} + H^{+} \qquad \text{I.A (2)}$$

where, A^{z} and B^{z-1} are the acid and the conjugate base respectively and $K_{a,w}$ is the acid dissociation constant and represented as $pK_{a,w}$. The acid-base indicators absorb light and the absorption by the protonated, A^{z} and that of the deprotonated, B^{z-1} species are different.[419] Depending on the medium pH, the equilibrium in Eq. I.A(2) shifts to the left or right with accompanying changes of color. A characteristic property of indicator dye is the pK_a, which is the pH of the aqueous indicator solution at which the activity of the acid form of the indicator dye is equal to that of the conjugate base form.

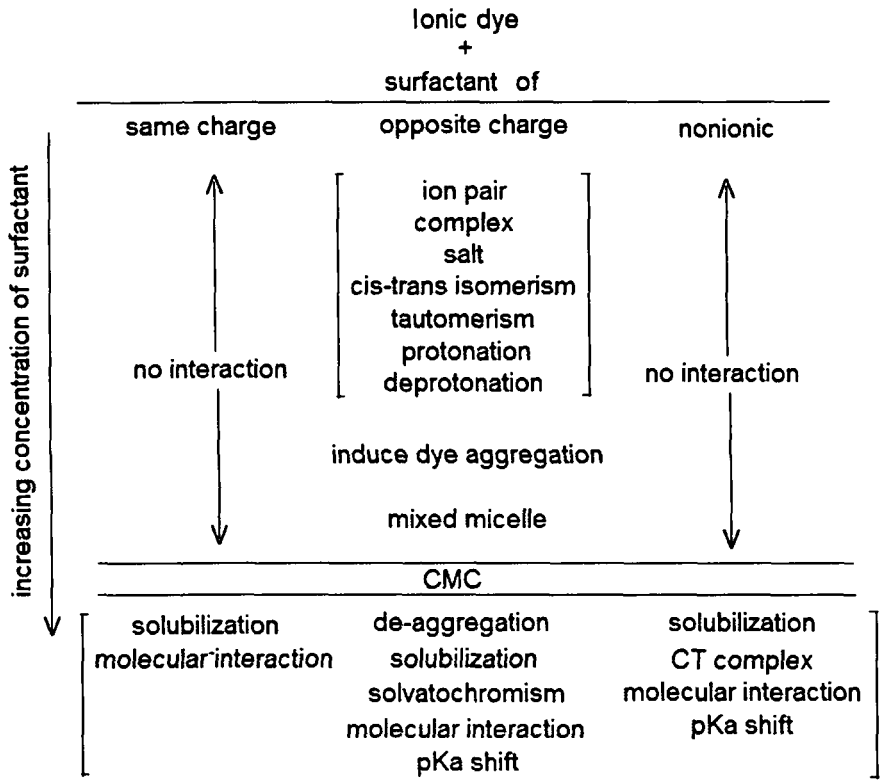

Fig. I.A.5: A schematic representation of the various interactions of ionic dyes with surfactants of various charge types as a function of the surfactant concentration.

Micellar system leads to the shift of acid-base equilibrium of dyes which was first observed by Hartley[48] and since then the acid-base properties of dyes were studied in micellar media for a number of dyes.[42,118,158,249,420] The protonation constants of several azo compounds in aqueous solutions of SDS surfactant were studied by Romero *et al.*[200] Reeves *et al.* studied the effect of DTAB and CTAB surfactants on the hydrazo-azo-tautomeric equilibrium of 4-phenylazo-1-naphthol-2,4'-di-sulphonate and the results obtained explained in terms of the formation of kinetically controlled small dye-surfactant aggregates.[192] The influence of nonionic surfactant TX-100 on the dissociation equilibrium of a number of phenols and nepthols are investigated by Tong and Glesmann.[421] In each case, an increase in pK_a was observed.

A number of researchers studied the effect of cationic and anionic surfactants on the dissociation equilibria of similar type of aromatic indicators.[47,118, 242,247,248,255,259,349,422] The shift in pK_a of the indicator has been attributed to the association of the dye with ionic micelles.[10,160,307,357] The color change of an anionic dye induced by a cationic surfactant is similar to the color change observed on increasing pH in absence of the surfactant.[158,191]

Minch *et al.* studied the effects of cationic micelles on the acid-base equilibrium of a number of carbon acids and phenols and from the results obtained they concluded that the shift in pK_a of the indicators depends on the hydrophobicity of the carbon acids and phenols.[423]

Hartley and Roe observed that the apparent shift of the pK_a in the micellar medium, is due to the change of the local interfacial proton activity at the surface of the charged micelle as compared to that in the bulk water.[182] Mukherjee and Banerjee opined that the total apparent shift of the pK_a value in the micellar solutions is due to a shift of the intrinsic pK_a as well as due to the change in local pH or interfacial potential at the micellar surface.[40] On the other hand, Pal and Jana interpreted that the acid-base equilibrium of an indicator dye, bound to micelle, may be affected not only by an electrostatic potential but also by a local environment.[424] Fernandez and Fromherz provided a quantitative description of the micelle-induced pK_a shifts of two coumarin dyes, bound to both anionic and cationic micelles by taking into account two factors, *viz.*, the shift due to polarity of the interface and the surface pH.[425] Funasaki suggested that the difference in the bulk and micellar pK_a values is due to lower dielectric constant at micellar surface.[426] According to Niazi *et al.* the acidity constant of the indicators *viz.*, methyl orange, methyl red and methyl violet are influenced as the percentages of the surfactants added to the solution of these indicators.[427]

Drummond *et al.* systematically investigated the acid-base equilibria of various weak acids and bases, *viz.*, sulphonephthalein indicators, azine derivatives and azo indicators in aqueous micellar medium of ionic and nonionic surfactants, ionic micelles having opposite charge to the ionic form of the indicators.[242,247,248] The variation in the apparent pK_a values in pure water and in the interfacial microenvironment of a micelle is attributed to the difference in intrinsic solvent characters, *i.e.*, dielectric constants of the two solvating media in case of nonionic surfactants. Whereas, in case of phenols, amines and carboxylic acids and the azo indicators were attributed to the contribution of electrostatic micellar surface potential in addition to that due to lower effective dielectric constant of the interface. However, the calculated and observed apparent pK_a of sulphonephthalein indicators in the interfacial microenvironment of micelles of DTAB and that of the azine indicators in micelles of SDS did not agree well. Therefore, in order to account for the differences between the observed and calculated values of the apparent pK_a, an additional parameter, 'interfacial salt-effect' was proposed. In the case of azine

derivatives, *viz.*, acridine and neutral red in SDS micelles, a specific molecular interaction (either ion-pair or hydrogen bond formation) was believed to contribute to the dielectric and electrostatic effects.

The acid-base equilibrium of indicator dyes depend on the concentration of the surfactants.[48,242,247,248] Rosendorfova and Sermoncova had reported that the pK_a of sulphonephthalein indicators decreased gradually with an increase in the concentration of cationic surfactant up to the CMC but remained constant above it.[249] It has been reported by some researchers that the pK_a values varied even when the concentration of the ionic surfactant were varied above CMC.[48,220,242,247,248,349,427,428]

The acid-base equilibrium of a dye and thus the apparent pK_a is largely affected by the ionic strength of the medium.[242,249] The cationic surfactant induced deprotonation of sulphonephthalein indicators are found to be suppressed by sodium chloride.[249] Diaz Gercia *et al.* observed an increase in pK_a of the dye-surfactant association complex with addition of electrolytes.[158] On the other hand, Miyashita and Hayane pointed out that addition of strong electrolytes might assist the process of inclusion of the dye into micelle.[259]

Some studies on the competitive counter ion binding results that the acid dissociation of an indicator at micellar surface is related to the concentration of the catalytically active ions such as H^+ and OH^- at the micellar surface.[316,426,429,430] A pseudophase ion exchange (PIE) model, has been developed and applied successfully to a number of protonation-deprotonation equilibria studies.[142,199,431,432-436] The PIE model sometimes fails near the CMC.[433] Bunton *et al.* carried out a quantitative treatment of the effects of cationic micelles on the K_b of benzimidazole, phenols and oximes by using the PIE model and the calculated parameters indicated the absence of a significant micellar effect on the K_b of these acids.[431] Funasaki investigated the acid dissociation constant of thymol blue and first order rate constants of the basic hydrolysis of *p*-nitrophenyl butyrate in presence of CTAB, sodium bromide and 2-amino-2-methyl-1,3-propanol/HBR buffer and treated the results applying the electrostatic and ion-exchange models and both the models were found to be similar under experimental conditions.[426] He *et al.* observed that the intrinsic acidity constant of the indicator, *viz.*, pyridine-2-azo-p-dimethylaniline (PADA) at micellar surface is close to that in water.[199] The Poission-Boltzmann Equation (PBE) model has been developed for the ionic distributions at micellar interfaces where

the ion distributions are computed using Poission-Boltzmann equation and was applied to many organic reactions at micellar surface involving H^+ and OH^- ions.[437-441]

Pesavento has introduced another model for treating protonation equilibria of indicator dyes.[156] The model considers micelles as a true microphase behaving like a strong ion exchange resin by setting Gibs-Donnan equilibria at the interface between the micelle and the bulk aqueous medium. Fuguet *et al.* employed a solvatochromic method to determine the CMC, partition coefficient of indicators and the solvation properties of the micellar system.[442] Saha *et al.* observed that the difference between the pK_a values of benzimidazoles, BI's in water and TW80 is due to smaller dielectric constant (D_{eff}) in the interfacial region, whereas, the difference in the pK_a values in water and SDS is due to low D_{eff}, surface potential and specific molecular interaction between the proton of the monocations of BI's and the sulfate head group of SDS micelles.[443] Ahmadi *et al.* carried out a study on the effect of anionic and cationic surfactants on dissociation constants of some azo dyes and observed that the anionic surfactant SDS can change the color of some indicators that do not bear SO^{3-} moiety in their structure by either repulsive negative forces or hydrogen bonding.[444]

Yuanqin *et al.* studied the effect of anionic, cationic and nonionic micelles on the acid-base equilibrium of thymol blue and bromothymol blue.[445] Saikia and Dutta studied the effect of nonionic surfactant micelles on the pK_a of sulphonenthalein dyes.[446] The pK_a values are found higher in micellar medium and the values increase with increasing surfactant concentrations.[446] Safavi *et al.* reported that the presence of imidazolium-based ionic liquids (ILs) leads to decreased pK_a values of sulfonated indicators because of the stronger electrostatic interaction of cationic ILs with the basic forms of the indicators with more negative charge.[447] Niazi, *et al* spectrophotometrically investigated the dissociation equilibrium of fluorescein in aqueous micellar solution at 298 K and at ionic strength of 0.1 mol dm^{-1}. They observed that the pK_a values of fluorescein are influenced as the percentages of an anionic and a cationic surfactant and the nonionic surfactant TX-100 only affects pK_{a1}.[428] Werawatganone and Muangsiri reported that in the presence of anionic and nonionic micelles the pK_a of bromothymol blue increases confirming the facilitation of neutral species (HB).[181] For NR, anionic micelles induce NRH^+ formation and an increase in pK_a is observed. On the other hand, the pK_a of NR decreases since NR formation is promoted in the presence of CTAB and TW80 micelles.[181]

Zarei *et al.* applied rank annihilation factor analysis (RAFA) for spectrophotometric analysis of acid-base equilibria of some sulfonephthalein dyes at 25°C and an ionic strength of 0.1 mol L^{-1}. They reported that interaction with surfactants induces significant pK_a shifts, which can be rationalized in terms of hydrophobicity and electrostatic interactions.[448] Wang *et al.* reported outstanding stabilization of the hydrophobic dye curcumin in aqueous cationic surfactant micelles due to strong interactions between the phenoxide ion of the dye and the cationic surfactant.[100] The strong interaction of Cur^{-1} with head groups of the cationic surfactant results in a lowering of the apparent pK_a values when micelles with bromide counterions are used. Protonation equilibria of indicators are also affected by micelle like other systems such as polyelectrolytes,[449] microemulsion,[386] proteins,[392] reversed micelles,[186] polymers,[388] etc.

I.C: *Polymer-surfactant interactions*

In an aqueous polymer-surfactant mixture the surfactant provides control over interfacial tension,[450] emulsification capacity[451,452] and colloidal stability,[453,454,455] while the polymer provides control of the rheological properties[456,457,458] as well as colloidal stability.[459] The high solubilization power of the mixed polymer-surfactant system makes such systems highly attractive for industrial applications.[460,461] Many types of surfactant-polymer interactions can occur depending upon the nature of both the surfactant (cationic, anionic, or nonionic) and the polymer (neutral or polyelectrolyte).[462] A number of excellent reviews and texts are available on this subject.[462-477] These literatures indicate that most of the research carried out in this field focused on the interaction of anionic surfactants (typically SDS) with a variety of polymers[108,458,478-483] and has involved a broad range of experimental methods including measurements of electrical conductivity,[484] viscosity,[485] surface tension,[484,486-488] cloud point[489-491] and solubility; binding studies using both dialysis and ion-specific electrodes; spectroscopic techniques, *viz.*, absorption spectroscopy,[455] fluorescence spectroscopy,[488,492] NMR spectroscopy,[493-495] light scattering[455,496-498] and small angle neutron scattering (SANS);[496,499,500] thermodynamic studies including calorimetry[498,502-505] and volumetric methods.[506-508]

Polymer-surfactant interaction involves a surfactant aggregation process analogous to the normal micellization process.[509] The onset of surfactant molecules binding on the polymers is signified as the critical aggregation concentration, CAC. If the value of CAC is greater than that of CMC, the situation would suggest that the surfactant molecules

would prefer to micellize with themselves instead of forming mixed micelles, which would otherwise indicate that no polymer-surfactant interactions exist at all.

The interaction of surfactants with water soluble polymers was first reported by Saito in 1950.[127] However, in 1967, Jones provided the conceptual framework to describe the interaction between surfactants and polymers that is still used today.[510] Based upon observations from NMR experiments using the SDS/PEO system, the model presented by Jones was further modified by Cabane which is known as the "necklace model" of Cabane.[493] From equilibrium dialysis and ion electrode measurements Nagarajan postulated that surfactant-polymer complex formation process is a cooperative one, though not as strongly cooperative as micelle formation itself.[511] Nagarajan's model has been used to predict the behaviour of various polymer-surfactant systems.[486]

The main driving force for association of surfactant molecules in presence of polymers is thought to be the hydrophobic interaction. It has been observed that cationic surfactants interact with nonionic polymers less strongly than anionic surfactants.[512] However, Dhara and Shah had showed that the interaction between water soluble synthetic polymers and SDS is not governed by the hydrophobicity of the polymers alone.[513] Nagarajan and Kalpakci viscometrically examined the polymer-micelle association monitoring the conformational changes induced in the polymer.[512]

Picullel *et al.*[514] reported that the nature of the polymer-micelle association is strongly influenced by the nature of the polymer. Medeiros and Costa have showed that for non-amphiphilic polymers the association process can be described as one in which the cooperative micelle formation process of the surfactant is facilitated by the polymer-micelle association.[515] However, a non-cooperative binding is observed in case of some amphiphilic or hydrophobically modified polymers.[516-520] The interactions between the binding of dodecyltrimethylammonium chloride (DTAC) to amphiphilic polyelectrolytes of different hydrophobicity has been investigated and it has been observed that, in aqueous surfactant free medium these polymers can form hydrophobic microdomains and are referred to as polysoaps.[519] Almgren *et al.* and Piculell *et al.* proposed that the interaction of surfactants with hydrophobically modified polymers is analogous to mixed micelle formation.[518,521,522] The mixed micellar behaviour of the binary mixtures of zwitterionic/cationic surfactants and triblock polymers have been reported by various researchers.[496,500,523,524] Using cryo-transmission electron spectroscopy (cryo-TEM) studies Shimoni and Danino reported the formation of polymer-surfactant mixed micelles

between nonionic block copolymer and surfactant mixtures with characteristic diameters.[525]

From isothermal titration calorimetry (ITC) studies Dai *et al.* showed that SDS does not bind with low molecular weight polyethylene glycols, PEG (MW 400 Daltons). While with increasing molecular weight of the polymers form 900 to 1450 Daltons, an endothermic peak which is attributed to the formation of an SDS-PEG aggregation complex has been observed. Again, when the molecular weight exceeds 3350 Daltons, an endothermic peak followed by an exothermic peak has been observed.[504,526] The results from the ITC curves suggested that the interaction between the polymer and the surfactant is controlled by a subtle balance of two mechanisms: the polymer induced micellization at low SDS concentrations (endothermic process) and re-hydration of the PEG chains to form the ion-dipole aggregation at high SDS concentrations (exothermic process).[527] From SANS studies Cabane suggested the formation of necklace-like structure in which the PEO can either be solubilised in the hydrophobic core of SDS micelles or absorbed on the surface of SDS micelles.[528,529] However, Wesley *et al.* also proposed the formation necklace structure between SDS and star PEO from SANS study.[530] Cui *et al.* reported that the anionic polyelectrolyte hydroxypropyl guar (HPG)-borate does not promote DTAB micellization or phase separation normally seen on mixing oppositely charged polyelectrolytes and surfactants.[531]

Freyssingeas *et al.* examined the effect of PEG on the SDS/pentanol bilayers in the lamellar phase. They observed that increase in PEG concentration decreases the repulsive forces between the lamellae.[532] Using ITC, ion-selective electrode (ISE), surface tension and dynamic light scattering measurements, Wang and Tam investigated the interaction of SDS with poly(acrylic acid) (PAA). They observed that the hydrocarbon chains of SDS cooperatively bind to apolar segments of PAA, driven by hydrophobic interaction. The interaction is entropically and enthalpically favoured.[533,534] They also examined the effect of polymer charge density of PAA at different degrees of neutralization (α) on the binding of DTAB to PAA by using calorimetric titration and light scattering techniques.[535]

Sachko *et al.* showed that pronounced associative processes occurred in aqueous systems containing an anionic polyelectrolyte (polymethacrylic acid) (PMAA) and an anionic sodium dodecylbenzenesulfonate (SDBS) surfactant. They reported that the hydrophobic interactions between the nonpolar SDBS moiety and PMAA macrochain hydrophobic fragments might play the key role.[536] Hansson theoretically analysed the

interaction of ionic surfactants with polyion networks of oppositely charged in an aqueous environment by applying the theory of surfactant ion-polyion complex salts.[537,538] Ali *et al.* had showed that gemini surfactants interact strongly with polyvinylpyrrolidone (PVP) as compared to conventional surfactants.[539]

Conductometric and surface tensiometric studies on the interaction of surfactants with bovine serum albumin (BSA) were carried out by a number of researchers.[540-545] The protein-surfactant association is a cooperative phenomenon, promoting micelle formation and stabilization.[540-545] The association of the gemini surfactants derived from cystine and a monomeric surfactant derived from cysteine with BSA were studied by Faustino *et al.*[546] The association of enantiomerically pure surfactants with BSA is favored when compared to the racemic mixture and pure L-stereochemistry is favored over D-stereochemistry.[546] Le *et al.* reported that bound surfactants largely minimise heat-induced protein intermolecular interactions and thus prevent heat-induced protein aggregation from a study of the effect of lysophospholipids, the main components of lysolecithins, as well as alternative surfactants, on heat induced whey protein aggregation.[547]

Chitosan is a positively charged linear polysaccharide,[548] it has many applications in the food and pharmaceutical industries,[549,550] etc. Using ITC, surfactant ion-selective electrodes (SISEs) and turbidity measurements, Thongngam *et al.* examined the influence of the solution, environmental conditions and ionic ratio on the interaction of the SDS/chitosan system.[551] Onesippe *et al.* used SISEs, surface tension measurements, ITC, turbidity and zeta potential measurements to study the binding of SDS to chitosan in aqueous solution.[552] They observed that at optimal ionic ratio, the SDS/chitosan system is capable of encapsulating hydrophobic molecules. Pepic *et al.* studied the bulk properties of the nonionic surfactants-chitosan mixtures by fluorescence spectroscopy, dynamic light scattering and zeta potential measurements. They observed that the addition of chitosan to triblock copolymers, Lutrol F127 systems in water had little effect on CMC values.[553,554]

Lam and Walker reported the *p*H induced alteration of the surfactant aggregates with polyelectrolyte those of oppositely charged from cylinder to a string-of-pearls structure (spherical micelles connected by the partially solubilized polyelectrolyte chain).[555] Pispas reported that well defined nanoassemblies can be formed in mixed solutions of a double hydrophilic anionic-neutral block copolymer, poly[(2-sulfamate-3-carboxylate)isoprene-b-ethylene oxide] (SCIEO) and the vesicle-forming surfactant, didodecyldimethylammonium bromide (DDAB) at certain mixing ratios through a

vesicles-to-micelles transition, driven by electrostatic interactions and packing constrains.[556]

Bellettini, *et al.* recently studied the aggregation of four modified hyperbranched polyethylene imines (PEI) in presence of SDS. The small-angle X-ray scattering (SAXS) data showed that the radius of gyration of the polymer molecules decreases with an increase in the alkyl chain length of the polymer, while the viscosity data indicated a decrease in the intrinsic viscosity under the same conditions.[488] Petkova *et al.* investigated the effects of polymer-surfactant interactions on the foamability and foam stability in mixed polymer-surfactant systems.[557] They clearly showed that the presence of opposite charges is not a necessary condition for boosting the foaminess and foam stability in the surfactant-polymer mixtures studied. Liu, *et al.* studied the interaction between a cationic surfactant (1-dodecyl-3-methylimidazolium bromide, C12mimBr) and a water-soluble polyanion (sodium carboxymethylcellulose, NaCMC) in aqueous solution by ITC, conductivity, surface tension and rheological measurements. They suggested that the electrostatic attraction between the cationic surfactant and anionic polyelectrolyte is an endothermic process and the C12mimBr monomer binding to the NaCMC chains through hydrophobic interaction is an exothermic process.[484]

I.D: ***Interaction of dyes with surfactants in presence of polymers***

The formation of polymer-surfactant complex can be realized from the marked change observed in the spectroscopic properties of dyes.[558,559] A very few spectrophotometric analysis of polymer-surfactant system has been carried out by using indicator dye as a probe.[560] Analysis of wavelength shift of a solution of a polymer, labeled with a dye, following addition of surfactant has been found to be successful in a number of studies.[133,561-565] Changes in the local microenvironment around the probe can produce measurable spectral changes which can be monitored easily. The spectral changes allow illumination of the influence of the immediate environment on the probe and give evidence of specific interactions.[256,566-570] Photochemical techniques such as luminescence techniques have been employed to determine micellar parameters such as aggregation number, CMC and partition of solute between the micellar and aqueous pseudo phase.[366,565,571,572]

Hayakawa *et al.* studied the spectroscopic properties of the cationic dyes, *viz.*, rhodamine 6G, proflavin and acridine orange in the presence of anionic polyelectrolytes,

i.e., sodium salts of dextran sulphate (DxS) and poly (vinyl sulfate) (PVS), with and without the cationic surfactant DTAB.[133] They reported that proflavin and rhodamine 6G dissolved into DTA^+-polyanion complexes in the monomeric form. They also examined the effective energy transfer from excited proflavin to rhodamine 6G when both are solubilised in DxS/DTAB and that of pyrene (donor) to proflavine (acceptor) when the dyes are solubilised in DxS/DTAB, DxS/DTAC, poly(vinyl sulfate)/DTAB and poly(styrenesulfonate)/DTAB aggregates, where no energy-transfer effect is observed in solutions of either the surfactant or the polymer alone.[573,574] The same group reported that the free energy of transfer of the water-insoluble dye, oil yellow OB from the solid phase to poly(vinyl sulfate)/alkyltrimethylammonium complex is found to be 3.1 kJ mol^{-1} from the solubilizing capacity.[575]

Kwak *et al.* used the ^1H NMR shifts to determine the location of aromatic solubilizates including probes in aggregates of Poly(maleic acid-co-butyl vinyl ether) (PMA-BVE) and cationic surfactants.[576,577] Das *et al.* studied the interactions of BSA and SDS using ethyl *p*-(dimethylamino)cinnamate as a fluorescence probe for monitoring the interactions.[566] Upon analysis of the fluorescence spectra of the probe resulted in cooperative protein-surfactant binding and the polarity of the BSA-SDS aggregates formed has been found in between that of hydrophobic regions of BSA and SDS micelles. Sen *et al.* studied the fluorescence anisotropy decay of two dyes *viz.*, merocyanine 540 and oxazine 1 in a system containing poly(vinylpyrrolidone) (PVP) and SDS aggregates.[578] Their results indicated that the microscopic friction in PVP-SDS aggregates is greater than that in an SDS micelle alone. Bloor *et al.* examined the binding of sodium alkylsulfates (C_8-C_{16}) to a copolymer of N-(vinylacryloyl) pyrrolidine and the covalently bonded chromophore 4-vinylpyridine dicyanomethylide by monitoring the wavelength shift of the chromophore band at 390 nm. They observed that the bound surfactant exists in the form of micellar type aggregates and the spectral data indicate that initially these aggregates preferentially bind to the chromophore on the polymer.[579]

Nayak *et al.* studied a polymer-surfactant micellar complex as a fluorescence resonance energy transfer donor to fluorescein-labeled DNA. From TEM microscopic study they showed the formation of a nanowire micellar complex of cationic poly(fluorene-co-phenylene) (c-PFP) and the surfactants.[580] Pu *et al.* examined the effect of surfactant on energy transfer between cationic conjugated polymer and dye-labeled oligonucleotide.[581] Sahoo *et al.* studied the interaction of SDS and amphiphilic block

copolymers polyethylene-*b*-polyethylene glycol by monitoring the sharp change of excited-state charge-transfer complex photophysics of 2-(4-(dimethylamino)styryl)-1-methylpyridinium iodide (DASPMI).[582] The enhancement of emission intensity of DASPMI incorporated inside of the nanostructure formed by micellar and polymeric chains indicates a completely different environment compared to that in the water and micellar system.[582] Nath *et al.* studied the interaction of capsular polysaccharide (an integral component of gram-negative bacteria) isolated from Klebsiella K18, with cationic dyes and surfactants.[583] Their studies provide an understanding on the effects of the surfactants on binding with the polymer (SPS). The binding was found to be electrostatic in origin and also hydrophobic in nature to a certain extent.

Iatridi *et al.* reported the interactions between anionic polyelectrolytes and the oppositely charged surfactant DTAC in dilute aqueous solution, exploiting the optical properties of nile red.[584] They had observed that the formation of ternary polymer/surfactant/Cu^{2+} complexes leads to a pronounced quenching of the luminescence of nile red. Bazylińska *et al.* investigated the influence of dicephalic ionic surfactant interactions with oppositely charged polyelectrolyte upon the in vitro dye release from oil core nanocapsules.[585]

Saikia and Dutta studied the acid-base equilibrium of three anionic sulfonephthalein dyes, *viz.*, bromothymol blue, thymol blue and cresol red in aqueous media containing the nonionic polymers, viz., polyvinyl alcohol (PVA) and PEG in the presence SDS.[256] They successfully employed the partition equilibrium method to determine the interacting parameter between the surfactant and the polymers.

I.E: *Curcumin- surfactant interactions*

I.E.1: *Curcumin*

Curcumin is a yellow pigment present in the spice turmeric (*Curcuma longa* Linn) that belongs to the ginger (Zingiberaceae) family.[586,587] Curcumin was first isolated in impure form in 1815 by Vogel and Pelletier and it was first prepared in pure and crystalline form by Daube in 1870 followed by Ivanov and Gajevsky almost three decades later.[587] Its chemical structure was determined in 1910 by J. Milobedzka and V. Lampe.[587] The use of curcumin in biliary diseases was first documented in 1937 (67 patients treated), then its antibacterial action in 1949 and its ability to decrease blood sugar levels in human subjects (i.e. its use as an antidiabetic) in 1972.[587] It has been termed as C.I. Natural Yellow 3 and

WHO (World Health Organization) and FAO (Food and Agriculture Organization) committees have approved it as a food additive.[586]

Chemically, curcumin is a bis-α,β-unsaturated *β*-diketone, commonly known as diferuloylmethane {(1E, 6E)-1,7-bis(4-hydroxy-3-methoxy phenyl)-1,6-heptadiene-3,5-dione} and it was suggested that under physiologic conditions exhibits keto-enol tautomerism, having a predominant keto form in acidic and neutral solutions and a stable enol form in alkaline media (*p*H > 8.00).[589] It has a molecular weight (MW) of 368.38, a melting point of 179-183°C and chemical formula is $C_{21}H_{20}O_6$. Commercially available curcumin is a mixture of curcuminoids, containing approximately 77% diferuloylmethane, 18% demethoxycurcumin and 5% bisdemethoxycurcumin.[587,588] Curcumin is practically insoluble in water at acidic and neutral *p*H condition (~11 ng/ml in plain aqueous buffer *p*H 5.00) and ether however it is moderately soluble in aqueous solutions of high *p*H[590,591] and in both polar protic and polar aprotic solvents.[592] In alkaline medium, the deprotonation of curcumin occurs first as a result of hydrolysis and produces *trans*-6-(4′-hydoxy-3′-methoxypenyl)-2,4-dioxo-5-hexenal.[593] The hydrolysed product then further degraded to smaller molecular components such as vanillin, feruloyl methane and ferulic acid.[593] Acidic conditions result in slower degradation of curcumin, with ~20% of total curcumin decomposed at 1 hour.[593]

Extensive research have been carried out about the medicinal properties of curcumin which indicated that curcumin possesses remarkable therapeutic properties including antioxidant, anti-inflammatory,[594-597] antimicrobial,[598-600] anticancer,[597,599,601-603] etc. In addition to this the hepato- and nephro-protective,[604,605] thrombosis suppressing,[606] myocardial infarction protective hypoglycaemic,[606-609] antirheumatic[610] effects of curcumin are also well established.[587] From the studies on different animal models [611,612] or human bodies[613-615] it has been established that curcumin is safe even at very high doses.[587]

I.E.2: *Interaction of curcumin with surfactants*

It has been showed that, micellar systems potentially play an important role in leading improved aqueous solubility and bioavailability of curcumin. Tønnesen studied the stabilisation of curcumin at *p*H 5.00 and *p*H 8.00 in different types of surfactant micelles including SDS, TX-100 and TTAB.[97] They observed that SDS and TX-100 micelles are

highly effective in stabilizing curcumin, while TTAB micelles are not as effective as SDS and TX-100 micelles at *p*H 8.00.[97]

Iwunze reported the thermodynamic stability of curcumin solubilised in cationic CTAB micellar medium with a free energy of transfer from the aqueous phase to micellar pseudophase of –13.74 kJ/mol.[98] Wang *et al.* showed that SDS, SDBS and protein can enhance the resonance light scattering (RLS) and also fluorescence intensity of curcumin.[616-618] They observed that the enhanced RLS is in proportion to the concentration of proteins. The same group also reported the nucleic acid enhancement of the RLS of curcumin in presence of CTAB.[619]

Leung et.al showed that curcumin can be encapsulated in cationic micelles of DTAB and CTAB surfactants which suppress the alkaline degradation of curcumin at *p*H 13.00.[99] The attractive electrostatic interactions between the cationic head groups of the surfactants and the deprotonated curcumin (Cur^{3-}) play the key role in stabilising Cur^{3-} in alkaline medium. The same research group investigated the interactions of curcumin with negatively and positively charged micelles and vesicles at different *p*H conditions.[100] There is a strong interaction between the Cur^{-1} phenoxide ion and the positively charged surfactants results in a change in the acidity of the phenolic hydrogen and a lowering of the apparent lowest pK_a value for curcumin. However, in anionic micellar medium or negatively charged bilayers, they observed that curcumin partitions as the Cur^{0} species. From femtosecond fluorescence upconversion experiments, Adhikary *et al.* reported that micelle-captured curcumin undergoes excited-state intramolecular hydrogen atom transfer.[620]

Recently, Ke *et al.* spectroscopically investigated the interaction of curcumin with cationic DTAB surfactant at *p*H 5.00.[621] From their results they suggested that at low surfactant concentrations the DTAB/curcumin complex is formed, while, at intermediate concentration of the surfactant the dye induced premicellar aggregates of DTAB are formed. At high surfactant concentrations, DTAB micelles are formed and curcumin solubilised in the micellar core predominantly as enol curcumin.

I.F: *Lacuna and rational*

Despite many investigations of dye-surfactant systems and on the behaviour of surfactant and dye mixtures, there are limited numbers of studies on the dye-surfactant interactions in the presence of polymers. Most of the studies have examined the nature and strength of

polymer-surfactant interactions as well as the nature of the aggregation phenomena and acid-base equilibrium of dyes in the polymer-surfactant systems. The existing interpretation, both in submicellar and postmicellar concentration of surfactants seems to be unable to give a clear picture about the mechanism underlying the interaction of dyes with surfactants and with both polymers and surfactants together. The interactive forces which facilitates the dye binding to surfactants and to both polymers and surfactants together are not yet clearly understood, which may be due to limited choice of dye-polymer-surfactant systems in the reported studies. Moreover, there is no report regarding the interaction of dye and surfactants of same charge in the presence of polymers. There is also hardly any literature available on the subject of the natural dye curcumin-polymer-surfactant system. It would be of interest, from both practical and academic perspectives, to investigate the interactive forces operative in these systems explicitly.

In the studies of acid-base equilibrium of dyes in micellized surfactants in the presence and absence of polymers, the spectroscopic properties of the dyes as a function of concentration of surfactants are expected to through some light on the mechanism underlying the dye binding to the surfactants in the presence of polymer, as well as nature of polymer-surfactant interactions. A study of the dimerization of a dye in an anionic surfactant-nonionic polymer system allows one to obtain precisely the critical concentration of surfactant that maximizes the dimer formation and the redissolution of the monomer in the polymer-surfactant complex. The investigations on the physicochemical properties of a natural dye in polymer-surfactant systems provide desirable information in solubilizing and stabilising of the dye. In addition, binding to a biopolymer can be used to monitor as a delivery system for administration of the dye as a drug, with implications on biological and medical applications.

Spectrophotometry is a commonly used technique for qualitative and quantitative determination of dye-polymer-surfactant interactions. It was therefore decided to carry out some systematic studies on various dye-surfactant-polymer interactions using UV-visible and fluorescence spectroscopic methods with different chosen synthetic and natural dyes. In case of the natural dye, for clear understanding of the physicochemical behaviour the dye in such systems, surfactant concentrations are chosen from submicellar to post micellar ranges.

I.G: ***Aim and objectives***

The aim of the present work was to carry out a systematic study on the acid-base equilibrium of two synthetic dyes of different charge types, the dimerization of another synthetic dye and the physicochemical behaviour of a natural dye in different surfactants and in polymer-surfactant systems. The different polymers and surfactants were varied without a tremendous change in structures.

The chosen anionic dye was a sulphonephthalein dye *viz.*, phenol red (PR). The anionic surfactant chosen for using with the anionic dye was SDS. The nonionic polymers chosen were polyvinyl alcohol (PVA) (M.W. 14,000), PVA (M.W. 1,25,000), PEG 200, PEG 400 and PEG 600. For a system, a phanizine dye, *viz.,* neutral red (NR) was chosen as a neutral dye. The nonionic surfactants were polyoxyethylene(20) sorbitan monolaurate (Tween-20), polyoxyethylene(20) sorbitan monopalmitate (Tween-40), polyoxyethylene(20) sorbitan monostearate (Tween-60) and polyoxyethylene(20) sorbitan monooleate (Tween-80). The nonionic polymers chosen for this system were PVA (M.W. 125,000), PEG 200, PEG 400 and PEG 600. The cationic dye chosen for surfactant-induced dimerization study was a thiazine dye, *viz.*, methylene blue (MB). The dimerization of MB was studied in the presence of an anionic surfactant *viz.*, SDS and a nonionic polymer, viz., PVA (M.W. 14,000).

A natural dye of versatile medicinal activity, *viz.*, curcumin, was chosen for the study. We examined the interactions of the dye with surfactants of different charge types as there are only a few studies reported on the physicochemical properties of curcumin in micellar systems. In submicellar medium, only one report with cationic surfactant is available.[629] The anionic surfactants chosen for using with curcumin were an alkylsulphate surfactant, *viz.*, SDS, an alkyl benzene sulfonate surfactant, *viz.*, SDBS and an alkyl sulfonate surfactant, *viz.*, sodium dodecylsulphonate (SDSN). The cationic surfactants chosen were some alkyltrimethylammonium halide surfactants of varying chain length, *viz.*, CTAB, TTAB and DTAB. The polymer chosen was a nonionic polymer, *viz.*, PVA (M.W 125,000). In a system of curcumin and a cationic biopolymer, the biopolymer chitosan was chosen along with TW80 and CTAB surfactants.

We have investigated the partition of the two chosen dyes between aqueous and micellar pseudophases to investigate the acid-base equilibrium of the dyes in polymer-surfactant medium using the partition equilibrium method based on UV-vis spectroscopy.[259,355] The induced dimerization was also studied using a spectroscopic

method. For the study of the stabilisation of the natural dye in polymer-surfactant medium, the fluorescence spectroscopic technique has been used.

The work was planned as described below:

- Preparation of the aqueous solutions of dyes, surfactants and polymers and their mixtures.
- Recording of electronic spectra of the aqueous dye solutions as a function of concentration of surfactants ranging from below the CMC of the surfactant to above the CMC in polymer free medium as well as in presence of polymers.
- Recording of electronic spectra of the aqueous dyes as a function of concentration of polymers in presence of surfactants of fixed concentrations.
- Calculation of thermodynamic parameters.
- Recording of fluorescence spectra of the aqueous dye a function of concentration of surfactants in absence of polymers and in presence of polymers.

At the end of the chapter the author would like to acknowledge all the authors cited in this thesis. The author also apologizes for any lapse which might have occurred due to oversight or error in judgement.

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CHAPTER-II

II. Experimental

II.A: *Materials*

Four dyes including three synthetic and one natural, ten surfactants of different charge types and six polymers including five nonionic and one cationic have been used in the present study. The detail description of the dyes, surfactants and polymers used has been given below:

II.A.1: *Dyes*

PR: PR (Product No. 61841500251730), IUPAC name: 4,4'-(1,1-Dioxido-3H-2,1-benzoxathiole-3,3-diyl)diphenol, FW 354.38 g/mol, (mp 300°C), of AR grade was obtained from Merck, Mumbai, India. The dye was recrystallised from water and dried before used. Transition interval: *p*H 6.80 (yellow) to 8.20 (red). Detailed description is given in **Table II.A(1)**. Structural formula is shown in **Fig. II.A.1**.

NR: NR (Product No. 1013760025, CAS No. 553-24-2), IUPAC name: 3-Amino-7-dimethylamino-2-methylphenazine hydrochloride, FW 288.78 g/mol, (mp 290°C), of AR grade was a product of Merck, Mumbai, India. It was recrystallised from water and dried before used. Transition interval: *p*H 6.80 (red) to 8.00 (yellow). Detailed description is given in **Table II.A(1)**. Structural formula is shown in **Fig. II.A.1**.

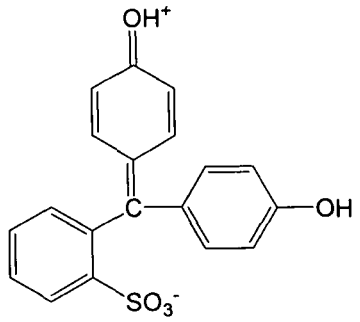
MB: (Product No. 44048, CAS No. 61-73-4), IUPAC name: [7-(Dimethylamino)phenothiazin-3-ylidene]-dimethylazanium chloride, FW 319.86 g/mol, (mp 100-110°C), of AR grade was obtained from S.D. Fine Chemicals, India. The dye was recrystallized from ethanol and dried before used. Detailed description is given in **Table II.A (1)**. Structural formula is shown in **Fig. II.A.1**.

Curcumin: (Product No. SL09143, CAS No. 458-37-7), IUPAC name: (1E,6E)-1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione, FW 368.39 g/mol, (mp 175°C), of LR grade was obtained from Sigma Aldrich, USA. The dye was used as such. Detailed description is given in **Table II.A(1)**. Structural formula is shown in **Fig. II.A.1**.

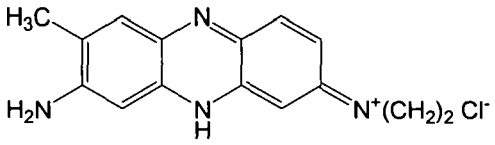
The purity of all the dyes after recrystallisation was further checked by spectrophotometry and melting point determination.

Table II.A(1): Detail description of the dyes used in the study.

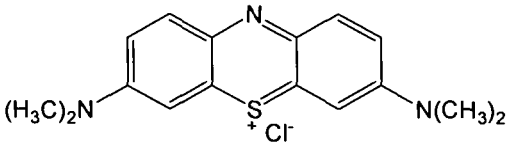
Serial No	Name	Charge type	Class	CI No	Abbreviation
1	Phenol Red	Anionic	Sulphonephthalein	45410	PR
2	Neutral Red	Neutral	Phenazine	50040	NR
3	Methylene Blue	Cationic	Thiazine	52015	MB
4	Curcumin	Neutral	Polyphenol	75300	Curcumin



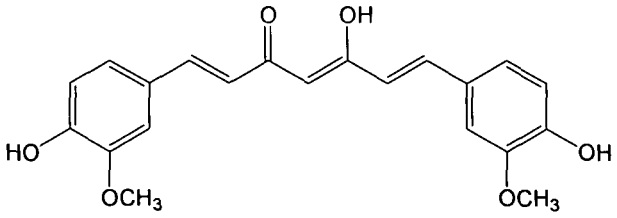
PR (**PR**$^-$ form)



NR (NRH$^+$ form)



MB



Curcumin (enol form)

Fig. II.A.1: Structural formulae of the dyes studied.

II.A.2: ***Surfactants***

SDS: SDS (Batch No. T8261190) FW 288.38 g/mol, of electrophoresis grade was obtained from Sisco Research Laboratory, Mumbai, India. The surfactant was stirred overnight in ether to remove the dodecanol impurities which is usually present in SDS as a result of hydrolysis of the surfactant. The samples were than recrystallised twice from ethanol-water mixture and dried thoroughly. By using Krüss Du Nuoy Tensiometer the CMC of the surfactant were determined and the results are in good agreement with the literature value (8.0x 10^{-3} mol dm^{-3}). The plot of surface tension *vs.* concentration of the surfactant did not show any minimum indicating absence of dodecanol in the purified surfactant (**Fig.II.A.3**). Structural formula is shown in **Fig. II.A.2**. Detail description of the surfactant is shown in **Table II.A(2)**.

SDSN: SDSN (Batch No. 10,643-7), FW 272.38 g/mol, was obtained from Aldrich Chemical Company, USA. The CMC of the aqueous surfactant solution was determined at 298 (±0.1) K and found in good agreement with the literature value (1.2x 10^{-2} mol dm^{-3}) and was used as such. Structural formula is shown in **Fig. II.A.2**. Detail description of the surfactant is shown in **Table II.A(2)**.

SDBS: SDBS (Lot No. 02728JI, Product No. 28,995-7) FW 348.48 g/mol, was obtained from Aldrich Chemical Company, USA. The CMC of the aqueous surfactant solution was measured at 298 (±0.1) K and found in good agreement with the literature value (1.2x 10^{-3} mol dm^{-3}) and was used as such. Structural formula is shown in **Fig. II.A.2**. Detail description of the surfactant is shown in **Table II.A(2)**.

CTAB: CTAB (Batch No. C01Y-0301-2202-13, Product No.37665), FW 364.45 g/mol, of LR grade was obtained from S.D. Fine Chemicals Limited, Mumbai, India. The CTAB was recrystallized from acetone and dried before use. The measured CMC value (9.1x 10^{-4} mol dm^{-3}) of the surfactant in pure water at 298 (±0.1) K has been found in good agreement with the literature value. Structural formula is shown in **Fig. II.A.2**. Detail description of the surfactant is shown in **Table II.A(2)**.

TTAB: TTAB (Lot No. FA005752, Product No. 86,042-5, CAS 1119-97-7), FW 336.41 g/mol, was obtained from Sigma, USA. The CMC of the aqueous surfactant solution was measured at 298 (±0.1) K and found in good agreement with the literature value (3.62x 10^{-3} mol dm^{-3}) and was used as such. Structural formula is shown in **Fig. II.A.2**. Detail description of the surfactant is shown in **Table II.A(2)**.

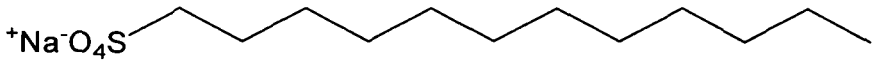
DTAB: DTAB (Lot No. 19805, Product No. 26876-3, CAS 1119-94-4), FW 308.35 g/mol, was obtained from Sigma, USA. The measured CMC value (16.0x 10^{-3} mol dm^{-3}) of the surfactant in pure water at 298 (±0.1) K has been found in good agreement with the literature value. Structural formula is shown in **Fig. II.A.2**. Detail description of the surfactant is given in **Table II.A(2)**.

TW80: TW80 (Product No. 056023), FW 1309.68 g/mol, was obtained from Central Drug House, Mumbai, India and used as such. The measured CMC value (1.0x 10^{-5} mol dm^{-3}) of the surfactant in pure water at 298 (±0.1) K has been found in good agreement with the literature value. Structural formula is shown in **Fig. II.A.2**. Detail description of the surfactant is given in **Table II.A.2**.

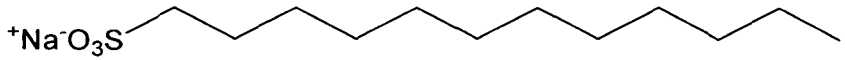
TW60: TW60 (Product No. 024295), FW 1131.9 g/mol, was obtained from Central Drug House, Mumbai, India and used as such. The measured CMC value (2.10x 10^{-5} mol dm^{-3}) of the surfactant in pure water at 298 (±0.1) K has been found in good agreement with the literature value. Structural formula is shown in **Fig. II.A.2**. Detail description of the surfactant is given in **Table II.A(2)**.

TW40: TW40 (Product No. 26876-3), FW 1283.84 g/mol, was obtained from Central Drug House, Mumbai, India and used as such. The measured CMC value (2.30x 10^{-5} mol dm^{-3}) of the surfactant in pure water at 298 (±0.1) K has been found in good agreement with the literature value. Structural formula is shown in **Fig. II.A.2**. Detail description of the surfactant is given in **Table II.A(2)**.

TW20: TW20 (Product No. 956020), FW 1227.54 g/mol, was obtained from Central Drug House, Mumbai, India and used as such. The measured CMC value (5.0x 10^{-5} mol dm^{-3}) of the surfactant in pure water at 298 (±0.1) K has been found in good agreement with the literature value. Structural formula is shown in **Fig. II.A.2**. Detail description of the surfactant is given in **Table II.A(2)**.



SDS



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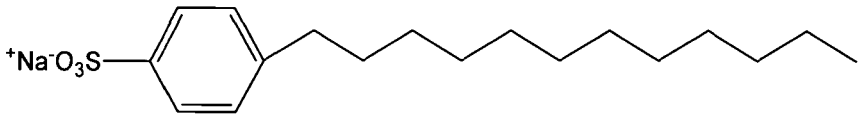

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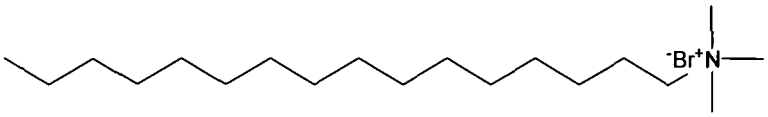
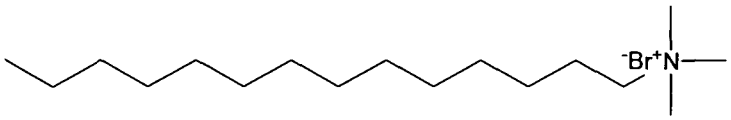
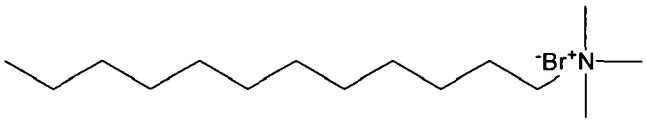


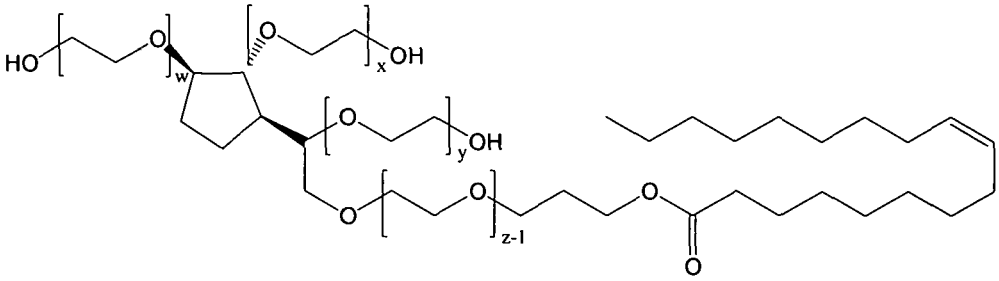
CTAB



TTAB

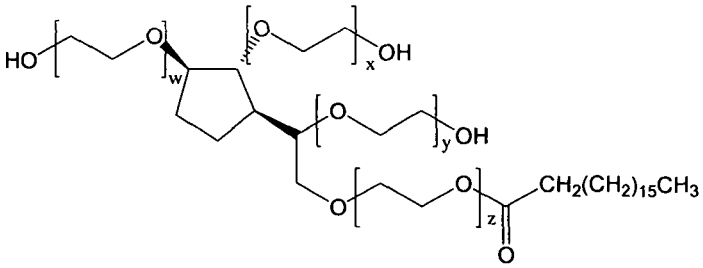


DTAB



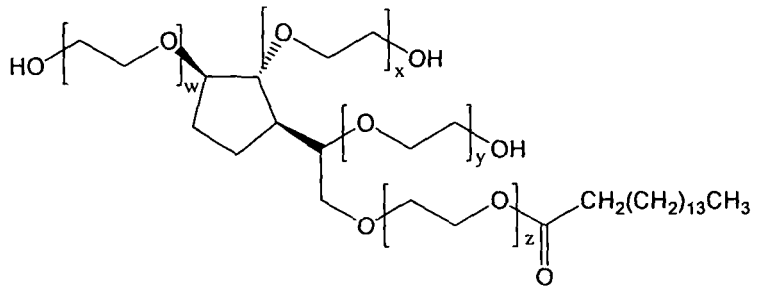
w+x+y+z = 20

TW80



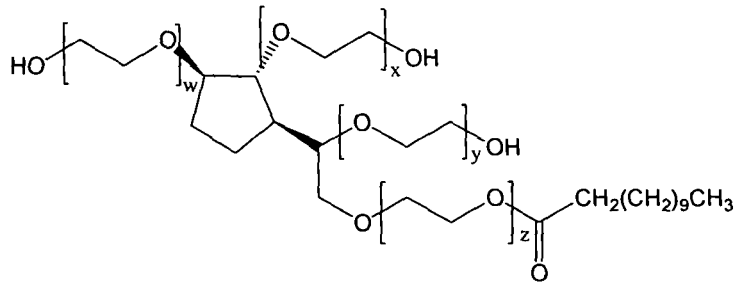
w+x+y+z = 20

TW60



w+x+y+z = 20

TW40



w+x+y+z = 20

TW20

Fig. II.A.2: Structural formulae of the surfactants studied.

Table II.A(2): Detail description of the surfactant used in the study.

Serial No	Name	Charge type	Abbreviation
1	Sodium dodecylsulphate	Anionic	SDS
2	Sodium dodecylbenzenesulphonate	Anionic	SDBS
3	Sodium dodecylsulphonate	Anionic	SDSN
4	Hexadecyltrimethylammonium bromide	Cationic	CTAB
5	Tetradecyltrimethylammonium bromide	Cationic	TTAB
6	Dodecyltrimethylammonium bromide	Cationic	DTAB
7	Polyoxyethylene(20) sorbitan monolaurate	Nonionic	TW20
8	Polyoxyethylene(20) sorbitan monopalmitate	Nonionic	TW40
9	Polyoxyethylene(20) sorbitan monostearate	Nonionic	TW60
10	Polyoxyethylene(20) sorbitan monooleate	Nonionic	TW80

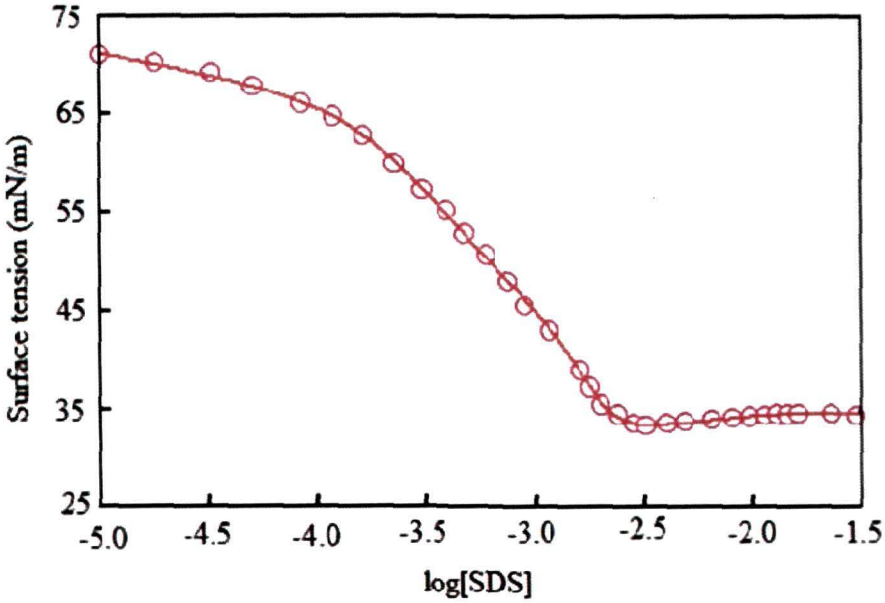


Fig.II.A.3: Plot of surface tension (mN/m) as a function of the logarithm of SDS concentrations at 298 (±0.1) K for determination of CMC of SDS.

II.A.3: ***Polymers***

PVA (MW ≈ 1,25,000)**:** PVA (CAS No., 9002-89-5, Product No., 1142660100), was obtained from Merck, Mumbai, India. The polymer was used as such. Detail description of the polymer is given in **Table II.A(3)**. Structural formula is shown in **Fig.II.A.4**.

PVA (MW ≈ 14,000)**:** PVA (CAS No., 9002-89-5, Product No., 030573), was obtained from Central Drug House Private Limited, Mumbai, India. The polymer was used as such. Detail description of the polymer is given in **Table II.A(3)**. Structural formula is shown in **Fig.II.A.4**.

PEG 600: PEG 600 (Batch No., SJ5S540600, Product No., 80748605001046), MW 570-630 g/mol was obtained from Merck, Mumbai, India. The polymer was used as such. Detail description of the polymer is given in **Table II.A(3)**. Structural formula is shown in **Fig.II.A.4**.

PEG 400: PEG 400 (Batch No., SG5S550435, Product No., 80748505001046), MW 380-420 g/mol was obtained from Merck, Mumbai, India. The polymer was used as such. Detail description of the polymer is given in **Table II.A(3)**. Structural formula is shown in **Fig.II.A.4**.

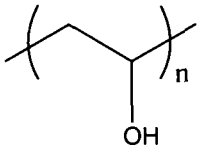
PEG 200: PEG 200 (Batch No., SC5S550107, Product No., 80748305001046), MW 190-210 g/mol was obtained from Merck, Mumbai, India. The polymer was used as such.

Detail description of the polymer is given in **Table II.A(3)**. Structural formula is shown in **Fig.II.A.4**.

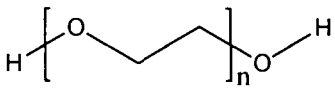
Chitosan: Chitosan (Product No., 448869, CAS No., 9012-76-4), MW ≈ 1,73,000 g/mol, degree of deacetylation (DDA), 80.5% was obtained from Sigma Aldrich, India. The polymer was used as such. Detail description of the polymer is given in **Table II.A(3)**. Structural formula is shown in **Fig.II.A.4**.

Table II.A(3): Detail description of the polymers used in the study.

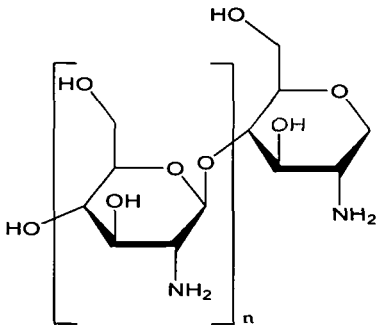
Serial No	Name	Charge type	MW (g/mol)	Abbreviation
1	Polyethylene glycol-200	Nonionic	190-210	PEG 200
2	Polyethylene glycol-400	Nonionic	380-420	PEG 400
3	Polyethylene glycol-600	Nonionic	570-630	PEG 600
4	Poly vinyl alcohol	Nonionic	1,25,000	PVA
5	Poly vinyl alcohol	Nonionic	14,000	PVA
6	Chitosan	Cationic	1,73,000	Chitosan



PVA



PEG



Chitosan

Fig. II.A.4: Structural formulae of the polymers studied.

In addition to the above mentioned dyes, surfactants and polymers, various buffer components, acids and bases have been used. The sources and purification of all the chemicals used are mentioned below.

II.A.4: *Buffer Components*

Perrin's low ionic strength (I= 0.01) buffer systems have been used throughout the study.[1] The buffer components, *viz.*, disodium hydrogen phosphate (Na_2HPO_4), potassium dihydrogen phosphate (KH_2PO_4), glycine ($H_2NCH_2CO_2H$), formic acid (H_2CO_2), potassium hydroxide (KOH), sodium hydrogen carbonate ($NaHCO_3$), sodium carbonate (Na_2CO_3), sodium metaborate ($Na_2B_4O_7.10\ H_2O$), boric acid (H_3BO_3), sodium chloride (NaCl), hydrochloride acid (HCl), perchloric acid ($HClO_4$), etc., were all of AR grade obtained from Merck, Mumbai and used as such.

II.B: *Preparations of solutions*

II.B.1: *Preparation of experimental solutions in buffer medium*

Double distilled water (conductivity ~0.1μS), prepared by adding $KMnO_4$ in the first distillation was used as solvent for preparing all solutions. To maintain the *p*H of the experimental solutions doubly concentrated buffer has been used. Experimental solutions with fixed dye concentration together with fixed polymer concentration and in a wide range of surfactant concentrations have been prepared by volume as shown in a representative table, **Table II.B(1)**. For covering a wide range of surfactant concentrations of the experimental solutions, surfactant stock solutions of different concentrations have been used as shown in the table. Fixed concentrations of the dyes were chosen in the order to have absorbance in a suitable range. As curcumin is poorly soluble in water, for the preparation of 2x 10^{-4}mol dm^{-3} curcumin solution, 25% methanol and 75% distilled water were used. In the final experimental solution the concentration of methanol is 3.0%. Doubly concentrated stock solutions of buffer components were prepared so that after mixing with the dye and surfactant/polymer solutions the resulting experimental solution contains the appropriate concentrations of the components required for the desired *p*H and ionic strength. The *p*H of the aqueous buffer solutions was found to be unchanged on the addition of the surfactants below their CMC.

Table II.B(1): Preparation of experimental solutions for the determination of equilibrium constant for an aqueous dye-surfactant-polymer system at a fixed *p*H.

Sl. No.	Buffer solution (ml) (doubly concentrated)	Aqueous surfactant * (ml)	Water (ml)	Aqueous dye (ml)	Aqueous polymer (ml)	Total solution volume (ml)	[Surfactant] in final solution (mol dm^{-3})
1	10	0	5.0	2.5	2.5	20	0
2	10	0.4(0.001)	4.6	2.5	2.5	20	2.0×10^{-5}
3	10	0.8(0.001)	4.2	2.5	2.5	20	4.0×10^{-5}
4	10	1.2(0.001)	3.8	2.5	2.5	20	6.0×10^{-5}
5	10	1.6 (0.001)	3.4	2.5	2.5	20	8.0×10^{-5}
6	10	2.0(0.001)	3.0	2.5	2.5	20	1.0×10^{-4}
7	10	4(0.001)	1.0	2.5	2.5	20	2.0×10^{-4}
8	10	0.8(0.01)	4.2	2.5	2.5	20	4.0×10^{-4}
9	10	1.2(0.01)	3.8	2.5	2.5	20	6.0×10^{-4}
10	10	1.6(0.01)	3.4	2.5	2.5	20	8.0×10^{-4}
11	10	2.0(0.01)	3.0	2.5	2.5	20	1.0×10^{-3}
12	10	4.0(0.01)	1.0	2.5	2.5	20	2.0×10^{-3}
13	10	0.8 (0.1)	4.2	2.5	2.5	20	4.0×10^{-3}
14	10	1.2(0.1)	3.8	2.5	2.5	20	6.0×10^{-3}
15	10	1.6(0.1)	3.4	2.5	2.5	20	8.0×10^{-3}
16	10	2.0(0.1)	3.0	2.5	2.5	20	1.0×10^{-2}
17	10	2.4(0.1)	2.6	2.5	2.5	20	1.2×10^{-2}
18	10	2.8(0.1)	2.2	2.5	2.5	20	1.4×10^{-2}

*Values within parenthesis indicate stock surfactant concentration.

II.C: ***Experimental measurements***

The UV-visible absorption spectra were recorded on Shimadzu U-2550 UV-visible spectrophotometer with matched pair of cells of 1 cm path length fitted in a thermostated cell holder. Temperature was maintained within ±0.5 K using a circulating cryostat bath attached to the spectrophotometer during the measurements. The sample cell was pre-rinsed with the respective solution to avoid any loss of dye by adsorption.

Fluorescence spectra were taken using a Hitachi F-2500 fluorescence spectrophotometer with the excitation and emission slit widths set at 5 nm. The temperatures were maintained within ±0.5 K using a circulating cryostat bath attached to the spectrometer during the measurements.

The surface tension readings for the determination of CMCs of the surfactants were carried out by using a Krüss Du Nouy tensiometer (Germany) model K9 (Accuracy: ± 0.1) using a platinum ring with a thermostated sample holder with temperature control by Thermo Hoake K10 (Temperature accuracy ±0.1 ^{o}C).

The *p*Hs were determined by using an Orion multiparameter kit ion meter (USA) or a Systronics (India), μ-*p*H systems. The *p*H-meter was calibrated properly with care before the measurements. All experiments were repeated at least thrice to check reproducibility.

II.D: ***Methods***

The acid-base equilibrium of an anionic and a nonionic dye shifts in surfactant micellar medium in presence of nonionic polymers. The equilibrium constants and thermodynamic parameters of the interactions between the anionic dye and anionic surfactant micelles in presence of nonionic polymers have been determined and will be described in the results and discussion section. The apparent acid dissociation constant of the neutral dye in nonionic surfactant micellar medium in presence of nonionic polymers have been determined and the methods used are described below. The monomer-dimer equilibrium of a cationic dye is shifted by anionic surfactant-polymer medium. The physicochemical behaviour of a natural dye is affected by submicellar cationic and anionic surfactants. The association constants have been determined and will be explained in the results and discussion section. The binding constants of the natural dye with surfactants in presence of polymers have been evaluated by electronic spectroscopy and fluorescence spectroscopic

techniques. Using the same spectroscopic techniques the binding constants of the natural dye with a biopolymer in presence of surfactants have been determined.

II.D.1: ***Calculation of the apparent acid dissociation constant of NR in nonionic surfactant micelles in presence of nonionic polymers***

The apparent acid dissociation constant of NR, $K_{a,app}$ in presence of any concentration of nonionic surfactant and/or polymer can be defined as,[2,3]

$$K_{a,app} = ([NR]_w + [NR]_m)\,[H^+_w] \,/\, ([NRH^+]_w + [NRH^+]_m) \qquad \text{II.D(1)}$$

where, $[NR_w]$ and $[NR_m]$ are the concentrations of the neutral form of NR in aqueous and the micellar pseudophase, respectively. $[NRH^+_w]$ and $[NR^+_m]$ are the concentrations of the acid form of the dye in aqueous and the micellar pseudophase, respectively. $[H^+_w]$ is the hydrogen ion concentration in aqueous phase.

The following 'FORTRAN' program was used for computation of $K_{a,app}$.[4]

1. **Symbols:**

Used in text	Used in the programme
$[NR_w]$	DW
$[NR_m]$	DM
$[NRH^+]_w$	DHW
$[NRH^+]_m$	DHM
$[H^+_w]$	Hw
$[H^+_m]$	Hm
CMC	cmc
K_{ass}	kass
K_s	ks
$K_{a,w}$	kaw
$K_{a,m}$	kam

2. **Program**

```
Real NRW, Kaw, Nr, Kam, Kass, NRWF
Open (unit=6, file= 'bornali.out')
f1=0.0000001
f2=0.00001
```

```
f3=0.000001
write (*,*)' NRW KAW   HW
Read (*,*) NRW,KAW, HW
Kaw=Kaw*f1
Hw=Hw*f1
write (*,*)'     Kass  Sm'
Read (*,*) Kass,Sm
Sm = SM*f2
write (*,*)' Kam'
Read (*,*) Kam
kam = kam*f3
NRWF=NRW
fact=Kaw/Hw
write (*, 10) NRW, KAW, HW
write (6, 31) NRW, KAW, HW
write (*,10) Kass, Sm
write (6, 32) KASS, SM
write (*,10) Kam
write (6, 33) KAM
DHW=NRW/ (1 + fact)
DW=NRW-DHM
write (*, 21) DW, DHW
write (6, 21) DW, DHW
fact1=Kass*sm
NR=NRW
NRWF=NR
NRW=NR/ (1 + fact1)
DM=NR-NRW
write (*, 22) NRW, DM
write (6, *) DW  DHW   NRW   DM    DHM'
KK=1
DHW=NRW/ (1. + fact)
DW=NRW-DHM
Kam=Kam
Hm=kaw*Hw/ Kam
format (5x, 4e16.7)
DM=NRW*Kass*Sm
Din=Kaw/HM
DHM=DM/Din
NRWF=NRW
NRW=NR- (DHM+DM)
Diff = abs (NRWF -NRW)
if ( diff. It. 0.0000000000005) go to 200
if (kk .gt. 40) go to 200
KK = KK+1
write (6, 10) dw, dhw, nrw, dm, dhm
```

```
go to 100
format (5E14.6)
format (5x, 'DW =' e15.7,' DHW =',e15.7)
format (5x, 'NRW =' e15.7,' DM =',e15.7)
format (5x, 'DHM =' e15.7,' NRW =',e15.7)
format (//5x, 'NRW =' e15.7,' KAW =',e15.7' HW =', e15.7)
format (5x, 'KASS =' e15.7,' SM =',e15.7)
format (5x, 'KAM =' e15.7//)
stop
end
```

3. An example of application of the program (NR-TW80 system)

Determination of $pK_{a,app}$ of NR (2.0x 10^{-5} mol dm^{-3}) at 298 (±0.1) K and at pH 7.00 in presence of TW80 (4x 10^{-4} mol dm^{-3}).

Inputs:

```
NRW =    .2000000E-04  KAW=    .3980000E-06  HW=    .1000000E-06
KASS=    .1210000E+04  SM =    .2900000E-03
KAM =    .3162000E-05
```

Outputs:

```
DW =    .1598394E-04  DHW =    .4016064E-05
  DW            DHW            NRW            DM            DHM
.118321E-04  .297288E-05  .146406E-04  .519506E-05  .164296E-06
.117008E-04  .293989E-05  .147001E-04  .513740E-05  .162473E-06
.117483E-04  .295183E-05  .146786E-04  .515827E-05  .163133E-06
.117311E-04  .294751E-05  .146864E-04  .515072E-05  .162894E-06
.117373E-04  .294907E-05  .146836E-04  .515345E-05  .162981E-06
.117351E-04  .294851E-05  .146846E-04  .515246E-05  .162950E-06
.117359E-04  .294871E-05  .146842E-04  .515282E-05  .162961E-06
.117356E-04  .294864E-05  .146844E-04  .515269E-05  .162957E-06
.117357E-04  .294866E-05  .146843E-04  .515274E-05  .162958E-06
.117356E-04  .294866E-05  .146843E-04  .515272E-05  .162958E-06
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.117357E-04  .294866E-05  .146843E-04  .515273E-05  .162958E-06
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.117357E-04  .294866E-05  .146843E-04  .515273E-05  .162958E-06
```

.117357E-04	.294866E-05	.146843E-04	.515273E-05	.162958E-06
.117357E-04	.294866E-05	.146843E-04	.515273E-05	.162958E-06
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.117357E-04	.294866E-05	.146843E-04	.515273E-05	.162958E-06
.117357E-04	.294866E-05	.146843E-04	.515273E-05	.162958E-06
.117357E-04	.294866E-05	.146843E-04	.515273E-05	.162958E-06
.117357E-04	.294866E-05	.146843E-04	.515273E-05	.162958E-06
.117357E-04	.294866E-05	.146843E-04	.515273E-05	.162958E-06
.117357E-04	.294866E-05	.146843E-04	.515273E-05	.162958E-06
.117357E-04	.294866E-05	.146843E-04	.515273E-05	.162958E-06

Calculation:

$[NR]_w = 1.173x\ 10^{-5}$ M

$[NR]_m = 5.153x\ 10^{-6}$ M

$[NRH^+]_w = 2.948x\ 10^{-6}$ M

$[NRH^+]_m = 1.63x\ 10^{-7}$ M

Now, given that, $K_{a,app} = ([NR]_w + [NR]_m)\ [H^+{}_w] / ([NRH^+]_w + [NRH^+]_m)$ II.D(1)

Thus, $K_{a,app} = 5.383 \times 10^{-7}$ M

$pK_{a,app} = 6.27$.

References:

1. Perrin, D.D. *Aust. J. Chem.* **16** (4), 572-578, 1963.
2. Dutta, R.K., et al. *J. Chem. Soc. Faraday Trans.* **91** (4), 681-686, 1995.
3. Saikia, P.M., et al. *J. Colloid Int. Sci.* **285** (1), 382-387, 2005.
4. Saikia, P.M. *A Study of Acid-Base Equilibrium of Dyes in Aqueous Micellar Systems*, Ph.D. Thesis, Tezpur University, India, 2005.

CHAPTER-III

III: Results and Discussion

In this chapter the experimental results and their analysis and interpretation have been discussed. For systematic organization, this chapter has been divided into three major sections which are described below.

III.A: *Acid-base equilibrium of dyes in aqueous polymer-surfactant medium*

The work on the acid-base equilibrium of the chosen dyes, *viz.*, phenol red (PR) and neutral red (NR) in aqueous polymer-surfactant media have been presented in two different subsections below.

III.A.1: *Acid-base equilibrium of phenol red in aqueous polymer-surfactant medium*

The acid-base equilibrium of PR has been studied in aqueous solutions and in aqueous surfactant solutions also in addition to aqueous polymer-surfactant solutions in order to assess the combined effects of polymer and surfactant on the aqueous dye.

Three forms of PR, *viz.*, DH_2, DH^-, D^{2-} (**Fig. III.A.1**) have been reported with corresponding absorption bands in the visible region with λ_{max} at 506 nm, 431 nm and 559 nm, respectively.[1-3] The pK_{a2} of the dye in water corresponding to the deprotonation of DH^- form to D^{2-} form is reported to be 7.74 in low ionic strength (I = 0.01) phosphate buffer medium.[1-4] The pK_{a1} of the dye in water corresponding to the first deprotonation equilibrium has been reported to be 0.90 in Glycine-NaCl-HCl buffer systems.[5]

It has been reported that anionic and nonionic surfactants showed no effect on PR in submicellar medium,[3,6] However, deprotonation of PR occurs in submicellar cationic surfactant medium.[3,4] The oppositely charged ion and the surfactant head groups form a closely packed ion-pairs.[3,6] In anionic and nonionic micellar medium, a shift in $pK_{a,w}$ of PR has been observed.[3,6] Moreover, in cationic micellar medium, solubilization of the dye by cationic micelles vanish the process of ion-pair formation between the oppositely charged dye and surfactant head groups.[7]

III.A.1(i): *Acid-base equilibrium of phenol red in polymer-anionic micellar medium*

a. Spectral behaviour

The spectra of PR (3.5×10^{-5} mol dm^{-3}) at *p*H 7.70 (phosphate buffer system) in aqueous solution of various concentration of SDS in presence of 5% PVA solution at 298 (±0.1) K are shown in **Fig. III.A.1**. The two bands with absorption maxima at 431 nm and 559 nm are attributed to the acid (*i.e.*, DH^-) and the base (*i.e.*, D^{2-}) forms of PR, respectively.[1-3] It was observed that with increase in concentration of SDS the absorbance of the basic form of PR decreases with the corresponding increase in the absorbance due to its acid form.

Similar trends are observed in presence of the polymers PEG 200, PEG 400 and PEG 600. The presence of a sharp isosbestic point at 475 nm suggests that equilibrium between the dye in bulk aqueous medium and in the micellar pseudophase exists.

Association of sulfonephthalein dyes with micelles is determined by a combination of hydrophobic attraction and electrostatic repulsion between the acid and base form of the dyes with micelles having same charge. The gradual disappearance of the absorption band due to D^{2-} form and corresponding increase in the absorption band due to the DH^- form indicates conversion of the D^{2-} forms to the DH^- form with the increase in the concentration of surfactant. This may be attributed to the increase in electrostatic repulsion between the D^{2-} forms of PR in the anionic SDS micelles bound to polymer chains. During the binding of the micelles or surfactant aggregates with the polymer chain, the head group region of the micelles get increasingly exposed through replacement of the water molecules around the head group area of the micelles. As a result the electrostatic repulsion between the D^{2-} forms of PR with the anionic SDS micelles bound to polymer chains have increased leading to greater conversion of the D^{2-} forms to the DH^- form of the dye.

However, for the same system as above under identical conditions, we observed a reverse trend in Tris buffer system of *p*H 7.70. The spectra of PR (3.5×10^{-5} mol dm^{-3}) at *p*H 7.70 (Tris buffer system) in aqueous solution of various concentration of SDS in presence of 5% PVA solution at 298 (±0.1) K are shown in **Fig. III.A.2**. It was observed that in the aqueous polymer medium the absorbance of the basic form of the dye increases while that of the corresponding acid form decreases gradually with the increase in concentration of SDS. This observation was against our expectation since the anionic micelles bound to the polymer chains should have favoured greater electrostatic repulsion for the doubly negative form than the mononegative form of PR as was observed in the former case. This contrasting observation may be due to the partition of the Tris buffer components between the aqueous phase and micellar pseudophase which results in shielding of the polar head group regions of the micelles bound to the polymer.

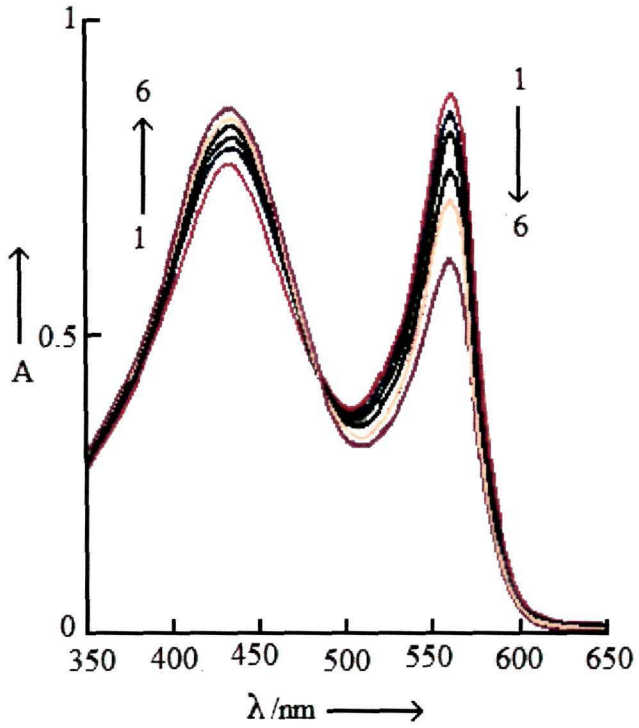


Fig. III.A.1: UV-visible absorption spectra of PR (3.50x 10^{-5} mol dm^{-3}) at various concentrations of SDS in presence of 5% PVA at *p*H 7.70 (phosphate buffer) at 298 (±0.1) K: [SDS] / 10^{-3} M = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5) 10.0 and (6) 12.0.

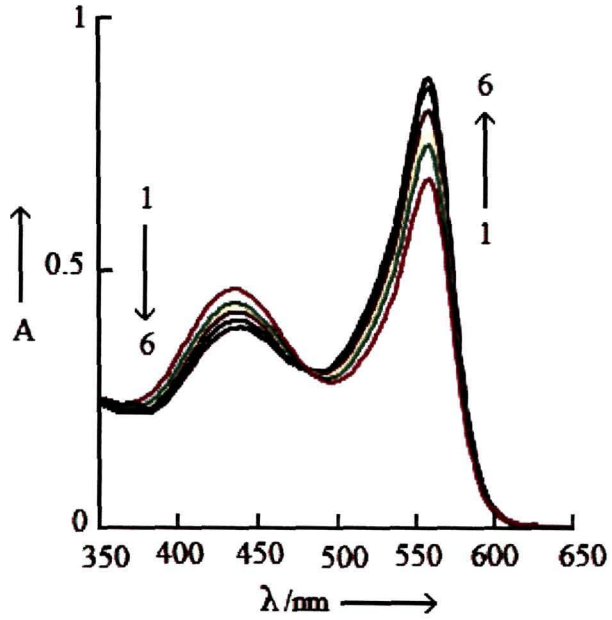


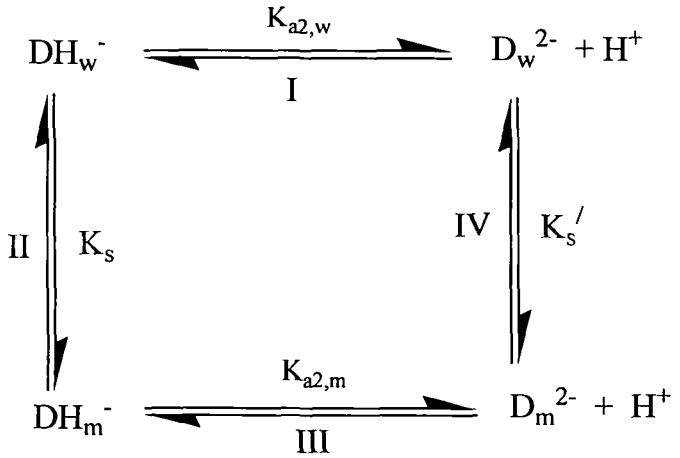
Fig. III.A.2: UV-visible absorption spectra of PR (3.50x 10^{-5} mol dm^{-3}) at *p*H of 7.70 (Tris buffer) in aqueous solution of various concentrations of SDS in presence of 5% PEG 200 at 298 (±0.1) K: [SDS] / 10^{-3} M = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5) 10.0 and (6) 12.0.

Increase in concentrations of the surfactant favoured greater partition of the buffer components and hence greater shielding of the electrostatic repulsion between the micelles and the doubly negative form of PR. This observation was analogous to the spectral change observed on increasing the polymer concentration which can be attributed to the formation of polymeric network around the micelles bound to it. In the present experimental condition the polymer backbone perhaps form bridges between the micelles and in this way the polymer self assembles through various interactions to form a transient network as reported earlier.[8-10] Formation of such polymeric network probably leads to the shielding of the head group region of the micelles bound to the polymer backbone. As a result, the D^{2-} form moves away from the aqueous pseudophase and a part of the dye in the DH^- form changes to the D^{2-} form in order to maintain constant ratio of the two forms since the aqueous pseudophase is buffered.

b. Determination of equilibrium constants and other thermodynamic parameters

The various equlibria involved in case of sulphonepthalein indicators in aqueous anionic micellar systems can be summarized as shown in **Scheme III.A(1)**. Here, DH_w^- and DH_m^- are the acid form of the dye, D_w^{2-} and D_m^{2-} are the base form of the dye, H_w^+ and H_m^+ are the hydrogen ion concentrations in the aqueous and micellar pseudophases, respectively. $K_{a2,w}$ and $K_{a2,m}$ are the acid dissociation constants of the dye in the aqueous and the micellar pseudophase, respectively.

The method described below, developed by Dutta *et al.* has been used to determine the equilibrium constants.[6,11]



Scheme III.A(1): The various equilibria and the species involved in the PR-micelle-polymer systems investigated.

Step 1

Considering the equilibrium I (Scheme III.A (2)), we have,

$$K_{a2,w} = [D_w^{2-}][H_w^+] / [DH_w^-] \qquad \text{III.A(1)}$$

or,

$$[D_w^{2-}] - (K_{a2,w} / [H_w^+])\,[DH_w^-] = 0 \qquad \text{III.A (2)}$$

In the absence of surfactant,

$$[D_w^{2-}] + [DH_w^-] = [D]_o \qquad \text{III.A (3)}$$

where $[D]_o$ is the total concentration of dye, which is known. Eq.s III.A(2) and III.A(3) can be solved to find $[D_w^{2-}]$ and $[DH_w^-]$.

Step 2

If, for the time being, we assume that only the mononegative forms of the dye associate with the micelles, i.e., only the following equilibrium exists,

$$[D_w] + [S_m] \overset{K_{ass}}{\rightleftharpoons} [DH_m^-] \qquad \text{III.A (4)}$$

where $[D_w]$ is the concentration of the dye in the aqueous solution, or

$$[DH_m^-]/ [D_w] = K_{ass}[S_m] \qquad \text{III.A (5)}$$

$$[DH_m^-]- K_{ass}[S_m]/ [D_w] = 0 \qquad \text{III.A (6)}$$

where $[S_m]$ is the total surfactant in micellar form.[6,11,12] The association constant, K_{ass}, can be determined using the Eq. III.A (7),[11]

$$(d_o - d) / (d - d_m) = K_{ass}[S_m] = - K_{ass}CMC + K_{ass}[S_o] \qquad \text{III.A (7)}$$

where K_{ass} is the association constant of the dye with micelles at constant *p*H, $[S_o]$ is the total concentration of the surfactant, $[S_m]$ is the concentration of the micellized surfactant and CMC represents the critical micelle concentration of the surfactant in the buffered medium. The CMC is replaced by CAC (critical aggregation concentration) in presence of polymer. Here the terms d_o, d, and d_m are the absorbances of the dye in the absence of surfactant, in the presence of surfactant of concentration [S], and in excess of surfactant, respectively, at fixed *p*H and at a wavelength of the band where absorbance decreases with increased concentration of the surfactant such that $d_o = \varepsilon_o[D]_o$, $d_m = \varepsilon_m[D]_o$, and $d = \varepsilon_m[D]_o + \varepsilon_0[D]_0 - \varepsilon_0[D_m]$, where ε_o and ε_m are the apparent molar absorption coefficients of the dye, and $[D]_o$ and $[D_m]$ are the total concentration of the dye and the concentration of micellized dye, respectively.[6] Thus, the quantity ($K_{ass}[S_m]$) in Eq. III.A (6) can be known. Again, under such conditions, the total dye concentration, $[D]_o$, is given by,

$$[D]_o = [DH_m^-] + [D_w] \qquad \text{III.A (8)}$$

The Eqs. III.A (6) and III.A (8) can be solved simultaneously to calculate $[DH_m^-]$ and $[D_w]$ and the revised values of $[D_w^{2-}]$ and $[DH_w^-]$ by repeating Step 1. Nevertheless, these values are obtained with the assumption that only the mononegative form of the dye is associated with the micelles, which is not correct.

Step 3

If we allow association of the doubly negative form of the dye also to the micelles of the nonionic surfactant, as in equilibrium IV in **Scheme III.A (1)**, then we have

$$K_{a2,m} = [D_m^{2-}][H_m^+] / [DH_m^-] \qquad \text{III.A (9)}$$

or,

$$[D_m^{2-}] - (K_{a2,m} / [H_m^+])\,[DH_m^-] = 0 \qquad \text{III.A(10)}$$

If we assume the acid dissociation constant to be an intrinsic property of the indicator dye and to remain the same in both the aqueous as well as in the micellar pseudophase, i.e., $pK_{a2,w} = pK_{a2,m}$, and attribute the shift in observed apparent $pK_{a2,m}$ to difference in *p*H of the micelle surface, then Eq. III.A(9) can be written as,

$$[D_m^{2-}] = (K_{a2,w} / [H_m^+])\,[DH_m^-] \qquad \text{III.A(11)}$$

On the other hand, the apparent pK_{a2} in micellar medium, $pK_{a2,m,app}$, defined by

$$[D_m^{2-}] = (K_{a2,m,app}/[H_w^+])\,[DH_m^-] \qquad \text{III.A(12)}$$

can be measured in the presence of excess concentrations of the surfactant when all of the dye can be assumed to be incorporated into the micelles. From Eq.s III.A(11) and III.A(12) we get,

$$K_{a2,m}/[H_m^+] = K_{a2,m,app}/[H_w^+] \qquad \text{III.A(13)}$$

or,

$$[H_m^+] = K_{a2,m}\,[H_w^+]/\,K_{a2,m,app} \qquad \text{III.A(14)}$$

Thus, $[H_m^+]$ or the pH_m can be known. Once $[H_m^+]$ is known, $[D_m^{2-}]$ can be calculated using Eq. III.A(11). Now, the total concentration of the dye is given by,

$$[D]_o = [D_w] + [DH_m^-] + [D_m^{2-}] \qquad \text{III.A(15)}$$

and the concentrations of $[D_w]$, $[DH_w^-]$, $[D_w^{2-}]$, $[DH_m^-]$, and $[D_m^{2-}]$can be recalculated by repeating Steps 1 and 2.

The pK_as of the indicators were determined experimentally using the following equation,

$$pH = pK_{a2} - \log\{(A_b - A_x)/(A_x - A_a)\} \qquad \text{III.A(16)}$$

where A_a, A_b, and A_x are the absorbances of the indicator in a strong acidic medium, in a strong basic medium, and at an intermediate pH, respectively, at λ_{max} of the acid or base form.

Step 4

An iteration of the Steps 1, 2, and 3 until one gets constant values of the concentrations of all the four species of the dye, *viz.*, DH_w^- , DH_m^- , D_w^{2-}, and D_m^{2-}, in a well-buffered medium and for a particular concentration of the surfactant.

$K_{a2,app}$ of the chosen sulfonephthalein indicator at any concentration of the surfactant can be defined as,[13]

$$K_{a2,app} = ([D_w^{2-}] + [D_m^{2-}])\,[H_w^+]/\,([DH_w^-] + [DH_m^-] \qquad \text{III.A(17)}$$

The $pK_{a2,app}$ were determined experimentally using Eq. III.A(17). The equilibrium constant K_s, which is independent of *p*H, can be related to K_{ass} by the equation,[11,12]

$$K_s = K_{ass}(1 + K_{a2,w}/\,[H_w^+]\,) \qquad \text{III.A(18)}$$

A plot of $(d_o - d)/\,(d - d_m)$ *vs.* $[S_o]$ should be linear with slope equal to K_{ass} and intercept of the abscissa equal to CAC (or the intercept of the ordinate equal to $-K_{ass}$ .CAC). The plots of $\{(d_o - d)\,/(d - d_m)\}$ *vs.* $[S_o]$ for PR in aqueous micellar solution of SDS in the presence of 5% PVA , 5% PEG 200, 5% PEG 400 and 5% PEG 800 solution at *p*H 7.70 and 298 (±0.1) K are shown in **Fig. III.A.3.**

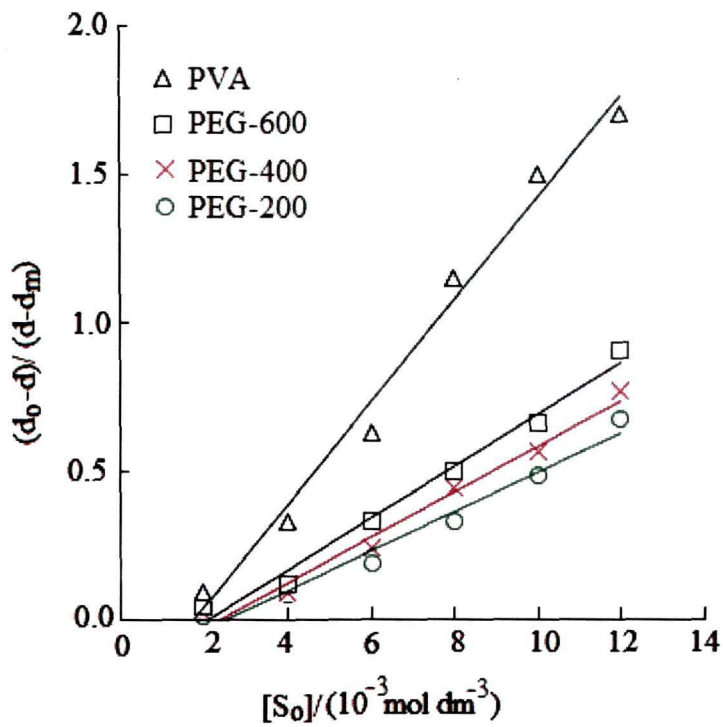


Fig. III.A.3: Linear plots of $\{(d_o–d)\,/\,(d–d_m)\}$ *vs.* $[S_o]$ for PR-SDS system in presence of different polymers (5%) at a *p*H of 7.70 and 298 (±0.1) K.

The plots have been found to be quite linear which indicates that the partition equilibrium method holds for the polymer-surfactant systems. The CAC of the system can be located easily from the plot. The CAC and K_{ass} values determined at 298 (±0.1) K for the different systems are shown in **Table III.A(1)**. From the Table, it has been observed that the CAC of the surfactant in the polymer-surfactant system is lower than its CMC in absence of polymer in otherwise identical conditions. This is probably due to the electrostatic stabilization of micelles, which takes place due to the decrease in the mutual head group repulsion. Another factor may be the reduction of interfacial area between the hydrophobic polymer segment and the exposed hydrophobic part of the aggregating surfactant as observed earlier in similar polymer-surfactant systems.[8,9]

The *p*H dependent association constants K_{ass} of PR with SDS-PEG systems increases with the increase in molecular weight of the polymer. It has been observed that at the same *p*H the value of K_{ass} is greater in Tris buffer system than in phosphate buffer system. This also indicates the partition of Tris buffer components between the aqueous phase and micellar pseudophase which probably shielded the head group region of the micelles reducing the electrostatic interactions and inducing greater hydrophobic interactions between the dye molecules and the micelles as reported earlier in aqueous surfactant systems in absence of polymer.[13]

The ΔG^o of the systems has been determined from the equation,

$$\Delta G^o = -RT \ln K_s \qquad \text{III.A(20)}$$

ΔH^o and ΔS^o for the SDS-PVA and SDS-PEG systems were determined using the van't Hoff plot assuming the ΔH^o to be nearly constant in the small experimental temperature range between 298 and 313 K using average value of K_s obtained at different *p*H. The van't-Hoff plots for the interaction of PR with SDS in presence of different nonionic polymers at *p*H 7.70 (Tris buffer) are shown in **Fig. III.A.4**. The various thermodynamic parameters for the interaction of PR with the PVA-SDS and PEG-SDS aqueous systems at *p*H 7.70 (Tris buffer) are shown in **Table III.A(2)**. The interactions are found to be endothermic and driven by entropy. The observed small positive enthalpy changes indicate weak dye-micelle interaction due to similar charge on both. The observed weaker interaction between the PR and SDS bound to the nonionic polymers may have

contributions from hydrophobic interaction. The large ΔS^o values can be attributed to more ordering in the bound system compared to the free dyes, polymer and micelles.

Table III.A(1): The CAC's of SDS in the buffered solutions (0.1 M TRIS + 0.1M HCl), *p*H dependent association constants*, K_{ass} and the *p*H independent equilibrium constants, K_s of PR with the surfactant in the polymer-surfactants systems at 298 (± 0.1) K.

*p*H	polymer	Mol. Wt. of polymer	CAC /10^{-3} moldm^{-3}	K_{ass} /dm^{-3}mol	K_s /dm^{-3}mol
	-	-	2.11[b]	368[b]	1046[b]
	PVA	125,000	0.84	235	668
			1.80[a]	171[a]	472[a]
7.70	PEG	200	1.35	126	358
			2.61[a]	71[a]	196[a]
	PEG	400	1.25	132	375
			2.45[a]	76[a]	210[a]
	PEG	600	1.12	145	412
			2.26[a]	82[a]	206[a]
	-	-	2.72[b]	268[b]	1049[b]
	PVA	125,000	1.02	171	670
7.90	PEG	200	1.52	92	360
	PEG	400	1.42	96	376
	PEG	600	1.36	106	415
	-	-	3.01[b]	168[b]	1053[b]
	PVA	125,000	1.20	99	676
8.20	PEG	200	1.75	53	362
	PEG	400	1.62	56	382
	PEG	600	1.46	61	417

*Experimental error limit = ± 5%

[a]In phosphate buffer system (0.02 M KH_2PO_4 + 0.01 M Na_2HPO_4).

[b]In polymer free micellar medium.

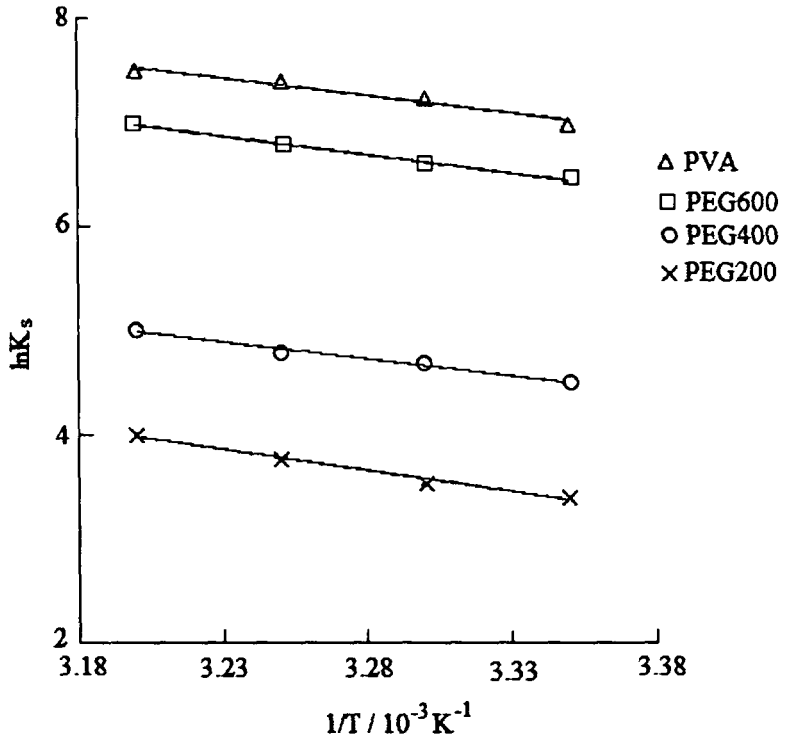


Fig. III.A.4: vant-Hoff plot for the interaction of PR with SDS in presence of different nonionic polymers at *p*H 7.70 (Tris buffer).

Table III.A(2): The thermodynamic parameters of the interaction of PR with SDS in PVA-SDS, PEG 200-SDS, PEG 400-SDS, PEG 600-SDS systems, at *p*H 7.70 (Tris buffer).

Polymer	**Surfactant**	**$-\Delta G^o$ /kJ mol^{-1}**	**ΔH^o /J mol^{-1}**	**ΔS^o /J mol^{-1}K^{-1}**
PVA	SDS	16.11	23.65	54.14
PEG200	SDS	14.57	24.15	48.97
PEG400	SDS	14.68	23.89	49.34
PEG600	SDS	14.91	23.05	50.11

Experimental error limit = ± 5%.

III.A.2: ***Acid-base equilibrium of neutral red in aqueous polymer-surfactant medium***

In aqueous medium at moderate *p*H, neutral red (NR) exists in equilibrium between the two forms, *viz.*, HD^+ and D.[14-16] The absorption maxima for base form, D is reported to be at 450 nm, while for acid form, HD^+ is reported in the range of 535 nm to 545 nm. The observed difference in the absorption maxima corresponds to the acid form HD^+ and also the pK_{a2} shift has been attributed to the effects of different buffer system used.[14] The absorption maxima for the HD^+ form is reported to be 527 nm and the corresponding pK_{a1} for the dissociation of HD^+ in water have been reported as 6.75 (± 0.02), in phosphate buffer medium.[14] A doubly protonated form of NR, H_2D^{2+} with an absorption maxima at 598 nm has been reported in highly acidic condition.[16] The pK_a of the dye corresponds to acid dissociation of the H_2D^{2+} form of NR in water, pK_{a2} has been reported as 0.26.[16]

Cationic and nonionic surfactants showed no effect on NR in submicellar medium.[6,17] However, it has been reported that, in aqueous submicellar SDS medium, the dicationic form, *viz.*, H_2D^{2+} of the dye also exists at *p*H 7.00.[14] The oppositely charged ion and the anionic head groups of the surfactants form a very closely packed ion-pair.[16,17] In the presence of nonionic and cationic micelles, the neutral form is predominant, and a pK_a shift of the dye has been observed.[14,18] While the negatively charged SDS micelles enhance the formation of the positively charged species (NRH^+) and at the same time, increases the solubilization of the neutral species (NR) shifting the acid-base equilibrium. Hence, the electrostatic and solubilization effects shift the acid-base equilibrium in opposite directions. Overall, the SDS micelles induce NRH^+ formation and an increase in pK_a is observed. On the other hand, CTAB and TW80 micelles enhance the formation of the neutral form of NR and decrease the pK_a.

III.A.2(i): ***Acid-base equilibrium of neutral red in polymer-nonionic micellar medium***

a. Spectral behaviour

The spectral changes of 5.0 x10^{-5} mol dm^{-3} aqueous NR induced by TW80 at *p*H 6.80 at 298 (±0.1) K are shown in **Fig.III.A.5**. The intensity of the 470 nm absorption band, which corresponds to the neutral form of the dye, increased gradually at the cost of absorbences of the 527 nm band, which corresponds to the NRH^+ form, on increasing the surfactant concentration. The observed spectral behaviour of the dye is in agreement with an earlier report with another nonionic surfactant, *viz.*, TX-100.[14] A sharp isosbestic point was observed at 478 nm. The presence of the sharp isosbestic point suggests the existence of equilibrium between the neutral and protonated forms of NR in the system. The gradual

disappearance of NRH^+ band on addition of TW80 indicates gradual conversion of the neutral form of the dye into the acid form. This happens because the neutral base form of the dye is preferentially incorporated into the nonionic micelles and as a result, the acid form of the dye is gradually converted into the neutral base form to maintain a constant ratio of the two forms of the dye in the buffered aqueous pseudophase.[11] The 527 nm band however did not disappear completely even in the presence of a high concentration of the surfactant at this *p*H suggesting that a significant fraction of the dye in the NRH^+ form is also incorporated to the micelles similar to that observed in the presence of TX-100.[14]

There is an electrostatic interaction between the oxygen atoms of the ethoxy chains of TW80 molecules and the hydrogen ion of NRH^+ as well as a hydrophobic interaction between the hydrophobic tail of the surfactant and the NR form of the dye. But, when some of the NRH^+ forms of the dye are incorporated with the nonionic micelles, the electrostatic repulsion between the cationic forms of the dye reduces further adsorption of the cationic acid form onto the micelles. As a result, the neutral base form of the dye associates to the micelles preferentially over the cationic acid form. A similar preferential incorporation of the monoanionic form of sulfonephthalein dyes to nonionic micelles over the dianionic form was reported in an earlier study by Saikia *et al.*[11] The strong affinity of the neutral form towards the nonionic micelles indicates specific hydrophobic interaction between the neutral form of the dye and the alkyl chain of the surfactant. Thus, the dye resides in the nonpolar core of the micelles of the surfactant,[13] where the polarity and so the dielectric constant of the microenvironment are much lower than that in bulk water. Thus, we observe a hypsochromic shift of the band corresponding to the neutral form from 470 nm to 460 nm.[19] Similar spectral trends of the dye have been observed with TW20, TW40 and TW60.

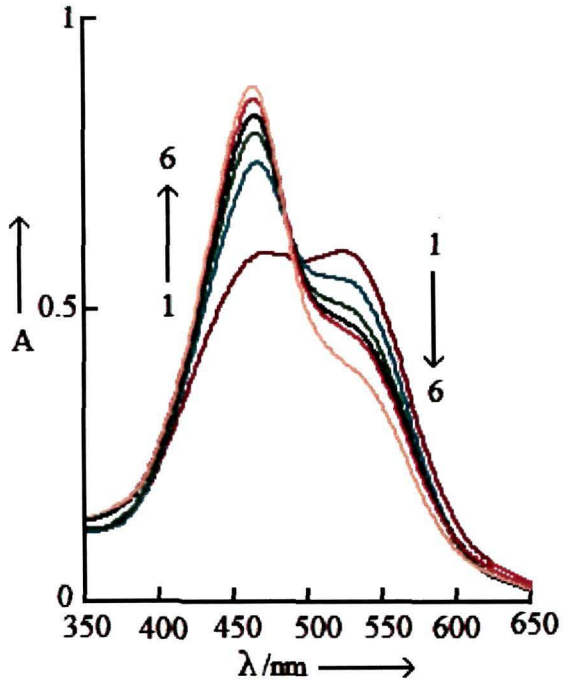


Fig. III.A.5: UV-visible absorption spectra of NR (5.0 x10^{-5} mol dm^{-3}) in presence of various concentrations of TW80 at *p*H 6.80 and temperature 298 (±0.1) K: [TW80]/(10^{-4} mol dm^{-3}) = (1) 0.00, (2) 0.40, (3) 0.80, (4) 1.20, (5)1.60 and (6) 2.00.

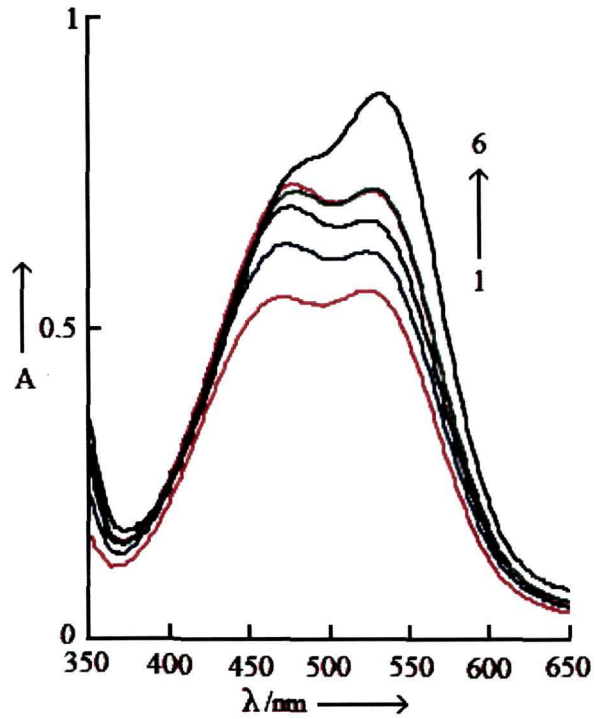


Fig. III.A.6: UV-visible absorption spectra of NR (5.0 x10^{-5} mol dm^{-3}) in presence of various concentrations of PVA (w/v %) at *p*H 6.80 and temperature 298 (±0.1) K: PVA/ w/v % = (1) 0.00, (2) 0.45, (3) 0.60, (4) 1.20, (5)0.75 and (6) 1.25.

It has been observed that, on increasing the concentration (weight%, w/v) of PVA at *p*H 6.80 at 298 (±0.1) K, the absorption intensities of both bands corresponding to the acid and the base forms increased initially as shown in **Fig.III.A.6** suggesting binding of both forms of the dye with the polymer. After a certain concentration of PVA, *viz.*, about 1.25% (w/v), the intensity of only one of the bands, *viz.*, the band corresponding to the NRH^+ form increased gradually as shown in the **Fig.III.A.6** suggesting a stronger interaction of the cationic form of the dye than the neutral form with the polymer at high concentrations of the polymer. Similar behaviour of the dye was observed on addition of PEG 600, PEG 400 and PEG 200 also. PVA is reported to form hydrogen bonding with water molecules with its –OH groups forming a transient polymer network.[20] The electrostatic interaction between the NH^+ part of NRH^+ and the oxygen atoms of PVA is increased with increasing PVA concentration. In addition to that, there may be hydrogen bond formation between the $-NH_2$ group of the dye molecule and the oxygen atoms of PVA. Thus, the observed bathochromic shift of the band of the NRH^+ form from 527nm to 535nm of can be attributed to the increasing hydrogen bond strengths in the presence of the polymer in the system.

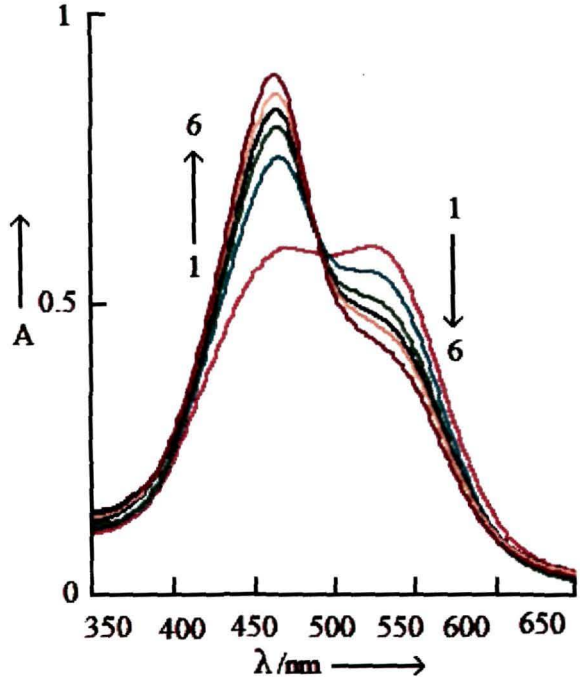
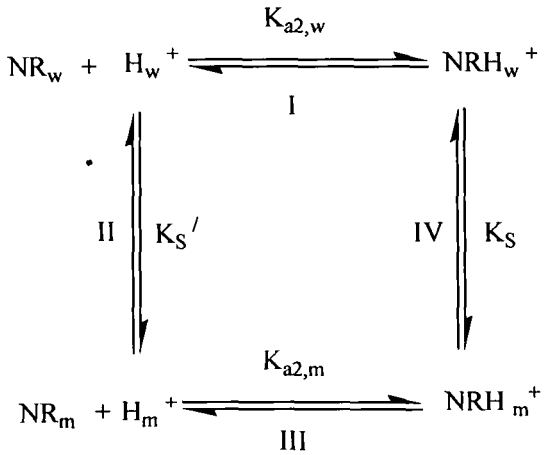


Fig. III.A.7: UV-visible absorption spectra of NR In presence of various concentrations of TW80 in presence of fixed concentration of 1.25% (w/v) PVA at *p*H 6.80 and temperature 298 (±0.1) K: [TW80] /(10^{-4} mol dm^{-3}) = (1) 0.00, (2) 0.30, (3) 0.60, (4) 0.90, (5) 1.20 and (6)1.50.

The spectral changes of the dye observed on addition of TW80 in the presence of a 1.25% (w/v) PVA at *p*H 6.80 at 298K are shown in **Fig.III.A.7**. The resemblance of this spectral trend with that observed with the surfactants alone indicates that the interactions of NR with the nonionic surfactant are stronger than that with the nonionic polymers alone. Similar trends were observed with the other Tween surfactants and PEG polymers also. The changes followed the same trend as was observed in the case of the surfactant alone indicating greater influence of the surfactant than the polymer on the dye.

b. Determination of equilibrium constants and other thermodynamic parameters

The various equlibria involved in case of NR in aqueous nonionic micellar systems can be summarized as shown in **Scheme III.A(2)**. Here, NRH^+_w and NRH^+_m are the cationic acid form of the dye, NR_w and NR_m are the neutral base form of the dye, H^+_w and H^+_m are the hydrogen ion concentrations in the aqueous and micellar pseudo phases, respectively.[11,17] Similarly, $K_{a,w}$ and $K_{a,m}$ are the acid dissociation constants of the dye in the aqueous and the micellar pseudo phases, respectively.[6,11] The concentrations of the various species in the system have been determined by the following procedure analogous to that described earlier for anionic sulfonephthalein dyes and nonionic surfactant systems.[11] As the experimental dye concentrations are very low, the concentrations of the various forms of the dyes have been considered equal to their activities.[21] However, the procedure used in the previous study for (–,2–) charge type sulfonephthalein indicator dye has been modified adequately to suit the present (+,0) charge type neutral red indicator dye.



Scheme III.A(2): A schematic representation of the various equilibria and the species involved in NR-nonionic micelle-polymer systems investigated.

It has been assumed that due to association of NR with nonionic micelles, the following equilibrium {Eq. III.A(21)} exists in the solution,

$$[NR_w] + [S_m] \underset{}{\overset{K_{ass}}{\rightleftharpoons}} [NR_m] \qquad \text{III.A(21)}$$

where, K_{ass} is the association constant of the dye with micelles at a constant experimental *p*H, $[NR_w]$ and $[NR_m]$ are the concentrations of the dye in aqueous and the micellar pseudophase and $[S_m]$ is the total concentration of the surfactant in micellar form. Eq. III.A(21) can be expressed as,

$$[NR_m] - K_{ass}[S_m][NR_w] = 0 \qquad \text{III.A(22)}$$

The association constant, K_{ass} at constant *p*H, the critical micelle concentration (CMC) (A term critical aggregation concentration (CAC) has been used for surfactant-polymer systems instead of CMC [25]) can be determined by using Eq. III.A(23),[6,11,12]

$$(d_o - d) / (d - d_m) = K_{ass}[S_m] = - K_{ass}.CMC + K_{ass}[S_o] \qquad \text{III.A (23)}$$

where, d_o, d and d_m are the absorbences of the dye at a chosen wavelength of the band in absence of surfactant, in the presence of surfactant of concentration [S], and in micellized form, respectively, at a fixed *p*H. A wavelength has been chosen from the band of the dye in which the absorbance decreases with increase in concentration of the surfactant. In such a case $d_o = \varepsilon_o[D]_o$, $d_m = \varepsilon_m[D]_o$ and $d = (\varepsilon_m[D]_o + \varepsilon_o[D]_o - \varepsilon_o[D_m])$ where, ε_o and ε_m are the molar absorption coefficients of the aqueous and micellized dye, $[D]_o$ and $[D_m]$ are the total concentration of the dye and the concentration of micellized dye, respectively.

The $K_{a,app}$ of NR in presence of any concentration of nonionic surfactant and/or polymer can be defined as,[6,22]

$$K_{a,app} = ([NR]_w + [NR]_m)\,[H^+{}_w] / ([NRH^+]_w + [NRH^+]_m) \qquad \text{III.A(24)}$$

The $pK_{a,app}$s were calculated by the present partition equilibrium (PE) method using Eq. III.A(24) by determining the concentration of all the four forms of the dye using a

FORTRAN program (described in Chapter-II) by a method similar to that described earlier.[6,11,12] The $pK_{a,w}$s of the dye have also been determined experimentally by using Eq. II.A(25),[3,11,12]

$$pH = pK_{a,w} - \log\{(A_b - A_x) / (A_x - A_a)\} \qquad \text{III.A(25)}$$

where, A_a, A_b, and A_x are absorbences of the dye in a strong acidic medium ($pH > 0.26$[16]), in a strong basic medium and at an intermediate pH, respectively, at λ_{max} of the acid or base form of the dye.

A pH independent equilibrium constant K_s {Scheme III.A(2)} has been calculated from K_{ass} using Eq. III.A (26),[14,23]

$$K_s = K_{ass}(1 + [H^+_w] / K_{a,w}) \qquad \text{III.A(26)}$$

The plots of $\{(d_o - d) / (d - d_m)\}$ *vs.* $[S_o]$ for NR-Tween systems in presence of 1.25% PVA at pH 7.00 and 298 (±0.1) K have been shown in **Fig.III.A.8**. The plots have been found to be quite linear which indicates the validity of the partition equilibrium (PE) method in the aqueous polymer-surfactant systems. The values of $[S_o]$ corresponding to the points where the straight lines meet the abscissa are the CMC (or CAC) of the surfactants in the respective media.[12] The points below $[S_o]$ = CMC (or CAC) fall on the abscissa due to the absence of micelles. The values of CMC or CAC, pH dependent association constant K_{ass} and the pH independent equilibrium constant K_s were determined at 298 (±0.1) K for the polymer-surfactant systems and have been shown in the **Tables III.A(3a-d)**.

Table III.A(3a): The *p*H dependent association constant, K_{ass} and *p*H independent equilibrium constant, K_s of NR with TW80 in presence of 1.25% (v/v) (PEG 200, PEG 400, PEG 600) and 1.25% (w/v) PVA at 298 (±0.1)K.

Polymer	**pH**	**CAC**** /(10^{-5}mol dm^{-3})	**K_{ass}**** /(10^3dm^3 mol^{-1})	**K_s**** /(10^4dm^3 mol^{-1})
PVA	6.80	1.04*	881*	1666*
		0.83	2321	4388
	7.00	0.95*	1068*	1668*
		0.77	2809	4387
	7.20	0.90*	1231*	1667*
		0.71	3245	4393
PEG 600	6.80	0.90	1341	2534
	7.00	0.82	1626	2540
	7.20	0.78	1879	2544
PEG 400	6.80	0.94	1156	2184
	7.00	0.86	1401	2188
	7.20	0.80	1618	2191
PEG 200	6.80	0.97	1021	1930
	7.00	0.90	1238	1933
	7.20	0.85	1432	1939

*In polymer free medium.

**Experimental error limits: ΔCMC = ±5%, ΔK_{ass} = ±5%, K_s = ±5%.

Table III.A(3b): The *p*H dependent association constant, K_{ass} and *p*H independent equilibrium constant, K_s of NR with TW60 in presence of 1.25% (v/v) (PEG 200, PEG 400, PEG 600) and 1.25% (w/v) PVA at 298 (±0.1)K.

Polymer	**pH**	**CAC**** /(10^{-5}mol dm^{-3})	**K_{ass}**** /(10^3dm^3 mol^{-1})	**K_s**** /(10^4dm^3 mol^{-1})
PVA	6.80	1.91*	786*	1486*
		1.58	2167	4097
	7.00	1.80*	955*	1491*
		1.46	2625	4100
	7.20	1.73*	1104*	1495*
		1.35	3031	4104
PEG 600	6.80	1.77	1192	2254
	7.00	1.68	1445	2257
	7.20	1.59	1667	2258
PEG 400	6.80	1.82	1012	1913
	7.00	1.74	1226	1915
	7.20	1.65	1417	1920
PEG 200	6.80	1.86	954	1804
	7.00	1.80	1157	1807
	7.20	1.72	1335	1809

*In polymer free medium.

**Experimental error limits: ΔCMC = ±5%, ΔK_{ass} = ±5%, K_s = ±5%.

Table III.A(3c): The *p*H dependent association constant, K_{ass} and *p*H independent equilibrium constant, K_s of NR with TW40 in presence of 1.25%(v/v) (PEG 200, PEG 400, PEG 600) and 1.25% (w/v) PVA at 298 (±0.1)K.

Polymer	pH	CAC** /(10^{-5}moldm^{-3})	K_{ass}** /(10^3dm^{3}mol^{-1})	K_s** /(10^4dm^{3}mol^{-1})
PVA	6.80	2.17*	702*	1327*
		1.67	2012	3822
	7.00	2.00*	850*	1328*
		1.53	2448	3824
	7.20	1.85*	981*	1329*
		1.36	2824	3826
PEG 600	6.80	1.88	1121	2121
	7.00	1.73	1359	2123
	7.20	1.62	1569	2125
PEG 400	6.80	1.96	1009	1908
	7.00	1.84	1223	1910
	7.20	1.72	1411	1911
PEG 200	6.80	2.08	956	1807
	7.00	1.94	1158	1809
	7.20	1.83	1336	1810

*In polymer free medium.

**Experimental error limits: ΔCMC = ±5%, ΔK_{ass} = ±5%, K_s = ±5%.

Table III.A(3d): The *p*H dependent association constant, K_{ass} and *p*H independent equilibrium constant, K_s of NR with TW40 in presence of 1.25% (v/v) (PEG 200, PEG 400, PEG 600) and 1.25% (w/v) PVA at 298 (±0.1)K.

Polymer	pH	CAC** /(10^{-5}moldm^{-3})	K_{ass}** /(10^3dm^{3}mol^{-1})	K_s** /(10^4dm^{3}mol^{-1})
PVA	6.80	4.32*	667*	1261*
		2.65	1910	3612
	7.00	4.14*	807*	1260*
		2.47	2313	3613
	7.20	3.91*	932*	1263*
		2.23	2666	3611
PEG 600	6.80	3.88	1063	2012
	7.00	3.69	1288	2012
	7.20	3.48	1487	2014
PEG 400	6.80	4.01	1002	1894
	7.00	3.84	1213	1895
	7.20	3. 62	1400	1897
PEG 200	6.80	4.20	921	1741
	7.00	3.97	1117	1745
	7.20	3.76	1286	1742

*In polymer free medium.

**Experimental error limits: ΔCMC = ±5%, ΔK_{ass} = ±5%, K_s = ±5%

From the above Tables **{Table III.A(3a-3d)}** it has been observed that the CMC as well as the CAC was found to decrease with increasing *p*H of the medium. This trend is just opposite to that reported with polymer-free anionic surfactants where the dyes used were some sulphonephthalein dyes.[12] The CMC of the polymer-free surfactants at a fixed *p*H decreased significantly in the following order: TW20 > TW40 > TW60> TW80 which is also in the reverse order to that observed with anionic surfactants and anionic dye systems.[12] These opposite trends can be attributed to a difference in the charge type of the surfactant and the dyes used which are affected in different ways by OH^- ions.

The values of the CACs were lower than the corresponding CMCs of the surfactants in polymer free medium which indicates facilitation of the aggregation of the surfactants by the nonionic polymers. Since, nonionic surfactants possess bulky head groups, the area of the (hydrophobic core)-water contact is limited and as a result association of these surfactants with polymer is insignificant.[24,25] But, the microenvironment of water located in the free space of the macromolecular coil has stronger interactions with the hydrocarbon core of the aggregates while it has weaker interactions with the head groups.[26] Thus, the surfactant aggregate below the CMC in the presence of the polymer as the free energy of formation of aggregate ($\Delta G^o = - RT\ln\chi_{cac}$) becomes more negative than that in the absence of polymer.[26]

It was also observed that the CAC of the surfactants in the presence of the polymers increased with changing the polymer in the order: PVA < PEG 600 < PEG 400 < PEG 200 which was in agreement with the earlier report of Saikia and Dutta[27] indicating weaker interaction of the surfactants with PEG than PVA and a decrease in surfactant-polymer aggregation with decreasing molecular weight.

The value of the K_{ass} increased slightly with increasing hydrocarbon chain length of the surfactants from TW20 to TW80, as can be seen in **Tables III.A(3a-3d)** indicating the presence of hydrophobic interactions between surfactants and the dye. This observed trend is just opposite of what was observed with the Tween surfactants and anionic sulphonephthalein dyes,[11] which can be attributed to difference in charge type of the surfactants and the dyes. The values of the *p*H-dependent equilibrium constants, K_{ass} have been found to be higher in the presence of the polymers, which is in agreement with previous report about similar systems.[27] The K_{ass} however increased with increasing *p*H of the polymer-surfactant systems unlike what was observed in the case of anionic surfactant and anionic dye reported (**Section III.A.1**). This opposite trend can also be attributed to

difference in the charge type of the surfactant and the dyes used which are affected in different ways by OH^- ions.

The association constant, K_{ass} of NR for the nonionic surfactant-polymer systems also increases with increasing molecular weight of the polymer which followed the same trend as was observed earlier (**Section III.A.1**). With increased molecular weight of the polymer, more polymer segments are available for binding and there should be greater adsorption of surfactant aggregates per polymer molecule onto it from water, and as a result, the dye should experience more hydrophobic force towards it and thus the association increases. However, in case of the short chain PEGs, more than one polymer molecule may interact with the surfactant aggregate and thus it may so happen that the PEGs are adsorbed at the surface of the surfactant micelle and the NR form of the dye occupies the inner core of the micelle with more hydrophobic forces.

The values of K_s, the *p*H independent equilibrium constant, calculated from Eq.III.A(26) are also included in **Tables III.A(3a-3d)**. The values of K_s are really insensitive to change in *p*H as observed in the previous cases which indicates the validity of the PE method to the present dye-surfactant-polymer systems.[11] The K_s were higher in the presence of the polymers than in their absence as was observed with K_{ass}. In the presence of the polymers, the K_s increased with an increase in the molecular weight of the polymer in the order: PEG 200 < PEG 400 < PEG 600 < PVA indicating that the association of the dye increases with increasing polymer surfactant interaction.

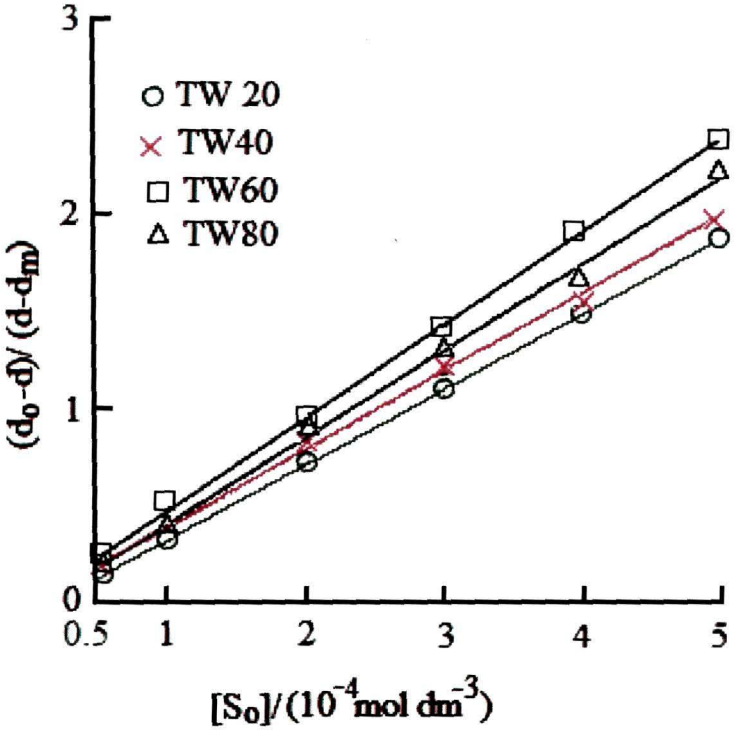


Fig. III.A.8: Plots of $\{(d_o-d) / (d-d_m)\}$ *vs.* surfactant concentration $[S_o]$ for NR-Tween systems in presence of PVA (w/v 1.25%) at *p*H 7.00 and 298 (±0.1) K.

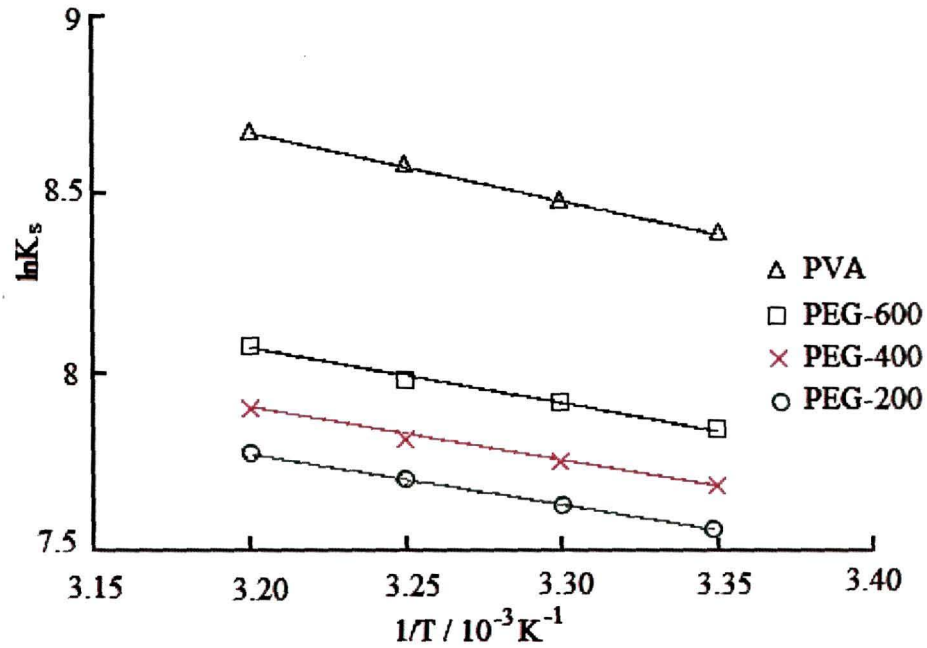


Fig. III.A.9: The van't-Hoff plots for the interaction of NR with TW80 in the presence of different nonionic polymers at *p*H 7.00.

The calculated standard thermodynamic parameters of the interaction of NR in the aqueous nonionic surfactant-polymer systems, *viz.*, ΔG^{o}, ΔH^{o} and ΔS^{o} are given in **Table III.A(4)**. The van't Hoff plots for the interaction of NR with TW80 in the presence of different nonionic polymers at *p*H 7.00 are shown in **Fig. III.A.9**. From the data in the table it is evident that the interactions are endothermic and the ΔH^{o} values are large for all the systems. The ΔH^{o} decreases with decreasing alkyl chain length of the surfactants as well as with decreasing molecular weight of the polymers. This indicates weaker interaction between the low molecular weight polymers with surfactants of lower hydrophobicity. The standard entropy changes, ΔS^{o} are positive and greater in the presence of the polymers and the ΔS^{o} also increased with an increase in the chain length of the surfactants and molecular weight of the polymers indicating a correlation of the strength of the interaction with hydrophobic interaction. The observed positive entropy changes may be due to a mixing and a more disordered water structure in the dye-surfactant-polymer system compared to the free dyes, polymer and micelles in solutions. Thus, the large negative free energy changes in the systems owe to the positive entropy changes in the system as in the case of PR described in the previous section (**Section III.A.2**).

The $pK_{a,app}$ values of NR in micellized systems of different nonionic surfactants in the presence of the polymers have been determined, which have been found to be lower than the $pK_{a,w}$ (6.75)[14] as shown in **Table III.A(5)**. This means that aqueous NR is a stronger acid in the surfactant-polymer systems than in the absence of them. The trend is just opposite of that observed with (–,2–) charge type sulfonephthalein dyes in the presence of nonionic surfactants,[11] as expected. The observed shift in pK_a can be attributed to the redistribution of the acid and base species between the aqueous and the micellar pseudophases. The $pK_{a,app}$ decreases with increase in alkyl chain length of the surfactants in the presence of PVA {**Table III.A(5)**}, which corresponds to the increase in the hydrophobic interaction between the dye and the surfactant indicating incorporation of more dye into the micelles with an increase in the surfactant hydrophobicity. In the presence of polymers, the value of $pK_{a,app}$ is lower than that in the absence of the polymer {**Table III.A(5)**} which indicates facilitation of the dye-surfactant interaction by the polymers. Thus, it has been seen that the overall acid dissociation of the dye increases with increase in the chain length or hydrophobicity of both the nonionic surfactant and the nonionic polymers.

Table III.A(4): The thermodynamic parameters of the interaction of NR with Tweens-PVA and Tweens-PEGs systems, at *p*H 7.00 (phosphate buffer).

Surfactant	Polymer	$-\Delta G^{o}$**/kJmol^{-1}	ΔH^{o}** /kJmol^{-1}	ΔS^{o}** /Jmol^{-1}K^{-1}
TW80	-	19.00*	10.46*	98*
	PVA	21.47	14.73	121.4
	PEG 600	20.21	12.60	107.3
	PEG 400	19.80	12.13	104.5
	PEG 200	19.46	11.31	102.1
TW60	-	18.79*	10.14*	95*
	PVA	21.31	12.08	109.57
	PEG 600	19.86	11.64	103
	PEG 400	19.44	10.97	99
	PEG 200	19.28	10.64	97
TW40	-	18.49*	9.53*	92*
	PVA	21.18	10.81	103
	PEG 600	19.69	10.37	98
	PEG 400	19.41	10.04	96
	PEG 200	19.26	9.74	94
TW20	-	18.33*	9.03*	89*
	PVA	21.05	10.24	102
	PEG 600	19.54	9.87	96
	PEG 400	19.38	9.56	94
	PEG 200	19.19	9.23	92

*In the absence of polymer.

** Experimental error limit: = ±5%.

Table III.A(5): The $pK_{a,app}$ values of NR in nonionic Tween surfactant- polymer systems at 298 (±0.1) K. [S] = $1x10^{-3}$ mol dm^{-3}.

Polymer	Surfactant (1x 10^{-3} mol dm^{-3})	$pK_{a,app}$ (±0.02)
		6.75#
PVA	TW80	6.27*
		6.01
	TW60	6.36*
		6.08
	TW40	6.38*
		6.11
	TW20	6.41*
		6.15
PEG 600	TW80	6.12
	TW60	6.143
	TW40	6.17
	TW20	6.182
PEG 400	TW80	6.14
	TW60	6.16
	TW40	6.175
	TW20	6.204
PEG 200	TW80	6.162
	TW60	6.187
	TW40	6.201
	TW20	6.234

$pK_{a,w}$, Ref.,[14] *in absence of polymer.

The distributions of the two forms of the dye between the bulk water and the micelles have been computed from the equilibrium constants by an iterative method using a FORTRAN program. The observed $pK_{a,app}$ values along with the ones predicted by the present method using FORTRAN and that by using Eq. III.A(24) of NR in solutions of various concentrations of TW20, TW40, TW60 and TW80 in the presence of 1.25% (w/v) of PVA at 298 (±0.1) K are shown in the **Fig. III.A.10**. The predicted $pK_{a,app}$ values have been found to be in very good agreement with the observed values as can be seen from the plots of $pK_{a,app}$ against the concentrations of the Tween ssurfactants in the **Fig. III.A.10**. This consolidates the assumption that in the case of nonionic micelles in the presence of the nonionic polymers, although a preferential incorporation of the electrically neutral form of NR to the micelles takes place, the association of the cationic conjugate acid form of the dye is also significant and cannot be neglected. Thus the agreement between the observed and the predicted $pK_{a,app}$ values indicates the validity of the PE method in the present nonionic surfactant-polymer systems and also that the dye behaves predictably in the systems.

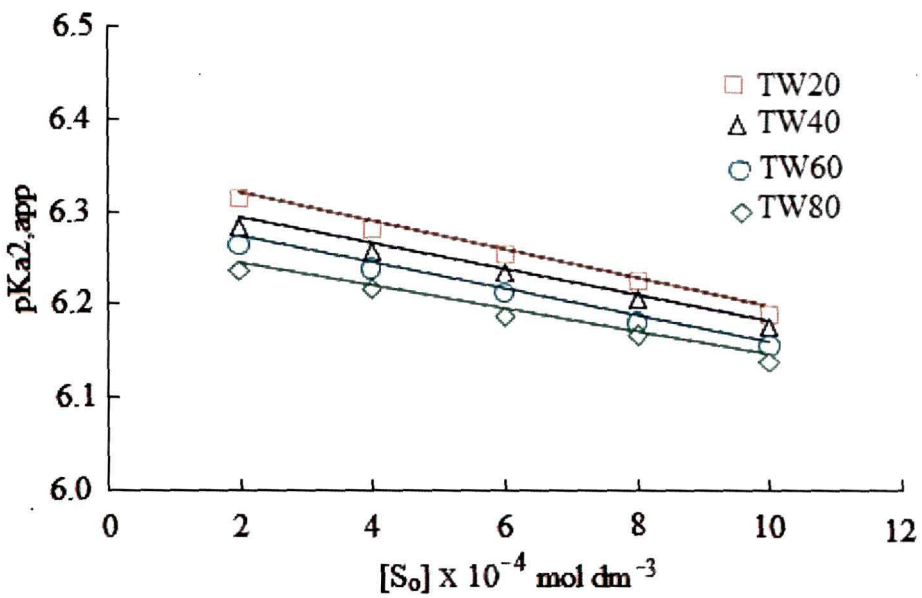


Fig. III.A.10: The $pK_{a,app}$ of NR in aqueous solutions of TW20, TW40, TW60 and TW80 in presence of PVA (1.25%) at pH 7.00 and 298 (±0.1) K. The solid lines are predicted by the present method. The symbols indicate experimental $pK_{a,app}$.

III.B: ***Monomer-dimer equlibrium of methylene blue in aqueous polymer-surfactant medium***

This section presents the results of the study of monomer-dimer equilibrium of methylene blue in aqueous nonionic polymer-anionic surfactant system.

In aqueous solution the two bands with λ_{max} at 612 and 664 nm can be attributed to the dimeric and monomeric forms of MB.[28-35] The monomer form of MB, has absorption bands in the visible region with λ_{max} at 660 nm, while that of the dimer form, *viz.*, MB_2 has absorption band at 660 nm.[28-35] It has been reported that changes in *p*H of the solutions have no detectable change in the spectra of MB.[34]

In submicellar anionic surfactant medium, *viz.*, in SDS the dye aggregates with SDS into insoluble salts.[30] However, cationic surfactants have no effect on the spectral change of MB.[35] In the intermediate range of SDS ([SDS] = 4x 10^{-3} mol dm^{-3}), the dissolution of the dye-surfactant aggregates occurred, which is a critical concentration of SDS, below the CMC of SDS homomicelle,[30] [SDS] = 8x 10^{-3} mol dm^{-3}.

III.B.1: ***Monomer-dimer equilibrium of methylene blue in polymer-anionic micellar medium***

a. Spectral behaviour

The spectral properties of MB have been summarized in **Table III.B(1)**. The absorption spectra of aqueous MB in absence and in the presence of SDS, PVA and SDS-PVA are shown in **Fig. III.B.1**. We have observed a small blue shift of the monomeric form in SDS and PVA-SDS system from 664 to 661 nm as shown in **Fig. III.B.1**.

The absorption spectra of MB (5x 10^{-5} mol dm^{-3}) in the presence of increasing concentration of SDS and PVA at 298K and *p*H 7.00 are shown in **Fig. III.B.2** and **Fig. III.B.3**. It has been observed that in case of SDS initially with increasing SDS concentration there is an increase in the absorption intensity at 612 nm at the cost of the absorption intensity at 661 nm. However as the concentration of SDS reaches 1x 10^{-2} mol dm^{-3} the absorption intensity at 661nm again increases and with higher concentration the spectrum becomes almost same as that of pure MB monomer as shown in **Fig. III.B.2**.

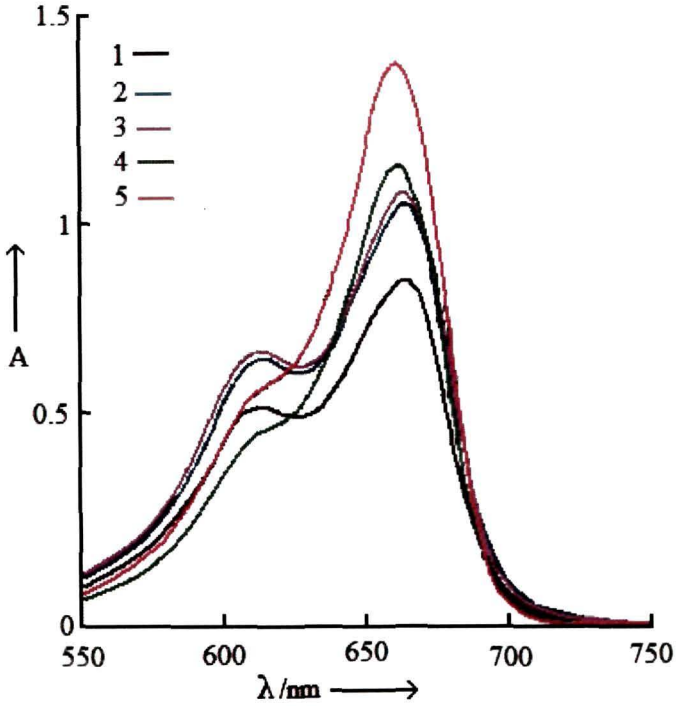


Fig. III.B.1: UV-visible absorption spectra of MB (5x 10^{-5} mol dm^{-3}) at *p*H 7.00 and 298 (±01) K: 1 (in water), 2 (in presence of 1.0 % PVA), 3{in presence of SDS (2.0x 10^{-3} mol dm^{-3} and PVA (1.0 %)}, 4{in presence of SDS (1x 10^{-1} mol dm^{-3})}and 5{ in presence of SDS (1.6x 10^{-2} mol dm^{-3})}.

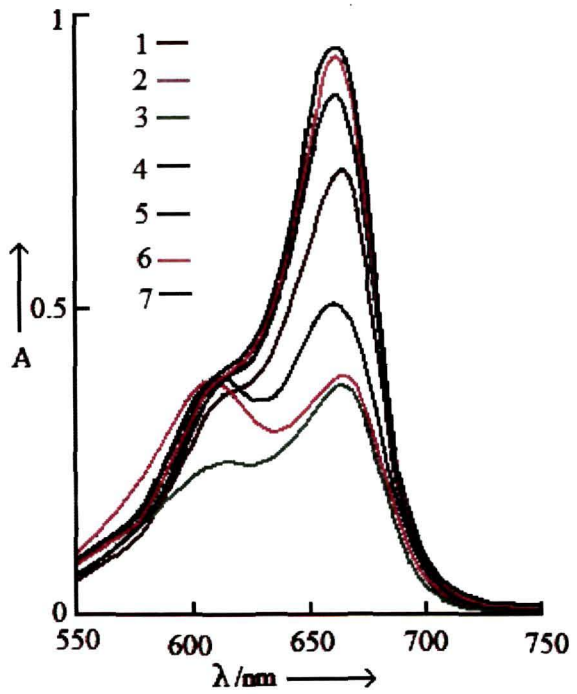


Fig. III.B.2: UV-visible absorption spectra of MB (5x 10^{-5} mol dm^{-3}) at *p*H 7.00 in presence of various concentration of SDS at 298 (±01) K: [SDS] / 10^{-3} mol dm^{-3} = 1(2.0), 2(4.0), 3(6.0), 4(8.0), 5(10.0), 6(12.0) and 7(14.0).

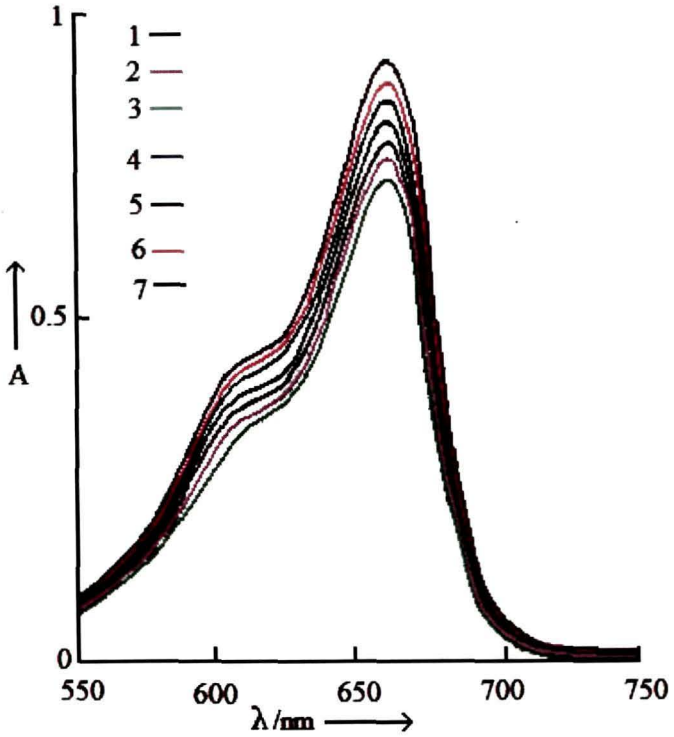


Fig. III.B.3: Spectra of MB (5x 10^{-5} M) at *p*H 7.00 in presence of various concentration of PVA (% w/v) at 298 (±0.1) K: [PVA] = 1(0.1%), 2(0.2%), 3(0.3%), 4(0.4%), 5(0.5%), 6(0.6%) and 7(0.7%).

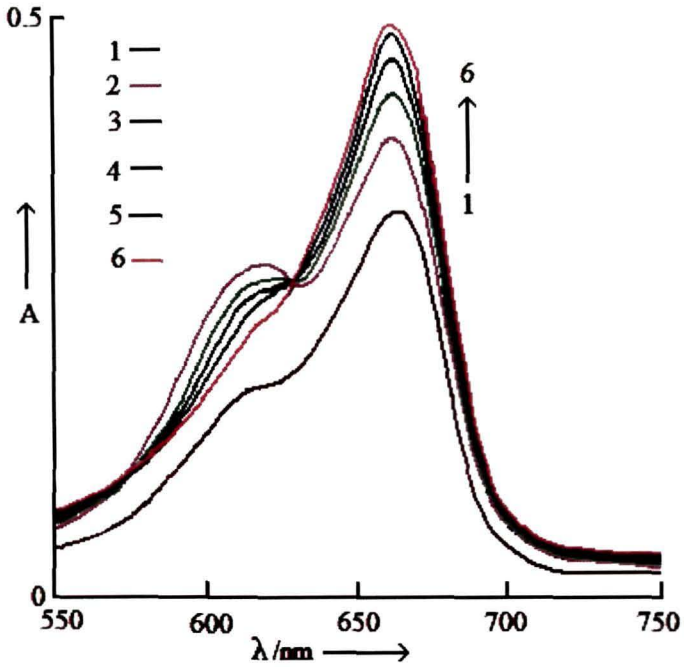


Fig. III.B.4: Spectra of MB (5x 10^{-5} mol dm^{-3}) at *p*H 7.00 in aqueous solution of varying concentration of SDS in presence of 5.0 % PVA (M.W. 14000) at 298(±01) K: [SDS] / 10^{-3}M = 1 (0.0), 2 (2.0), 3(4.0), 4(6.0), 5(8.8) and 6(12.0).

However, in case of PVA the absorption intensity at both 661 nm and 612 nm decreases initially with increasing concentration of PVA and when the PVA concentration reaches 0.4% the absorption intensity at both the wavelength increases as shown in **Fig.III.B.3**. This indicates specific hydrophobic interaction between the cationic dye and the nonionic polymer. Saikia *et al.* reported in an earlier study that there is stacking of the dye molecules both in monomeric and dimeric forms at low polymer concentration.[27] However when all the dye molecules are attached to the polymer chains, any further increase in polymer concentration only results in formation of transient network structures dislocating the stacked dye molecules which results in recovery of the absorption bands at both the wavelength.[27,36]

The spectra of MB in PVA-SDS system as a function of SDS concentration at 298K and *p*H 7.00 is shown in **Fig. III.B.4**. In the presence of PVA (5%) the absorption intensity of MB at 612 nm increases with the reduction in the absorption intensity at 661 nm indicating aggregation of the dye. With the addition of SDS the absorption intensity of MB at 661 nm initially decreases at the cost of the absorption intensity at 612 nm which is similar to the spectral feature of the dye in presence of SDS alone. However, when concentration of SDS exceeds 4.0x 10^{-3} mol dm^{-3} there is recovery in intensity and a small shift of the monomer band towards shorter wavelength. At very high concentration of SDS the 612 nm dimer absorbance band completely disappears. A clear isosbestic point was observed at 630 nm. The above spectral observations indicates that in surfactant free aqueous solution of nonionic polymer PVA, there is cooperative binding of the cationic MB dye leading to stacking of the dye on the polymer domain. On addition of anionic surfactant SDS there is competition for binding site on PVA between MB and SDS, where SDS exhibits stronger binding to PVA.[28,35] When surfactant concentration exceeds the critical aggregation concentration (CAC) and surfactant aggregates are formed, the dye dissolves in monomeric form in the hydrophobic SDS-PVA complexes.

b. Determination of effective dimerization constant ($^{eff}K_D$) and other thermodynamic parameters

In the experimental concentration range of MB it was assumed that only monomer-dimer equilibrium is possible, in accordance with the process,

$$2M \overset{K_D}{\rightleftharpoons} D \qquad \text{III.B(1)}$$

where, M and D are the monomer and the dimer species of MB respectively and K_D is the dimerization constant which can be defined as,

$$K_D = C_D / (C_M)^2 \qquad \text{III.B(2)}$$

where, C_D and C_M are the concentrations of the dimers and the monomers, respectively. The components concentration can be expressed by the following mass balance equation,

$$C_M + 2C_D = C_o \qquad \text{III.B(3)}$$

where, C_o is the analytical molar concentration of the dye.

or, $$x_i^M + x_i^D = 1 \qquad \text{III.B(4)}$$

where x_i^M and x_i^D are the respective mole fractions of the monomer and the dimer which can be defined as,

$$x_i^M = C_M / C_o \qquad \text{III.B(5)}$$

and

$$x_i^D = C_D / C_o \qquad \text{III.B(6)}$$

Using Eq.'s III.B(2), III.B(4), III.B(5) and III.B(6) we have,

$$K_D = x_i^D / 2C_o (x_i^M)^2 = (1 - x_i^M) / 2C_o (x_i^M)^2 \qquad \text{III.B(7)}$$

Further, considering the monomer-dimer process in SDS-PVA system we have for the 1.0 cm path length cuvette,

$$A = \varepsilon_M^f C_M^f + \varepsilon_M^b C_M^b + \varepsilon_D^f C_D^f + \varepsilon_D^b C_D^b \qquad \text{III.B(8)}$$

where ε_M^f, ε_M^b, ε_D^f and ε_D^b are the molar extinction coefficient and C_M^f, C_M^b, C_D^f and C_D^b are the concentrations of the respective free and bound monomer and dimer species of MB. If we assume that $\varepsilon_M^f = \varepsilon_M^b$ and $\varepsilon_D^f = \varepsilon_D^b$, then Eq. III.B(8) reduces to,

$$A = \varepsilon_M C_M + \varepsilon_D C_D \qquad \text{III.B(9)}$$

where, C_M and C_D are the total concentrations of the monomer and dimer species, respectively, i.e., $C_M = C_M^f + C_M^b$ and $C_D = C_D^f + C_D^b$ and ε_M and ε_D are the molar extinction coefficients of the monomer and dimer of MB at the monomer band maximum.

Regardless of the final location of the species (i.e., in water, micellar pseudophase or surfactant bound polymer surface), we can define the effective dimerization constant (${}^{eff}K_D$) from deviation value of absorbance from the absorbance value provided by Beer's-Lambert's law, ΔA as follows,

$${}^{eff}K_D = 2(\Delta A)(\Delta\varepsilon) / (2A - C_o\varepsilon_D)^2 \qquad \text{III.B(10)}$$

where, $\Delta A = (C_o\varepsilon_M - A)$ and $\Delta\varepsilon = (\varepsilon_M - \varepsilon_D/2)$.
Eq.III.B(10) can be transformed into the following linear equation,[36]

$$\frac{1}{\sqrt{\Delta A}} = (C_o / \Delta A)\, b - a \qquad \text{III.B(11)}$$

where, $a = (\sqrt{2\ {}^{eff}K_D}) / (\sqrt{\Delta\varepsilon})$ and $b = \sqrt{2\ {}^{eff}K_D\ \Delta\varepsilon}$. Therefore, $\Delta\varepsilon = b/a$ and ${}^{eff}K_D = (ab) / 2$. The ${}^{eff}K_D$ and the $\Delta\varepsilon$ values have been determined from the slope of the plot described by Eq. III.B(11).

For determination of ${}^{eff}K_D$ a series of solutions at progressively increasing concentration of the dye, C_o was prepared in water, in fixed concentration of SDS (3×10^{-3} mol dm^{-3}) and in fixed concentration of PVA (5.0%) for each set of experiment. The intensity of absorbance, A at 664 nm (monomer) was measured as a function of dye

concentration in water and for the other systems the 661 nm was considered. The molar extinction coefficient of the monomer (ε_M) was determined from the absorbance of the most dilute dye solutions (i.e., 1.35x 10^{-6} mol dm^{-3}) that were used. The molar extinction coefficient of the dimer (ε_D) was determined from the $\Delta\varepsilon$ values. The values of ε_M and ε_D determined by the present method {**Table III.B(1)**} are in good agreement with the reported values.[31, 33,37,38,40]. It may be noted that the present experiments were carried out in a well buffered medium of *p*H 7.00 (Perrin's table).[27] The value of $^{eff}K_D$ determined for the above experiments are also in good agreement of those reported by other methods as shown in **Table III.B(2)**.[31,33] We observed that the value of $^{eff}K_D$ of MB in water (3.88x 10^3 dm^3mol^{-1}) is about 10 times greater than its value in SDS micellar medium (3.61x 10^2 dm^3mol^{-1}) while its value is comparable to that observed in aqueous PVA-SDS system (2.25x 10^3 dm^3mol^{-1}). This indicates that there is decrease in hydrophobic interaction between the dye molecules in micellar medium compared with the hydrophobic interactions in water or in aqueous PVA-SDS system. In case of aqueous PVA-SDS system all the SDS micelles associates with the PVA chains and the excess polymer chain probably wraps around the micelles through transient bridge like structures as reported for similar systems.[8,27] As a result, the reduction of hydrophobic interactions between the MB molecules by micelles becomes less in the presence of PVA.

The increase in the dimerization at low concentrations of the surfactant was attributed by some researchers to a small volume of the micellar pseudophase under these conditions inducing higher local concentration of MB in the micelles enhancing dimer formation.[28,31,36] However, it can be noted that the increase in the dimerization has been observed when the SDS concentration is far below the CMC of the surfactant where micelle formation is unlikely. Moreover, reversal of the dye to the monomeric form at higher concentration of SDS indicates that the micelles rather favour the monomeric form.

Table III.B(1): Spectral properties of MB.

Species	In aqueous solution		In SDS micellar medium		In SDS-PVA medium	
	λ / nm	ε / 10^4 $dm^3mol^{-1}cm^{-1}$	λ / nm	ε / 10^4 dm^3mol^{-1} cm^{-1}	λ / nm	ε / 10^4 dm^3mol^{-1} cm^{-1}
Monomer(MB^+)	664	8.3	661	11.4	661	10.2
	665[a]	7.3[b]	665[e]			
		9.5[c]				
Dimer $(MB^+)_2$	612	12.8	612	15.6	612	14.8
	610[d]	13.2[c]	580[e]			

[a]Ref[37], [b]Ref[33], [c]Ref[38], [d]Ref[40], [e]Ref[31].

Table III.B(2): Effective dimerization constants of MB at 298 (±0.1) K.

Medium	Effective Dimerization Constant ($^{eff}K_D$ /10^3 dm^3mol^{-1})
In aqueous medium	3.88
	3.80[a]
	3.90[b]
In presence of SDS	0.361
	0.295[a]
In presence of PVA	0.213
In presence of SDS-PVA	2.25

[a]Ref[31], [b]Ref[33].

Gibbs free energy change for the monomer-dimer process of MB has been determined by using Eq. III.B(12),

$$\Delta G^o = -RT \ln {}^{eff}K_D \qquad \text{III.B(12)}$$

ΔH^o has been estimated from the slope of the approximating line according to the van't Hoff's relation,

$$\frac{d(\ln effK_D)}{d(\frac{1}{T})} = \frac{\Delta H^o}{R} \qquad \text{III.B(13)}$$

Some representative van't Hoff's plots are shown in **Fig. III.B.5**. The linearity of the plots indicates the validity of the present method. ΔS^o values were derived from ΔG^o and ΔH^o values.

$$\Delta S^o = -(\Delta G^o - \Delta H^o) / T \qquad \text{III.B(14)}$$

The values of the thermodynamic parameters are shown in **Table III.B(3)**. The relatively large negative ΔH^o values indicate that the monomer-dimer process of MB in aqueous medium in the systems studied is exothermic. The ΔH^o value is much lower in presence of surfactant or polymer as expected. The negative ΔS^o values indicate that the monomer-dimer process of MB is not driven by entropy as expected for more ordered dimer formation. Hydrophobic interactions probably help the system to get rid of the thermodynamically unfavorable state which is reflected in the large negative ΔH^o. The results are also in consistent with dispersive van der Waals interaction of aromatic dye chromophore during aggregation as observed in some earlier reports.[36,40,41] Such interactions are characterized by both negative enthalpy and negative entropy.[36,40,41] Hence, monomer-dimer process of MB in aqueous medium, in presence of surfactant or polymer or both has an enthalpic origin.

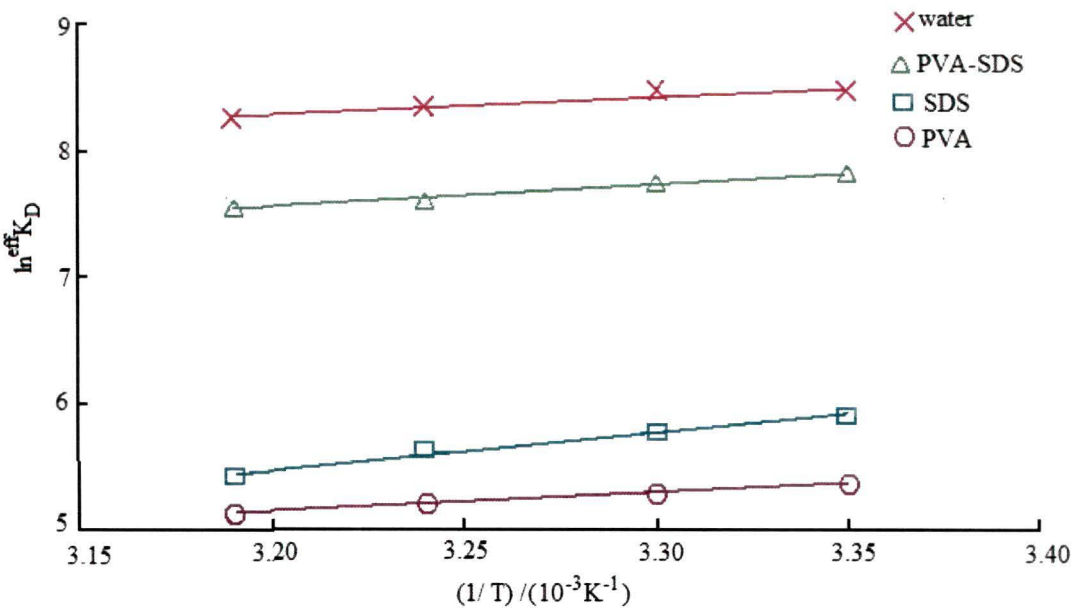


Fig. III.B.5: van't Hoff plot for monomer-dimer process of MB at *p*H 7.00 (phosphate buffer).

Table III.B(3): Thermodynamic parameters for monomer-dimer process of MB at 298 (±0.1) K.

	$-\Delta G^o$/ k J mol^{-1}	$-\Delta S^o$/ J mol^{-1} K^{-1}	$-\Delta H^o$/ kJ mol^{-1}
In aqueous medium	20.5	64.7	39.8
	20.0[a]	116[b]	59.1[b]
In presence of SDS	14.6	25.5	22.2
In presence of PVA	13.3	7.7	15.6
In presence of SDS-PVA	19.2	31.8	28.7

[a]Ref[33], [b]Ref[40].

III.C: ***Interaction of curcumin with surfactants and polymers in aqueous medium***

This section presents the experimental results of the study of the interactions of curcumin with both submicellar and micellar region of the surfactants in presence of a nonionic polymer. The results of the interactions of curcumin with a biopolymer chitosan in presence of surfactants have also been described in this section. For systematic organization, this section has been further divided into three sub-sections.

III.C.1: ***Interaction of curcumin with submicellar surfactants in absence and presence of polymers***

The results and their interpretation of the study of the interactions of curcumin with submicellar surfactants in absence and presence of polymers have been described in this sub-section.

Curcumin, bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione, is a bis-α,β-unsaturated *β*-diketone, commonly known as diferuloylmethane.[42] The enol form of curcumin dominates in aqueous solutions.[43] It is suggested that, in slightly acidic medium and possibly in cell membrane it may also exist in the keto form.[44] At *p*H < 1.00, the aqueous solution of curcumin has a red colour which indicates the protonated form (H_4Cur^+).[45,46] In the *p*H range 1.00-7.00, the majority of curcumin species have been reported to be exist in the neutral form (H_3Cur).[45,46] Water solubility is very low in this *p*H range and solutions are yellow.[45,46] At *p*H >7.50, the colour changes to red which indicates the deprotonated forms of curcumin, *viz.*, H_2Cur^-, $HCur^{2-}$ and Cur^{3-}, respectively, with increasing *p*H of the solutions (**Fig. III.C.1**).[45,46] It was reported that the enol form of curcumin has three ionizable protons, corresponding to the enolic group and two phenolic groups.[43] Thus, three acidity constants (pK_as) has been reported for curcumin both theoretically and experimentally.[43,44,46-50] The 1st deprotonation occurs at a *p*H range of 7.00-9.00, 2nd at the range of 9.00-11.00 and 3rd one occur at higher *p*H like 11.00-14.00.[43] From photochemical studies the lowest pK_a of curcumin has been reported as 8.55, which assigned to the dissociation of the enolic group.[45] However, some researchers have attributed the lowest pK_a for curcumin to the dissociation of phenolic proton.[47,49-51] Aqueous curcumin shows an absorption band at ~ 419 nm,[43] and a shoulder at 365 nm.[47,51] The absorption maximum at ~419 nm has been assigned to the π-π^* transitions in the enolic form in solution while the 365 nm shoulder is due to the nonplanar diketo form of curcumin.[43,51,52]

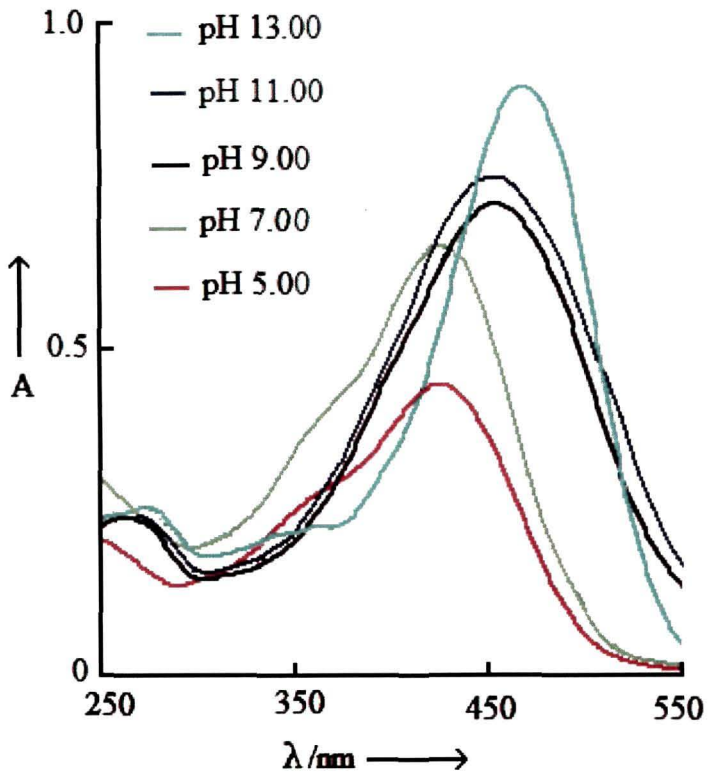


Fig. III.C.1: UV-Visible spectra of curcumin (2.5 x10^{-5} mol dm^{-3}) at various *p*H of the medium at 298 (±0.1) K.

Some information on the interactions of curcumin with both submicellar and micellar surfactants have been described in this division. At submicellar concentration of cationic surfactants, *viz.*, DTAB at *p*H 5.00 the DTAB/curcumin complex is reported to be formed through the electrostatic interaction between the cationic head group of DTAB and central β-diketonate group of curcumin.[53] While, at intermediate concentration of the surfactant ([DTAB] = 10-15 mM), the dye is reported to induce premicellar aggregates of DTAB which diminish the complex formation process.[53] All types of micelles can stabilize and solubilize curcumin predominantly in the enol form as reported in some earlier studies.[52-56] Curcumin decomposes in alkaline conditions but its encaptulation in cationic and nonionic micelles suppress the alkaline degradation.[56] However, anionic SDS micelle has been found to be ineffective in preventing the alkaline degradation of curcumin.[56]

III.C.1(i): ***Interaction of curcumin with submicellar cationic surfactants in absence and in presence of polymer***

The surfactant induced spectral behaviour of curcumin in submicellar cationic surfactants in absence and presence of a nonionic polymer and subsequent interactions of curcumin with such systems have been described in this division.

a. Spectral behaviour

We observed spectral changes in aqueous curcumin due to addition of CTAB and TTAB similar to that reported by Ke *et al.*[53] with DTAB at *p*H 5.00. As expected, the concentration of the surfactant required to effect the same change was smaller for higher homologues of the surfactants. **Fig. III.C.2** illustrates the effects of different concentrations of CTAB on the absorption spectra of buffered curcumin at *p*H 7.00 and at 298 (±0.1) K. The absorption spectrum of curcumin (2.5x 10^{-5} mol dm^{-3}) in the aqueous buffer has a broad absorption band at 425 nm with a shoulder peak at 355 nm which is similar to the absorption characteristics of curcumin reported earlier for aqueous buffers.[53,57-59] Successive additions of small concentrations of CTAB decrease the intensity of the absorption band at 425 nm corresponding to the enol form of curcumin[43,51,52] with simultaneous appearance of the new band at *ca.* 358 nm which corresponds to the keto form of curcumin.[43,51,52] The new band at 358 nm appears in the same manner at *p*H 5.00 and 2.00 of the solution. In presence of cationic surfactant molecules, the twisted diketonic form of curcumin[43] might be stabilised with the formation of dye-surfactant complex between CTAB and curcumin. The cationic head group of CTAB might interact with the negatively charged oxygen atoms of the diketone moiety and the conjugation of the aromatic system is vanished. As shown in **Fig. III.C.2**, with the addition of more surfactants the intensity of the ultraviolet region band increases with a shift in λ_{max} from 358 nm to 370 nm. The bathochromic shift can be attributed to the change in microenvironment from a less polar environment to a more polar environment around curcumin. The intensity of the new UV band reached a maximum at a CTAB concentration of 1.8x 10^{-4} M, and then rapidly disappeared with the reappearance of the original band as shown in **Fig. III.C.2**. Further increase in concentration of the surfactant resulted in an increase in the intensity of the original band, which can be attributed to the encapsulation of the keto-enol curcumin with the micellar core as reported in some earlier studies.[53,54,56,57]

In our experiments using CTAB, TTAB and DTAB surfactants at small concentrations, the appearance of the new UV band (~ 350 nm-370 nm) has been observed in the *p*H range from 2.00 to 7.00. The appearance of the new band in the UV region of the spectrum was observed only in acidic and neutral buffered medium but not without buffer or not in basic conditions with or without buffer. The position of the new band of curcumin is slightly shifted on changing the surfactant and its concentration but was not changed with change in the *p*H in the range of 2.00-7.00. The new submicellar absorption band appears at 352 nm in presence of 1x 10^{-4} mol dm^{-3} TTAB. A red shift of 352 nm to 365 nm is observed in going the TTAB concentration from 1x 10^{-4} M to 1.2x 10^{-3} mol dm^{-3} (**Fig. III.C.3**). In presence of DTAB, the new λ_{max} shifted from 350 nm to 355 nm in going the concentration of DTAB from 4x 10^{-4} mol dm^{-3} to 2.8x 10^{-3} mol dm^{-3} (**Fig. III.C.4**). The increased red shift of the new band have been observed in the order DTAB < TTAB < CTAB at a fixed concentration of curcumin and the same *p*H condition.

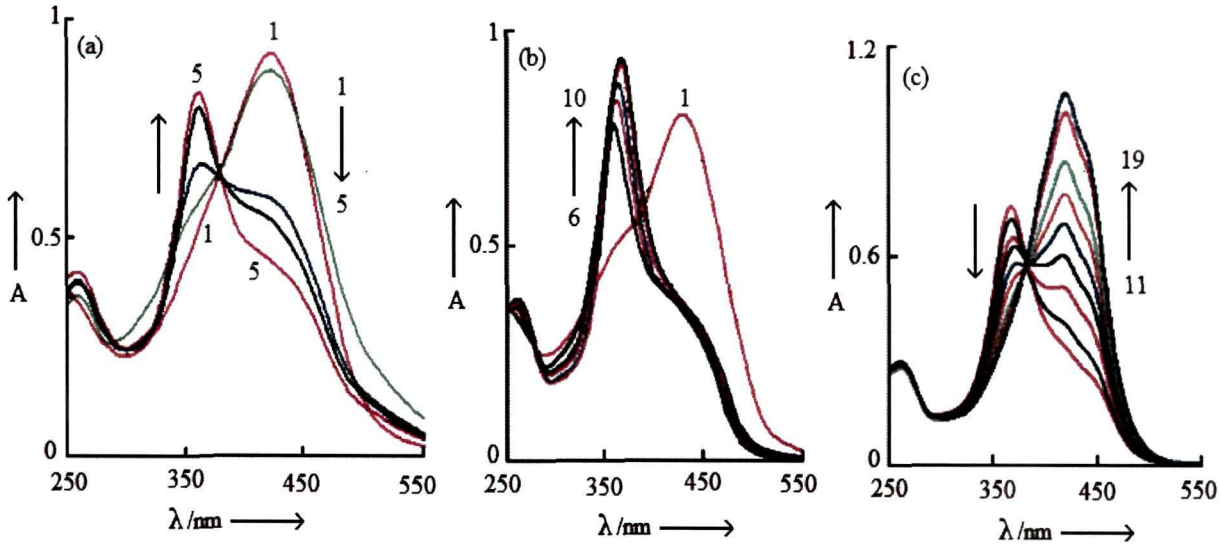


Fig. III.C.2: UV-visible spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in presence of various concentrations of CTAB at *p*H 7.00 and temperature 298(±0.1) K: [CTAB] / (10^{-5} mol dm^{-3}) = {**(a):** (1) 0.00, (2) 1.0, (3) 2.0, (4) 4.0 and (5) 6.0; **(b):** (6) 8.0, (7) 12.0, (8)14.0, (9)16.0 and (10) 18.0; **(c):** (11) 20.0, (12) 22.0, (13) 24.0, (14) 26.0, (15) 28.0, (16) 30.0, (17) 40.0, (18) 50.0 and (19) 60.0.

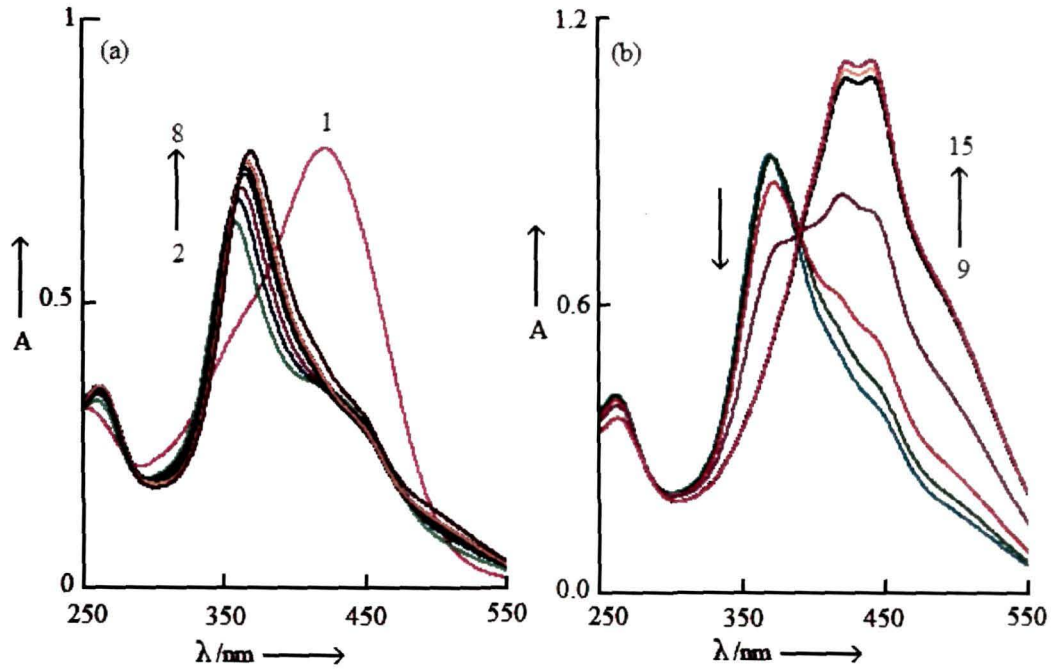


Fig. III.C.3: UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in presence of various concentrations of TTAB at *p*H 7.00 and temperature 298K (±0.1): [TTAB]/ (10^{-4} mol dm^{-3}){**(a):** (1) 0.0, (2)1.0, (3) 2.0, (4) 3.0, (6) 6.0, (7) 9.0 and (8) 12.0; **(b):** (9)15.0, (10)18.0, (11) 21.0, (12) 24.0, (13) 27.0, (14) 30.0 and (15) 40.0}.

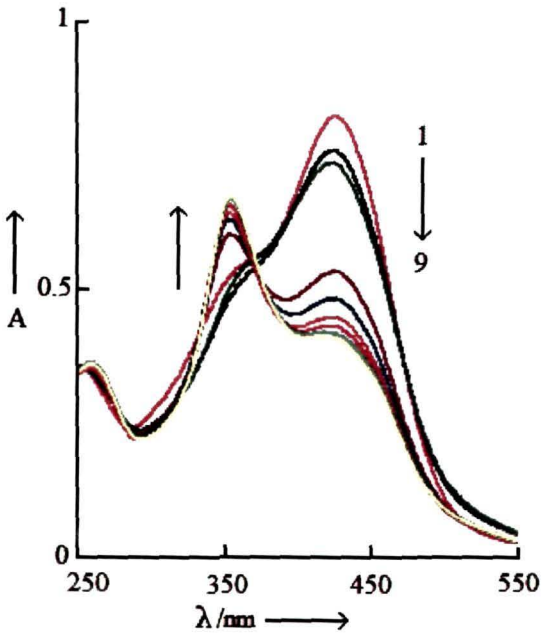


Fig. III.C.4: UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in presence of various concentrations of DTAB at *p*H 7.00 and temperature 298(±0.1) K: [DTAB]/ (10^{-4} mol dm^{-3}) = (1) 0.00, (2) 1.0, (3) 2.0, (4) 4.0, (5) 8.0, (6)12.0, (7)16.0, (8) 20.0 and (9) 24.0.

We have performed fluorescence spectroscopic measurements of curcumin in aqueous solution and in presence of the submicellar cationic surfactants. After excitation at 425 nm, an intense fluorescence-maximum at ~550 nm in aqueous buffered solution of curcumin have been observed similar to the ealier reports.[60,61] **Fig. III.C.5** depicted the influence of submicellar CTAB concentrations on the fluorescence spectra of curcumin at *p*H 7.00. Addition of increasing amounts of CTAB quenched the fluorescence of curcumin without significantly affecting the fluorescence maximum (~550 nm) as was reported earlier with DTAB.[53] In presence of submicellar CTAB, curcumin may experience a more polar environment through increased exposure to more hydrophilic region and hence the fluorescence quenching. The presence of bromide ion may partly affect the fluorescence intensity (FI) as reported for DTAB surfactant.[53] The FI decreases up to a concentration of CTAB at 1.8x 10^{-4} mol dm^{-3}. However, the FI of curcumin in presence of CTAB micelles are higher than that in aqueous solution.[56] Similar observations have been made for curcumin in TTAB and DTAB surfactants, where concentrations of the surfactants were insufficient to form micelle. The FI reached a minimum at 1x 10^{-4} M TTAB and then showed a significant increase in the case of TTAB. At *p*H 7.00, in presence of 2x 10^{-4} mol dm^{-3} DTAB solutions, the magnitude of the FI reached the minimum. Thus, the concentration of surfactant required to bring the FI to the minimum increased with decrease in the chain length of the surfactant. We have also observed, over the range of *p*H 2.00-7.00, that the FI of curcumin was not affected significantly with the change in *p*H in aqueous medium.

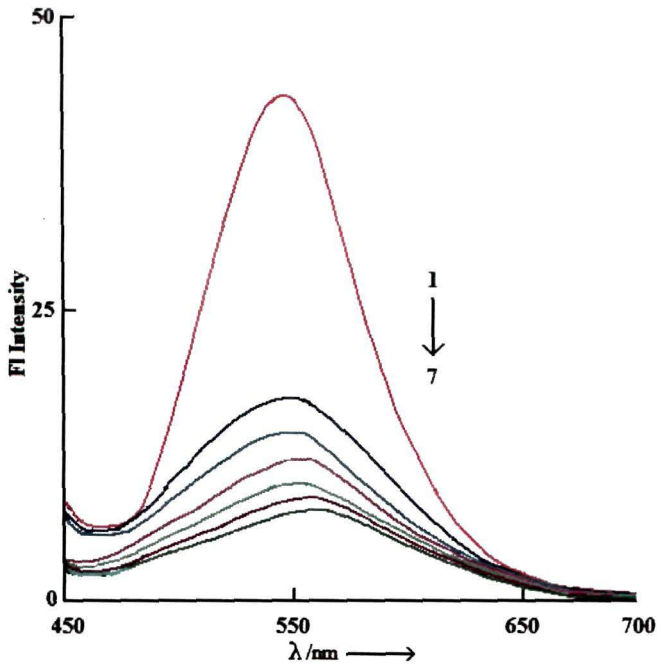


Fig. III.C.5: Fluorescence spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in presence of various concentrations of CTAB at *p*H 7.00 and temperature 298 (±0.1) K: [CTAB]/ (10^{-5} mol dm^{-3}) = (1) 0.00, (2) 2.0, (3) 4.0, (4) 8.0, (5) 10.0, (6)14.0 and (7)18.0.

The UV-visible absorption spectra of aqueous buffered curcumin (2.5x 10^{-5} mol dm^{-3}) at various concentrations of CTAB in the presence of fixed concentration of PVA (1%, w/v) at *p*H 7.00 and at a temperature of 298 (±0.1) K are shown in **Fig. III.C.6.** On addition of CTAB above 2.0x 10^{-5} mol dm^{-3}, the intensity of the 425 nm band corresponding to the enol form of curcumin increases. In this case, curcumin might strongly interacts with the nonionic polymer PVA as reported earlier.[61] It is interesting to note that in the presence of the polymer the shoulder at 355 nm gradually disappeared on addition of the surfactant. Which can be attributed as conversion of whatever diketo form was present in the system into the keto-enol form.

As shown in **Fig. III.C.7**, the FI of aqueous buffered curcumin in presence of the polymer increases with increasing concentration of CTAB in the submicellar concentration region. This may be attributed to formation of polymer-surfactant aggregates providing a nonpolar environment to the dye. In presence of the polymer, a blue shift of ~ 50 nm in the fluorescence maxima has been observed which also may be due to the hydrophobic environment of the polymer around the dye as observed for some earlier reports.[60,61]

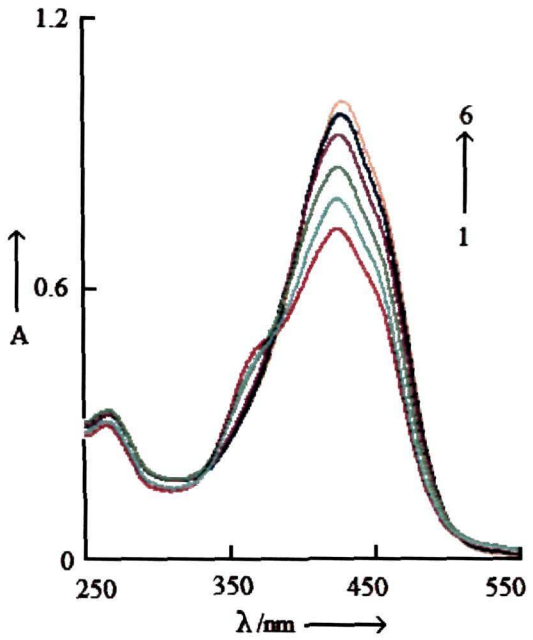


Fig. III.C.6: UV-visible absorption spectra of curcumin ($2.5x10^{-5}$ mol dm^{-3}) in various concentrations of CTAB in presence of 1% (w/v) PVA at *p*H 7.00 and temperature 298 (±0.1) K: [CTAB]/ (10^{-5} mol dm^{-3}) = (1) 0.00, (2) 2.0, (3) 4.0, (4) 6.0, (5) 9.0 and (6)12.0.

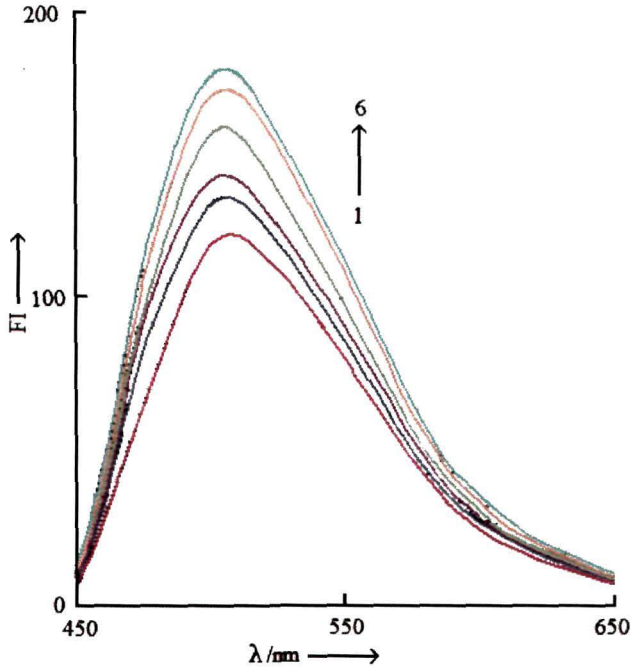


Fig. III.C.7: Fluorescence spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of CTAB in presence of 1% (w/v) PVA at *p*H 7.00 and temperature 298 (±0.1) K: [CTAB]/ (10^{-5} mol dm^{-3}) = (1) 0.00, (2) 2.0, (3) 4.0, (4) 6.0, (5) 9.0 and (6)12.0.

b. Determination of binding constants

An isosbestic point at 378 nm is observed for the curcumin-CTAB system in the concentration range of the surfactant between 2.0x 10^{-5} mol dm^{-3} and 1.8x 10^{-4} mol dm^{-3} indicates the formation of a complex between curcumin and the surfactant.[53] The values of the equilibrium constants of the complex formation have been determined by using a known method described below.[62,63] Assuming the complex to be a 1:1 complex we express the following equilibrium between the free curcumin and the proposed curcumin-surfactant complex,

$$S^+ + C^{\partial-} \underset{}{\overset{K_c}{\rightleftharpoons}} S^+C^{\partial-} \qquad \text{III.C(1)}$$

where, $[S^+]$ and $[C^{\partial-}]$ represent the concentrations of the surfactants and the dye respectively.

The equilibrium binding constant, K_c can be expressed as,

$$K_c = \frac{[S^+C^{\partial-}]}{[S^+][C^{\partial-}]} \qquad \text{III.C(2)}$$

taking $[S^+C^{\partial-}] = C_c$, $[C^{\partial-}] = C_d$, and $[S] = C_s$, Eq. III.C(8) can be written as,

$$K_c = \frac{C_c}{(C_d - C_c)(C_s - C_c)} \qquad \text{III.C(3)}$$

According to the Beer-Lambert law,

$$C_d = \frac{d_o}{\varepsilon_d \times l} \qquad \text{III.C(4)}$$

and

$$C_c = \frac{d_o - d}{\varepsilon_c \times l} \qquad \text{III.C(5)}$$

where, d and d_o are the absorbances of curcumin in the presence and absence of a surfactant, respectively, at λ_{max} of the dye, l is the light path of the cuvette (1 cm) and ε_d

and ε_c are molar extinction coefficients of a dye and its complex, respectively. Eq. III.C(6) can be derived from Eqs. III.C(4) and III.C(5),[62,63]

$$\frac{d_o}{d-d_o} = \frac{\varepsilon_d}{\varepsilon_c} + \frac{\varepsilon_d}{\varepsilon_c K_c}\left(\frac{1}{C_s}\right) \qquad \text{III.C(6)}$$

Therefore, plotting 1/ $(d\text{-}d_o)$ versus $1/C_s$ should result in a linear plot, and K_c can be obtained from the intercept to the slope ratio.

As shown in the **Table III.C(1)**, K_c decreased on changing the surfactant in the order CTAB > TTAB > DTAB indicating that the binding of the diketo form of curcumin with the surfactants increases with increasing chain length of the cationic surfactant in the experimental *p*H range. This indicates a strong interaction between the $CTA^+/DTA^+/TTA^+$ cationic head groups with the partially negatively charged oxygen atoms of the diketone form of curcumin which stabilised the twisted diketone form of curcumin. The quaternary ammonium ions can associate with the β-diketone form of curcumin through the electron-rich oxygen atoms. With a particular surfactant, the K_c increases with *p*H variation in the order of *p*H 2.00<7.00<5.00. This indicates roles of some more factors, in addition to hydrogen ion concentration, in the complex formation.

Table III.C(1): The association constant, K_c of curcumin with cationic surfactants at 298 (±0.1) K.

Surfactant	pH	*$K_c/(10^3\ mol^{-1}\ dm^3)$
	7.00	3.263
CTAB	5.00	3.465
	2.00	3.121
	7.00	2.825
TTAB	5.00	2.987
	2.00	2.678
	7.00	2.467
DTAB	5.00	2.588
	2.00	2.287

*Experimental error limit = ±5%.

III.C.1(ii): ***Interactions of curcumin with submicellar anionic surfactants in absence and presence of polymer***

The results and the analysis and interpretation of the study of interaction of curcumin with submicellar anionic surfactants in both absence and presence of a nonionic polymer have been depicted in this division.

a. Spectral behaviour

Fig. III.C.8 shows the variation in spectral properties of 2.5x 10^{-5} mol dm^{-3} of aqueous (~ 3.0% methanol) curcumin solution in presence of different concentrations of SDS at *p*H 7.00 (phosphate buffer) and 298 (±0.1) K. On addition of SDS the intensity of the 425 nm (~419 nm[43]) band of curcumin corresponding to the neutral enol form of curcumin decreases gradually with simultaneous appearance of a new band at *ca.* 5x 10^{-5} mol dm^{-3} SDS with λ_{max} at 355 nm band attributed to the β-diketo form of curcumin. Further addition of surfactant increases the intensity of the new UV-band with corresponding decrease of the 425 nm band with a slight bathochromic shift from 355 nm to 362 nm. The new band at 355 nm appears in the same manner at *p*H 5.00 and 2.00 also. The intensity of the UV band increased up to 2.0x 10^{-3} mol dm^{-3} of SDS and rapidly disappeared thereafter with reappearance of the original visible band at about [SDS] ≈7.2x 10^{-3} mol dm^{-3}.

In submicellar SDSN surfactant, the λ_{max} values of the submicellar band of the dye match those in presence of SDS at the same *p*H condition. Addition of small quantities of SDSN results the new band at 355 nm, accompanied by a reduction in the 425 nm band of curcumin (**Fig. III.C.9**). A slight red shift from 355 nm to 365 nm is observed in going SDSN concentration from 3.0x 10^{-4} mol dm^{-3} to 1.0x 10^{-3} mol dm^{-3}.

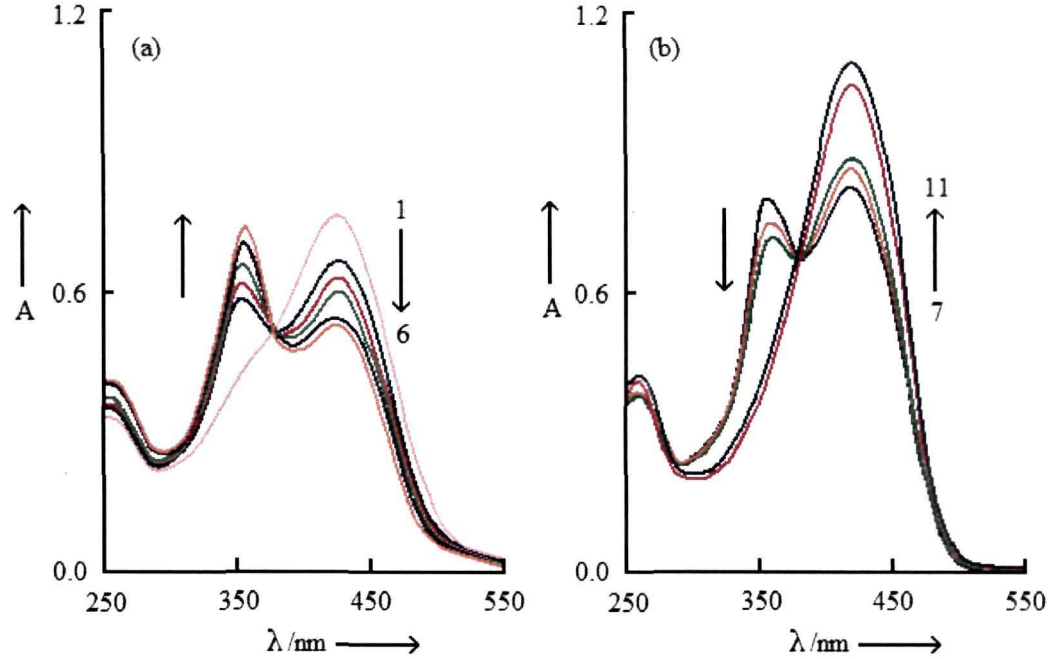


Fig. III.C.8: UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of SDS at *p*H 7.00 and temperature 298 (±0.1) K: [SDS] /10^{-4} mol dm^{-3} {**(a):** (1) 0.0 (2) 5.0 (3) 8.0 (4) 10.0 (5) 14.0 and (6) 18.0; **(b):** (7) 20.0 (8) 30.0 (9) 40.0 (10) 60.0 and (11) 80.0}.

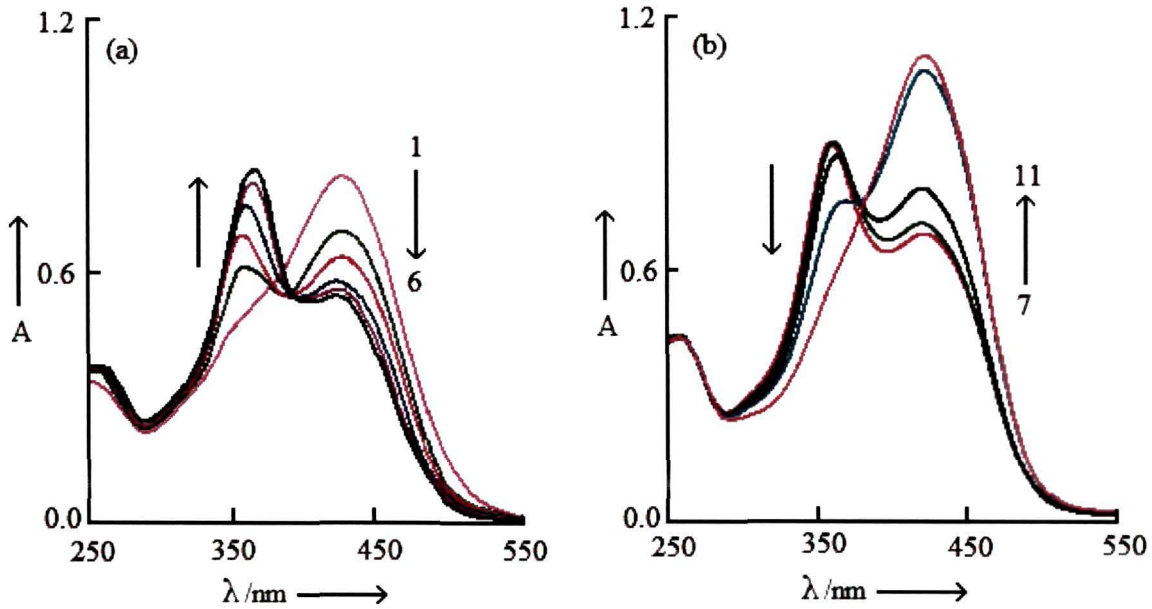


Fig. III.C.9: UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in presence of various concentrations of SDSN at *p*H 7.00 and temperature 298 (±0.1) K: [SDSN]/ (10^{-4} mol dm^{-3}) {**(a):** (0) 0.00, (1) 3.0, (2) 4.0, (3) 6.0, (4) 8.0 and (5) 10.0; **(b):** (6) 12.0, (7) 15.0, (8) 18.0, (9) 20.0 and (10) 30.0}.

Fig III.C.10 shows the absorption spectra of curcumin in buffered aqueous medium in presence of various concentrations of SDBS at *p*H 7.00. In presence of SDBS, the spectral variations of aqueous buffered curcumin were similar to those with SDS. The new submicellar absorption band appears at 360 nm in presence of 3.0x 10^{-4} mol dm^{-3} of SDBS. A red shift of 360 nm to 387 nm is observed on going from 3.0x 10^{-4} M of SDBS to 3.0x 10^{-3} mol dm^{-3} of SDBS. The visible band reappears at 416 nm at a concentration of the surfactant of 1.1x 10^{-3} mol dm^{-3}. The inclusion of a benzene ring on SDBS may lead to the π-π interaction between the surfactant monomer and the keto-enol tautomeric form of curcumin. Though the π-π interaction is not strong as hydrophobic and electrostatic interactions,[64] interaction of the aromatic π-bonds of SDBS with curcumin disturbs the hydrogen bond formation and as a consequence the diketo curcumin-surfactant complex no longer exists. As more and more surfactant is added to the aqueous curcumin solution the di-keto curcumin converts rapidly to the keto-enol form to retain its conjugation.

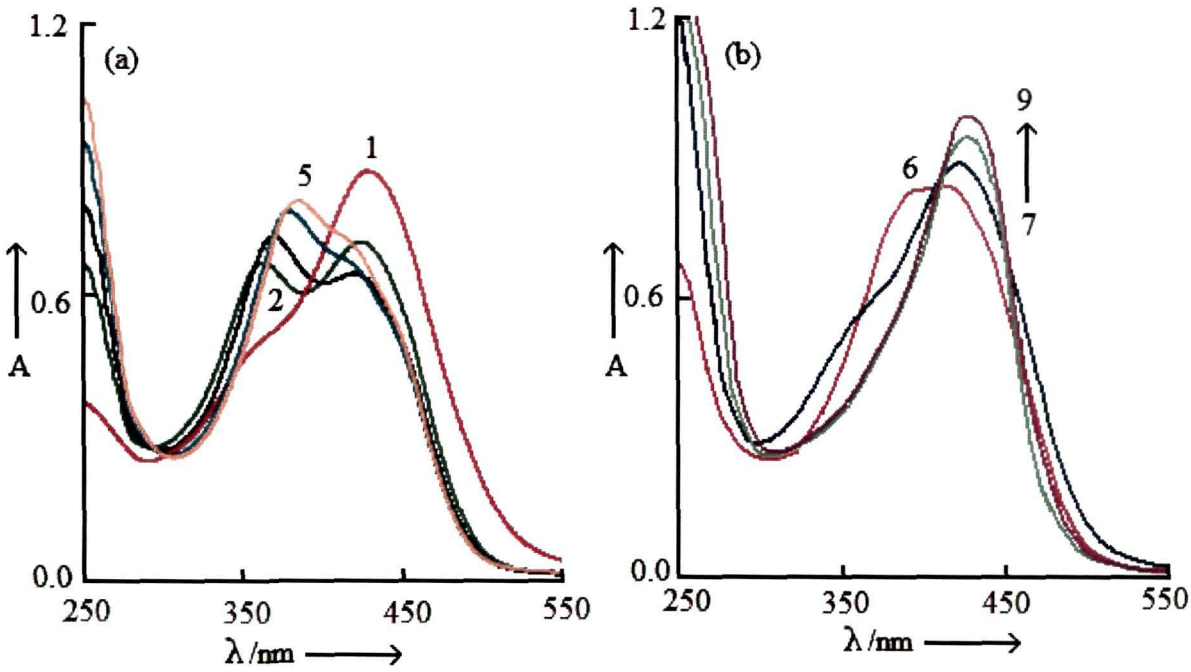


Fig. III.C.10: UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in presence of various concentrations of SDBS at pH 7.00 and temperature 298 (±0.1) K: [SDBS]/ (10^{-5} mol dm^{-3}) {**(a):** (0) 0.00, (1) 3, (2) 6, (3) 8 and (4) 10; **(b):** (5) 11.0, (6) 12.0, (7) 15.0 and (8) 20.0}.

The steady state fluorescence spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) at different concentrations of SDS at *p*H 7.00 and at a temperature of 298 (±0.1) K are shown in **Fig. III.C.11.** The FI of the band with λ_{max} of 550 nm of 2.5x10^{-5} mol dm^{-3} buffered curcumin decreased slightly as [SDS] increased above 2.5x 10^{-4} mol dm^{-3}, reached a minimum at 1.0 x10^{-3} mol dm^{-3} of SDS and then showed a marked increase above that concentration of the surfactant. While the marked increase in the intensity at higher concentrations of the surfactant can be attributed to curcumin solubilized in nonpolar environment of the micelle core.[53,55-57,60,65] The initial decrease in the intensity is indicative of a more polar environment of the dye due to binding with the surfactant head group. The increase in the FI above 2.0x 10^{-3} mol dm^{-3} of SDS coincided with the disappearance of the visible absorption band of the diketo form (**Fig. III.C.11**). Therefore, the observed curcumin-surfactant binding leading to the UV band must be through the β-diketo group breaking the conjugation of the dye. It is an unusual interaction between the anionic surfactant and the electron-rich diketo group of curcumin. Upon micellization, the complex breaks down and is solubilized in the nonpolar core of the micelle.

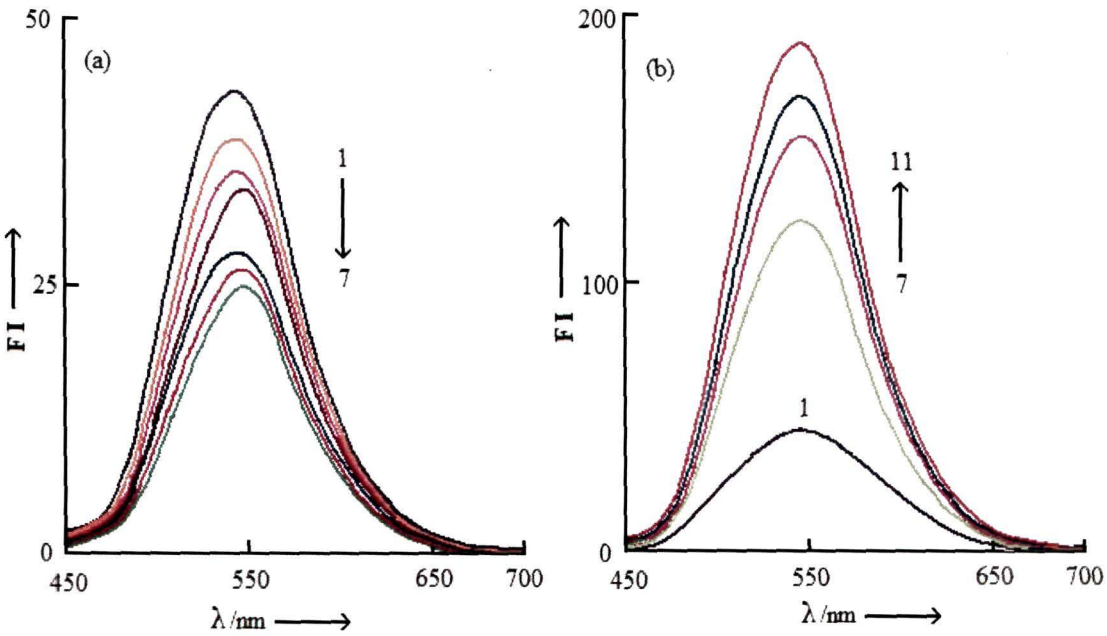


Fig. III.C.11: Fluorescence spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in presence of various concentrations of SDS at *p*H 7.00 and temperature 298 (±0.1) K: [SDS]/ (10^{-4} mol dm^{-3}) {**(a):** (1) 0.0 (2) 5.0 (3) 8.0 (4) 10.0 (5) 14.0 and (6) 18.0; **(b):** (7) 20.0 (8) 30.0 (9) 40.0 (10) 60.0 and (11) 80.0}.

The SDBS and SDSN induced changes in the fluorescence spectra of aqueous buffered 2.5x 10^{-5} mol dm^{-3} curcumin are comparable with that induced by SDS. The FI intensity of 550 nm of buffered curcumin decreased slightly as [SDSN] increased above 3.0x 10^{-4} mol dm^{-3}, reached a minimum at 1.0x 10^{-3} mol dm^{-3} of SDSN and then showed a distinct increase. Similarly, the FI of 550 nm band decreased with increasing concentration of SDBS reached minimum at 1.0x 10^{-3} mol dm^{-3} of SDBS and then increased with increasing concentration of SDBS.

The UV-visible absorption spectra of aqueous buffered curcumin (2.5x 10^{-5} mol dm^{-3}) at varying SDS concentrations in the presence of fixed concentration of PVA (1%, w/v) at *p*H 7.00 and at a temperature of 298 (±0.1) K are shown in **Fig. III.C.12.** On addition of SDS above 2.0x 10^{-4} mol dm^{-3}, the intensity of the 425 nm band corresponding to the enol form of curcumin increases. In this case curcumin may bind to the hydrophobic pockets of PVA as was reported in absence of surfactant.[61] With increasing concentration of SDS the curcumin solubility increases in the system and as a consequence the intensity of absorbance at the λ_{max} of 425 nm increases.

There was an increase in the FI of aqueous curcumin in the presence of the polymer with increase in the concentration of the surfactant, as shown in **Fig. III.C.13**, which indicates more nonpolar environment of the dye in presence of the micelles. An observed blue shift of ~ 50 nm in the fluorescence maxima in presence of the polymer may also be attributed to the hydrophobic microenvironment around curcumin.[60,61]

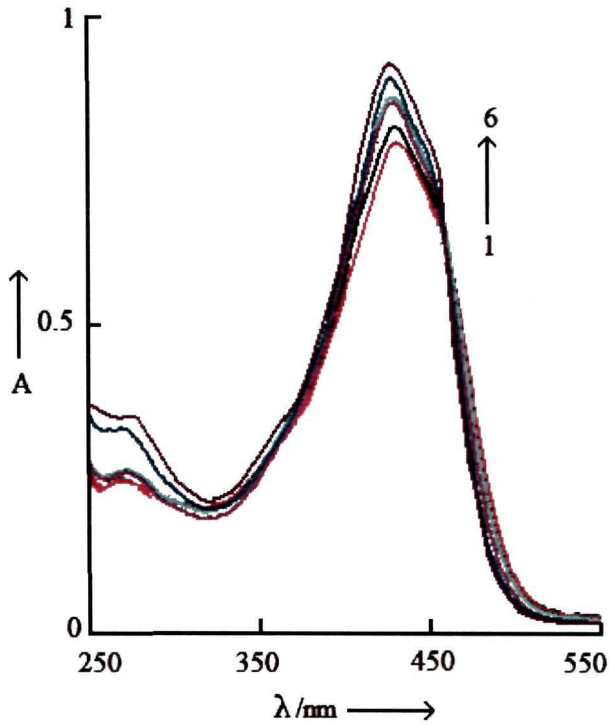


Fig. III.C.12: UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of SDS in presence of 1% (w/v) PVA at *p*H 7.00 and temperature 298(±0.1) K: [SDS] /10^{-4} mol dm^{-3} = (1) 0.0, (2) 5.0, (3) 8.0, (4) 12.0, (5) 16.0 and (6) 20.0.

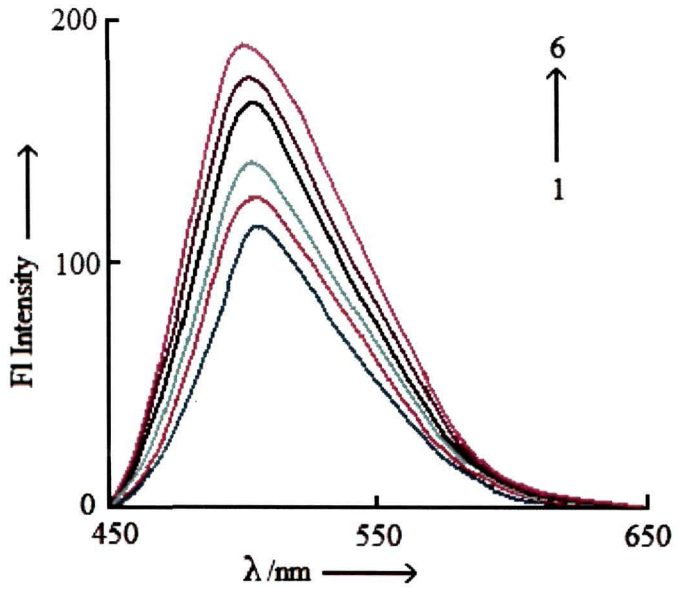


Fig. III.C.13: Fluorescence spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of SDS in presence of 1% (w/v) PVA at *p*H 7.00 and temperature 298(±0.1) K: [SDS] /10^{-4} mol dm^{-3} = (1) 0.0, (2) 5.0, (3) 8.0, (4) 12.0, (5) 16.0 and (6) 20.0.

b. Determination of binding constants

The spectra aqueous buffered curcumin recorded between 5.0×10^{-4} mol $dm^{-3}$and 2.0×10^{-3} mol dm^{-3} of SDS concentrations passed through a clear isosbestic point at 374 nm (**Fig. III.C.8**) indicating equilibrium between free curcumin and the curcumin bound to SDS.

$$[S] + [Cur] \overset{K_c}{\rightleftharpoons} [S \bullet Cur] \qquad \text{III.C(7)}$$

The equilibrium binding constant can be expressed as,[65,66]

$$K_c = \frac{[S \bullet Cur]}{[S][Cur]} \qquad \text{III.C(8)}$$

where, [S] and [Cur] represent the concentrations of the surfactants and the dye respectively. Assuming that, [S•Cur] = C_c, [Cur] = C_d, and [S] = C_s, as in the case of the cationic surfactant, we can determine the K_c using **Eq.III.C(6)**.

The binding constant (K_c) has been found to be 1.3×10^3 dm^3mol^{-1} with SDS at *p*H 7.00. The K_c decreased on changing the surfactant in the order SDS > SDBS > SDSN at *p*H 7.00 but the order was SDS > SDSN > SDBS at *p*H 5.00 and 2.00 {**TableIII.C(2)**}. With a particular surfactant, on varying the *p*H, the K_c increased in the order of *p*H: 2.00 <7.00 <5.00.

Table III.C(2): The association constant, K_c of curcumin with anionic surfactants at 298 (±0.1) K.

Surfactant	**pH**	***K_c/($10^3 dm^3$ mol^{-1})**
	7.00	1.328
SDS	5.00	1.477
	2.00	1.133
	7.00	1.194
SDBS	5.00	1.283
	2.00	1.027
	7.00	1.132
SDSN	5.00	1.341
	2.00	1.109

*Experimental error limit = ±5%

III.C.2: ***Interaction of curcumin with micellar surfactants in presence of PVA***

This subsection provides the results and the analysis of the study of the interactions of curcumin with surfactants of various types in absence and presence of a nonionic polymer, *viz.*, PVA.

a. Spectral behaviour in SDS-PVA system

As shown in **Fig. III.C.14** the intensity of the absorption band at 425 nm due to a stable enol form of curcumin[43] (2.5x 10^{-5} mol dm^{-3}) increases on increasing the concentration of SDS up to 12.0x 10^{-3} mol dm^{-3} at *p*H 7.00 which is accompanied by a red shift from 425 nm to 433 nm. Curcumin exhibits a absorption band in the SDS micelle similar to that observed for curcumin in water, which was reported to have strong interaction with the water molecules in the Stern layer of the micelle.[65]

Curcumin is reported to exhibit a very weak fluorescence band at ~ 550 nm in aqueous buffer solutions on excitation at 425 nm.[60,61] As shown in the **Fig. III.C.15** aqueous curcumin (2.5x 10^{-5} mol dm^{-3}) has been found to show a broad fluorescence spectrum peaked at 549 nm in the SDS micelle at *p*H 7.00 and 298 (±0.1) K. On addition of increasing concentration of SDS the FI considerably increases. The position of the emission maximum is identical to those of curcumin in water and pure methanol and thus was suggested that curcumin is located near the Stern layer of the SDS micelle.[65]

The changes in the UV-visible absorption spectra of 2.5x 10^{-5} mol dm^{-3} aqueous curcumin at various concentrations of SDS, in the presence of 1.0% (w/v) PVA at *p*H 7.00 and at 298 (±0.1) K are shown in **Fig. III.C.16.** On addition of SDS micelle to the aqueous curcumin solution, there is a significant increase in the intensity of the absorption band at 426 nm with the appearance of a small shoulder of absorption at 445 nm. The UV-visible absorption spectra of curcumin in the SDS micelle in presence of 1.0% (w/v) PVA is similar to that in nonionic TX-100 micelle as well as in aprotic solvents, *viz.*, chloroform and toluene, which indicates that the SDS-PVA environment is similar to hydrophobic environment.[60,65] Curcumin was reported to be strongly bound to the hydrophobic pockets of PVA.[61] In the present case, the SDS-PVA system also provides a hydrophobic environment to curcumin.

As shown in the in **Fig. III.C.17**, upon excitation at 425 nm, the FI of the aqueous buffered curcumin (2.5x 10^{-5} mol dm^{-3}) is greatly enhanced by SDS in presence of 1.0% (w/v) PVA. The emission peak is shifted from 550 nm to 502 nm. It has been well established that in a hydrophobic environment, the FI intensity of curcumin is found to

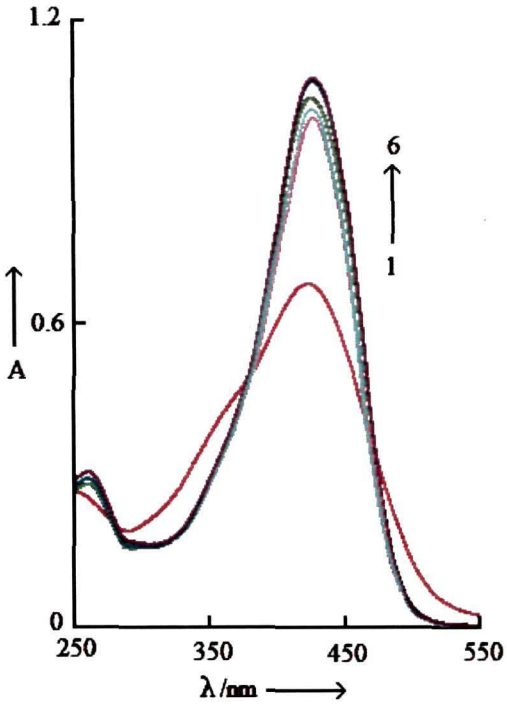


Fig. III.C.14: UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of SDS at *p*H 7.00 and temperature 298 (±0.1) K: [SDS] /10^{-3} $moldm^{-3}$ = (1) 0.0, (2) 5.0, (3) 8.0, (4) 10.0, (5)14.0 and (6) 18.0.

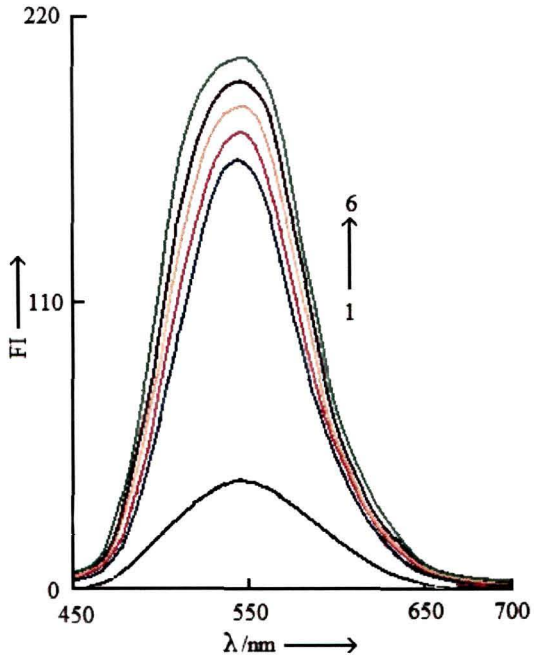


Fig. III.C.15: Fluorescence spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of SDS at *p*H 7.00 and temperature 298 (±0.1) K: [SDS] /10^{-3} mol dm^{-3} = (1) 0.0, (2) 5.0, (3) 8.0, (4) 10.0, (5)14.0 and (6) 18.0.

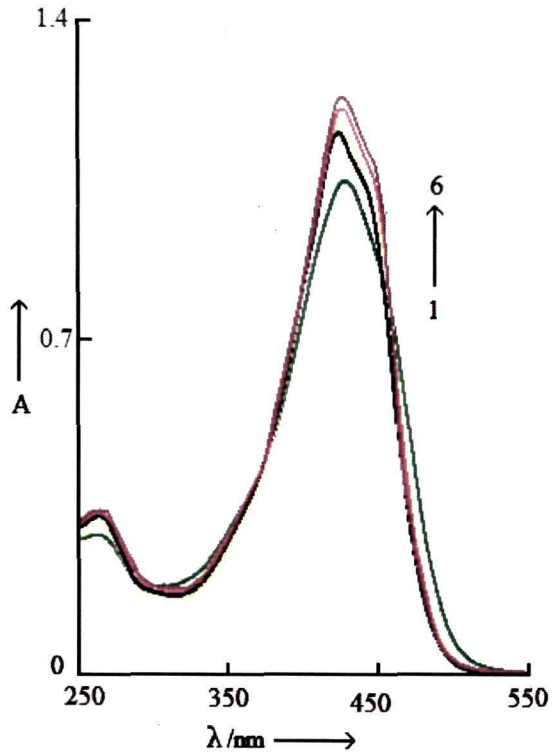


Fig. III.C.16: UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of SDS in presence of 1.0% (w/v) PVA at *p*H 7.00 and temperature 298 (±0.1) K: [SDS]/ 10^{-3} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)10.0 and (6) 12.0.

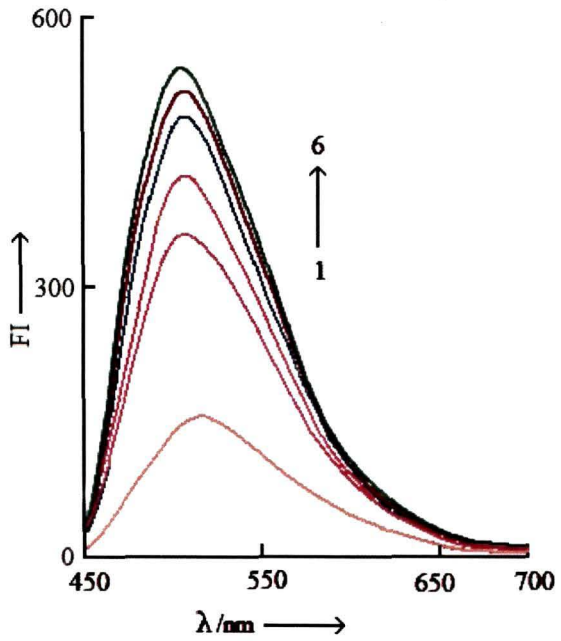


Fig. III.C.17: Fluorescence spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of SDS in presence of 1.0% (w/v) PVA at *p*H 7.00 and temperature 298 (±0.1) K: [SDS]/10^{-3} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)10.0 and (6) 12.0.

increase, with a blue shift in the fluorescence maximum.[60,61] From the fluorescence measurements it is clear that the SDS-PVA system provides a hydrophobic environment of lower polarity than polymer free SDS micelle to the aqueous curcumin. The SDS-PVA complex probably acts as a barrier between curcumin and water, thereby wrapping the curcumin molecules inside its hydrophobic core.

b. Spectral behaviour in CTAB-PVA system

Aqueous curcumin exhibits a broad and intense absorption peak at 421 nm in the presence of CTAB micelles with a shoulder of absorption at 443 nm (**Fig. III.C.18**).[55] The intensity of 421 nm band increases significantly with corresponding increase in the concentration of CTAB which can be attributed to binding of curcumin to the CTAB micelle. The CTAB micelles with lower polarity can promote the absorption of solubilized curcumin.[55] Curcumin is probably located in the palisade layer of the CTAB micelle.[65]

Fig. III.C.19 shows the fluorescence spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in *p*H 7.00 and at 298 (±0.1) K at various concentrations of CTAB. The FI of the aqueous curcumin markedly increases with increasing concentration of CTAB, owing to the non-polar like micellar environment of CTAB. The bromide ions present in the CTAB micelle is reported not to affect the FI significantly as they remain outside.[53] Thus, both absorption and fluorescence spectra showed that curcumin is located inside the CTAB micelle.

The UV-visible absorption spectra of 2.5x 10^{-5} mol dm^{-3} aqueous curcumin induced by CTAB in the presence of 1.0 % (w/v) PVA at *p*H 7.00 and 298 (± 0.1) K are shown in **Fig. III.C.20**. The intensity of the absorption band at 421 nm of aqueous curcumin increases with increase in the concentration of CTAB, which suggests strong interactions between curcumin, CTAB and PVA. The CTAB-PVA aggregates may solubilize the keto-enol curcumin.

As shown in **Fig. III.C.21** the FI at the fluorescence maxima of aqueous curcumin increases with increasing concentrations of CTAB in presence of 1.0% PVA at a *p*H of 7.00 and 298 (± 0.1) K. From the fluorescence characteristics it is clear that the CTAB-PVA system provides a hydrophobic environment to curcumin.

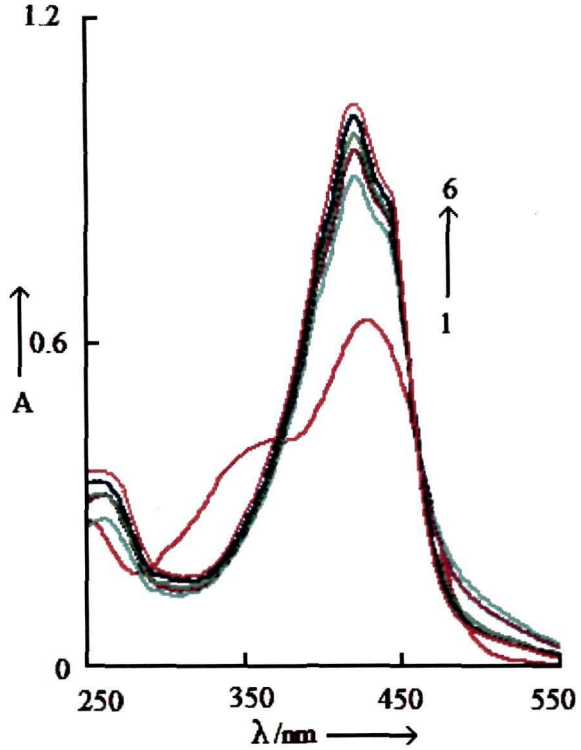


Fig. III.C.18: UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of CTAB at *p*H 7.00 and temperature 298 (±0.1) K: [CTAB]/ 10^{-4} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 16.0.

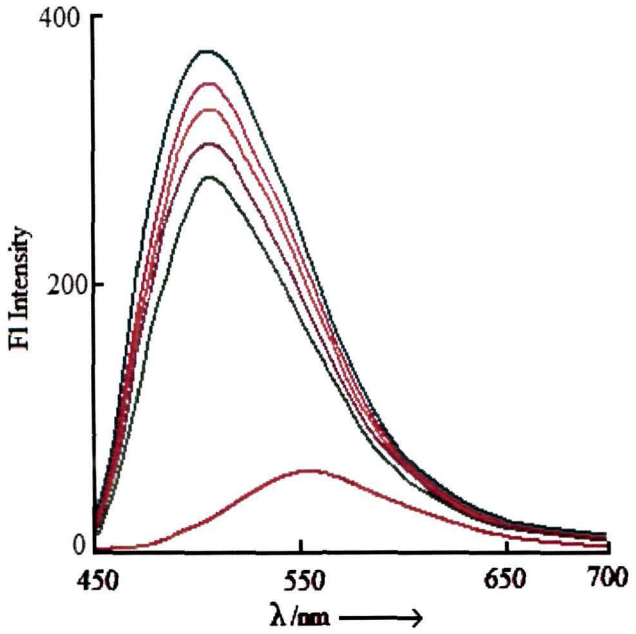


Fig. III.C.19: Fluorescence spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of CTAB at *p*H 7.00 and temperature 298 (±0.1) K: [CTAB] /10^{-4} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 16.0.

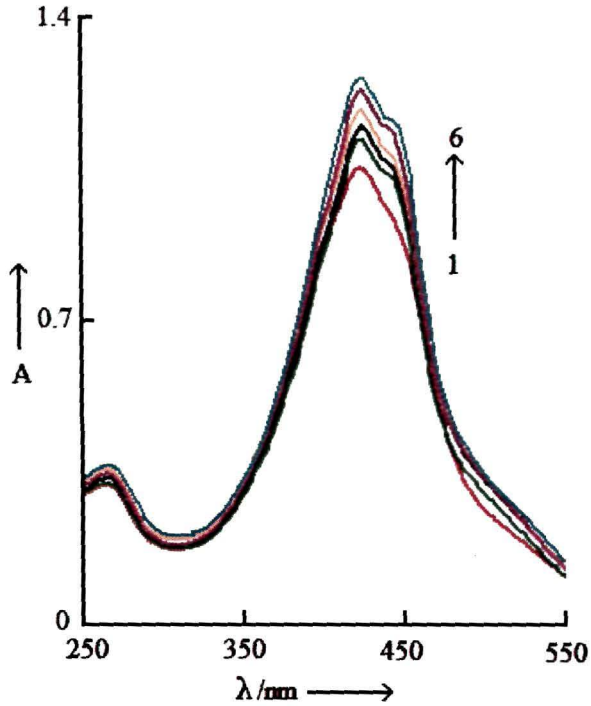


Fig. III.C.20: UV-visible spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of CTAB in presence of 1.0% (w/v) PVA at *p*H 7.00 and temperature 298 (±0.1) K: [CTAB] /10^{-4} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 16.0.

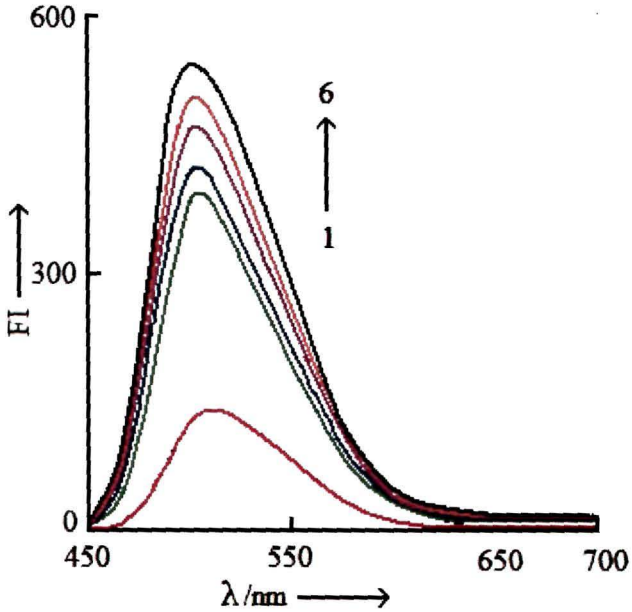


Fig. III.C.21: Fluorescence spectra of curcumin (2.5x10^{-5} mol dm^{-3}) in various concentrations of CTAB in presence of 1.0% (w/v) PVA at *p*H 7.00 and temperature 298 (±0.1) K: [CTAB]/ 10^{-4} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 16.0.

c. Spectral behaviour in TW80-PVA system

The absorption spectra of curcumin in TW80 micelle resemble those of curcumin in cationic CTAB micelle and also are very similar to that in polar protic solvents (**Fig. III.C.22**).[60,65] An enhancement in the absorption intensity of the absorption band at 425 nm band with a shoulder at 445 nm was observed on addition of increasing concentrations of TW80. The observed high absorbances near 250 nm are due to absorption by the surfactant. It was reported earlier that curcumin is located in the palisade layer of the non ionic TX-100 micelle.[65]

From the fluorescence spectra of curcumin in various concentration of TW80 it has been observed that FI of the aqueous curcumin increases markedly with increasing concentration of TW80 (**Fig. III.C.23**). It can be assumed that TW80 micelles being composed of high number of C-O groups may interact with curcumin through hydrogen bonding.[65] The intramolecular H-bond in curcumin may be perturbed to a greater extent through a stronger hydration of the TW80 micelle.[66]

The UV-visible absorption spectra of 2.5x 10^{-5} mol dm^{-3} aqueous curcumin induced by TW80 in the presence of 1.0 % (w/v) PVA at *p*H 7.00 and 298 (± 0.1) K are shown in **Fig. III.C.24**. With increasing concentrations of TW80 the intensity of the absorption band at 415 nm increases suggesting binding of the dye with the TW80-PVA aggregates.

The enhancement of FI of the fluorescence spectra of aqueous curcumin (2.5x 10^{-5} mol dm^{-3}) also suggests strong interactions between curcumin with the TW80-PVA aggregates (**Fig. III.C.25**).

d. Determination of binding constants

The association constant of curcumin with surfactant micelles can be represented as,[55]

$$[S_m] + [Cur] \overset{K_S}{\rightleftharpoons} [Cur_m] \qquad \text{III.C(9)}$$

The equilibrium constant K_s for the above equilibrium can be written as,

$$K_s = [Cur_m] / [Cur][S_m] \qquad \text{III.C(10)}$$

where, $[S_m]$ is the concentration of micellized surfactant, $[Cur_m]$ is the concentration of

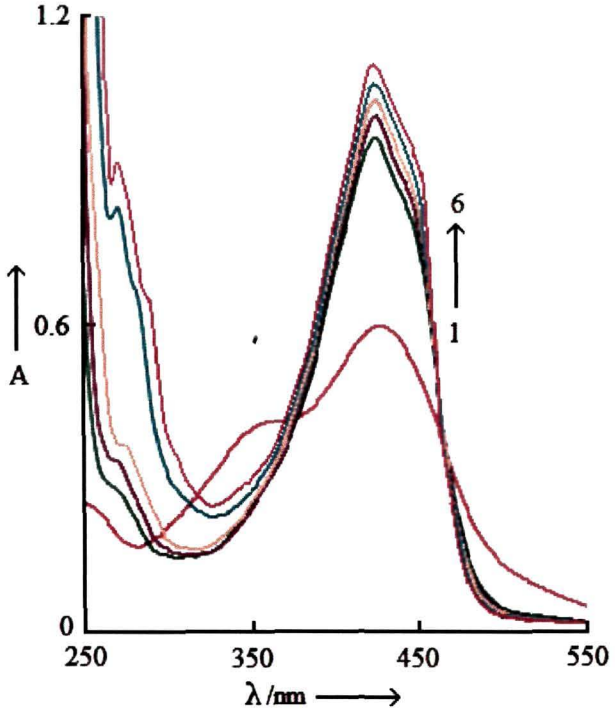


Fig. III.C.22: UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of TW80 at *p*H 7.00 and temperature 298 (±0.1) K: [TW80]/ 10^{-4} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 16.0.

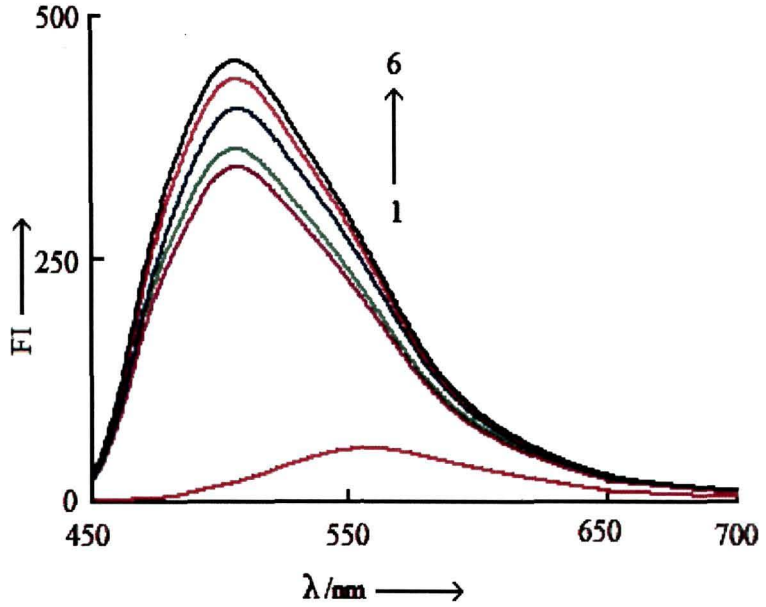


Fig. III.C.23: Fluorescence spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of TW80 at *p*H 7.00 and temperature 298 (±0.1) K: [TW80]/ 10^{-4} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 16.0.

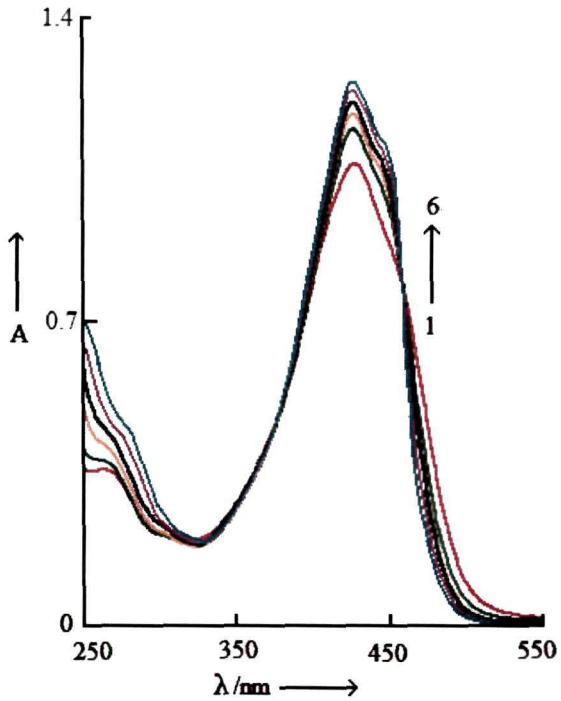


Fig. III.C.24: UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in various concentrations of TW80 in presence of 1% (w/v) PVA at *p*H 7.00 and temperature 298 (±0.1) K: [TW80] /10^{-4} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 16.0.

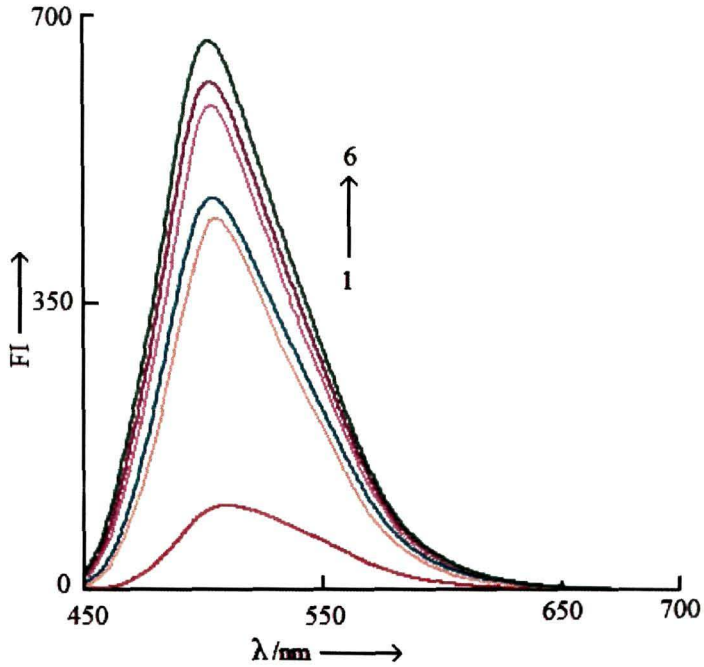


Fig. III.C.25: Fluorescence spectra of curcumin (2.5x 10^{-5} M) in various concentrations of TW80 in presence of 1% (w/v) PVA at *p*H 7.00 and temperature 298 (±0.1) K: [TW80] / 10^{-4} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 16.0.

curcumin in the micellar pseudophase. 'm' refers to micellar pseudophase. K_s is the equilibrium constant of association of curcumin with micelles or the curcumin-micelle binding constant. Linear plot can be made by following absorbance changes at a suitable wavelength as a function of reciprocal concentration of surfactants according to the Eq. III.C(11), the modified Benesi–Hildebrand equation given below,[67-69]

$$\frac{1}{\Delta A} = \frac{1}{K_s \Delta\varepsilon[cur_m]}\left(\frac{1}{[S_m]}\right) + \frac{1}{\Delta\varepsilon[cur_m]} \qquad \text{III.C(11)}$$

Here, ΔA and $\Delta\varepsilon$ correspond to the change in the absorbance and the molar extinction coefficient at the chosen wavelength and $[S_m]$ is the concentration of the micellized surfactant, ([S] – CMC).[70]

The binding constants have been estimated by following the fluorescence changes also. The FI of curcumin increases significantly in presence of micelles. The changes in FI at 425 nm due to curcumin were followed as a function of concentration of surfactant according to Eq. III.C(12) to estimate the binding constant, K_s,[71-73]

$$\frac{F_m - F_o}{F_t - F_o} = 1 + \left(\frac{1}{K_s[S_m]}\right) \qquad \text{III.C(12)}$$

here, F_m, F_o and F_t are the relative FIs of curcumin at a suitable wavelength in of 540-550 nm at micellised surfactant, in the absence of micelles and in the presence of intermediate concentration of surfactants, respectively. $[S_m]$ is the concentration of the micellized surfactant, ([S] – CMC).[70] In fluorescence method, the values of the binding constants, K_s are obtained from the plot of $(F_m - F_o)/(F_t - F_o)$ versus $[M]^{-1}$.

The partition of curcumin between aqueous phase and micellar pseudophase can be expressed as mole fraction from the relation,[55]

$$K_x = X_m / X_w, \qquad \text{III.C(13)}$$

where X_m and X_w are the mole fraction of curcumin in micellar and aqueous pseudophase. Expressing the mole fraction in conventional way, the equation becomes,[55]

$$K_x = 55.5K_s / (1 + K_s [Cur]) \quad \text{III.C(14)}$$

Since, $K_s[Cur] << 1$, we have,

$$K_x \doteq 55.5K_s. \quad \text{III.C(15)}$$

From the results obtained {**Table III.C(3)**} it has been observed that binding constant, K_s of curcumin-micelle binding increases in the order: SDS < CTAB < TW80. The binding constant, K_s of curcumin-surfactant-polymer binding has also been found in the order: SDS-PVA< CTAB-PVA < TW80-PVA. The observed large value of partition coefficient, K_x again indicates that the most of the curcumin molecules is partitioned to the polymer bound nonionic micelles. The binding in curcumin-surfactant-polymer systems were stronger than that in curcumin-surfactant systems.

Table III.C(3): The binding constant, K_s, partition coefficient, K_x of curcumin in surfactant-polymer systems at *p*H 7.00 and 298 (±0.1) K.

Surfactant	**Polymer**	**K_s* (absorption method) dm^3mol^{-1}**	**K_s* {fluorescence method) dm^3mol^{-1}**	**K_x* (absorption method) dm^3mol^{-1}**	**K_x* (fluorescence method) dm^3mol^{-1}**
SDS	-	2.41×10^2	2.46×10^2	1.32×10^4	1.35×10^4
SDS	PVA	3.18×10^4	3.22×10^4	17.50×10^5	17.71×10^5
CTAB	-	1.42×10^3	1.47×10^3	7.81×10^4	8.08×10^4
CTAB	PVA	2.67×10^4	2.73×10^4	14.6×10^5	1.51×10^5
TW80	-	4.62×10^3	4.65×10^3	2.54×10^5	2.56×10^5
TW80	PVA	5.28×10^4	5.31×10^4	28.80×10^5	29.21×10^5

*Experimental error limit = ±5%.

III.C.3: ***Interaction of curcumin with chitosan in presence of surfactants***

This subsection provides the results and their interpretation of the study of the interactions of curcumin with the biopolymer chitosan in absence and presence of a cationic and a nonionic surfactant. The anionic surfactants were excluded from the study because chitosan solution becomes turbid in presence of anionic surfactant. A physiological *p*H of 7.40 was chosen for the study due to the relevance of curcumin activities in physiological conditions.

a. Spectral behaviour

The absorption intensity of the 425 nm band of aqueous buffered curcumin (2.5x 10^{-5} mol dm^{-3}) increases with increase in the chitosan concentrations at the fixed *p*H of 7.40 (**Fig. III.C.26**). Although the spectra of curcumin bound to chitosan are similar to that in absence of chitosan in aqueous buffer medium,[53,57-59] the intensity of the 425 nm band increases significantly on addition of chitosan which indicates that curcumin interacts with the biopolymer. However, the nature of the chitosan induced absorption spectra of curcumin indicates that chitosan provides an environment similar to that of the 1:4 methanol-water system.[60] In solution of higher *p*H (*p*H > 6.50), the free amino groups of chitosan molecules become less protonated and the hydrophobic character along the chitosan chain becomes stronger.[74] Therefore, the chitosan self-aggregates may be formed in phosphate buffer solutions by intra and inter-molecular hydrophobic interactions.[74] The agglomerates of chitosan that are formed may entrap the neutral keto-enol curcumin. Moreover, there may be intermolecular hydrogen bond formation between curcumin and the hydroxyl groups of the glucosamine unit of chitosan. The hydrogen bond interaction has also been pictured out between curcumin and phosphatidylcholine in addition to the hydrophobic interaction.[75] Within this concentration range of chitosan the λ_{max} of curcumin slightly shifts from 425 nm to 422 nm. Unlike other macromolecules[61,76-78] chitosan neither generates any slightly red shifted spectrum of curcumin or nor it experiences any chemical denaturation due to curcumin. Indeed, the spectrum of curcumin induced by chitosan is slightly blue shifted.

In general, a blue shifted absorption spectrum is obtained for the keto form in nonpolar medium, as keto form is less polar than the cis-enol form.[79] In the present case, the slight blue shifted absorption band is for the π-π^* transition in the enolic form in

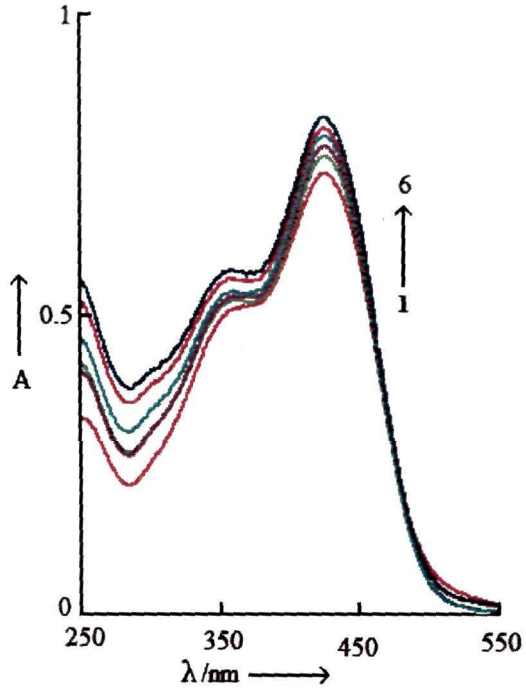


Fig. III.C.26: UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in presence of various concentrations of chitosan at *p*H 7.40 and 298 (±0.1) K: [chitosan] / 10^{-6} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 14.0.

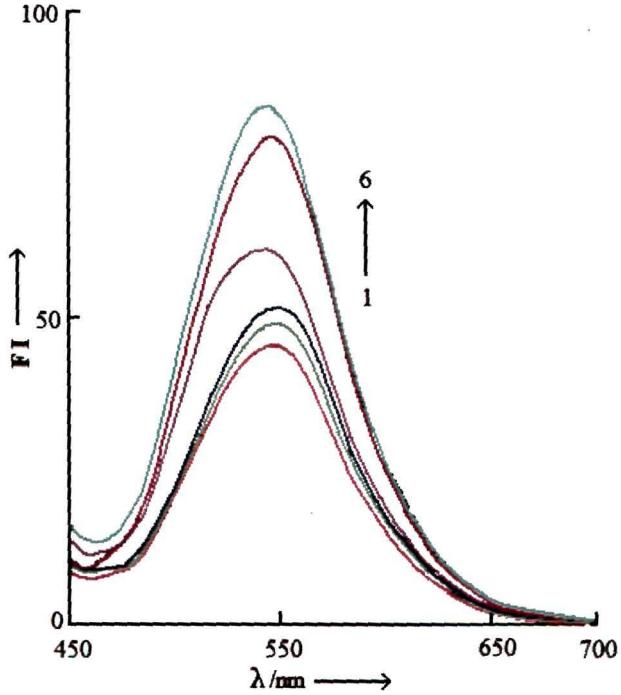


Fig. III.C.27: Fluorescence spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) in presence of various concentrations of chitosan at *p*H 7.40 and 298 (±0.1) K: [chitosan] / 10^{-6} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 14.0.

aqueous chitosan medium.[43] However, it can be seen from the spectra that the intensity of both the maximum absorption peak and the shoulder peak increases simultaneously with increasing concentration of chitosan. Thus, both the diketo form and the cis-enol form of curcumin effectively bind to chitosan.

The changes in fluorescence behaviour of curcumin has been attributed to the solute-solvent interactions, intramolecular charge transfer character, intermolecular hydrogen bonding with polar solvents, and π-π interaction with molecules possessing aromatic moiety.[80] The fluorescence spectra of curcumin have been reported to be independent of the excitation wavelength from 300-470 nm.[81] Curcumin exhibits a very weak fluorescence band at ~ 550 nm in aqueous buffer solutions after excitation at 425 nm.[60] It has been reported that in hydrophobic macromolecular environment, the FI significantly increases with a Stokes shift of about ~ 80 nm.[61] However, on the addition of increasing amount of chitosan at a fixed concentration of curcumin (2.5x 10^{-5} mol dm^{-3}), the fluorescence spectrum becomes sharp and FI considerably increases with a slight hypsochromic shift from 550 nm to 539 nm due to binding of curcumin with chitosan (**Fig. III.C.27**). The hydrophobic regions are available within chitosan molecule in aqueous solution into which a fraction of curcumin partitions and fluoresces considerably. The number of hydrophobic regions per unit volume increases as more chitosan is added to the solutions and protects curcumin from the fluorescence quenching in aqueous surroundings. As a consequence, when the concentration of chitosan increases in the bulk solution the FI of chitosan bound curcumin increases spectacularly. The slight spectral shift in the λ_{em} has been observed upon the complexation of curcumin with chitosan as the microenvironment of curcumin was changed. The dye is supposed to reside in the slightly nonpolar region of the polymer where the polarity and so the dielectric constant of the microenvironment are much lower than that in bulk water.

The changes in the UV-visible absorption spectra of 2.5x 10^{-5} mol dm^{-3} curcumin at various concentrations of chitosan at *p*H 7.40, varying concentration of chitosan from 2.0x 10^{-6} mol dm^{-3} to 14x 10^{-6} mol dm^{-3} in a fixed concentration of 1.5x 10^{-3} mol $dm^{-3}$of CTAB and at 298 (±0.1) K are shown in **Fig. III.C.28**. The absorption maximum slightly shifted from 425 nm to 420 nm in the presence of CTAB micelles due to microenvironment effect. On increasing the concentration of chitosan above 2.0x 10^{-6} mol dm^{-3}, the absorbances of the 365 nm shoulder completely disappeared and the absorbances of the 420 nm band increased considerably suggesting significant binding of the hydrogen

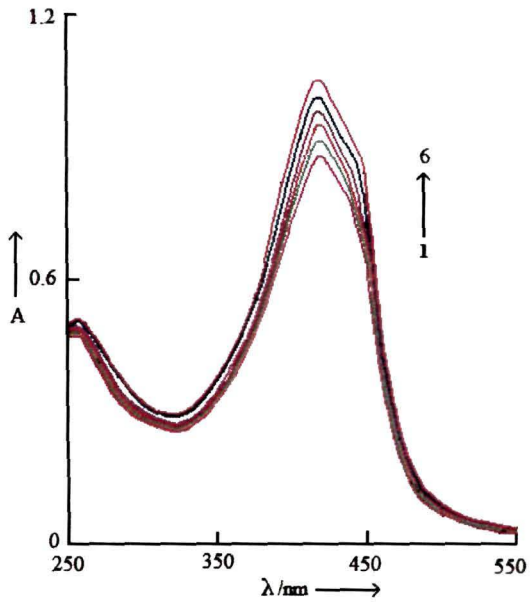


Fig. III.C.28: Absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) at various concentrations of chitosan in presence of 1.5x 10^{-3} mol dm^{-3} of CTAB at *p*H 7.40 and 298 (±0.1) K: [chitosan] / 10^{-6} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 14.0.

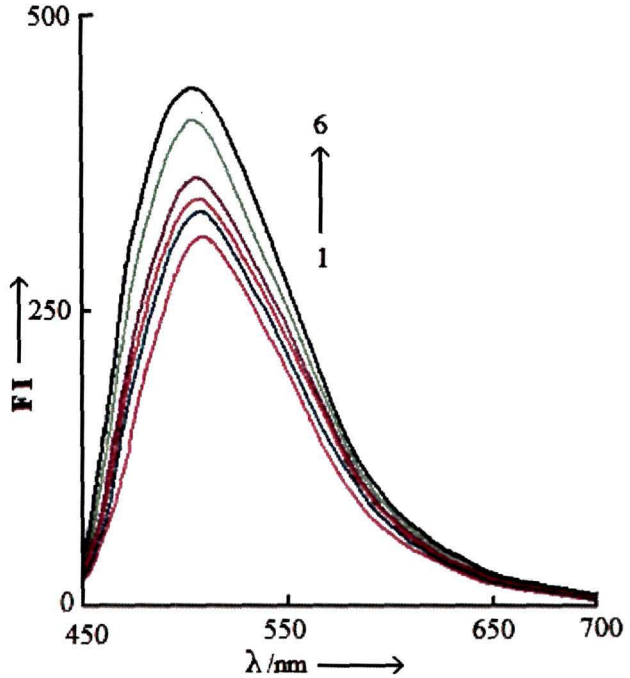


Fig. III.C.29: Fluorescence spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) at various concentrations of chitosan in presence of 1.5x 10^{-3} mol dm^{-3} of CTAB at *p*H 7.40 and 298(±0.1) K: [chitosan] / 10^{-6} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 14.0.

As shown in the **Fig. III.C.29**, upon excitation at 420 nm, the FI of the aqueous curcumin is greatly enhanced by chitosan in presence of CTAB. The emission peak is shifted from 550 nm to 500 nm. This large hypsochromic shift of ~50 nm can be attributed a change in microenvironment from a polar field to a less polar field. From the fluorescence data, it is clear that the chitosan-CTAB system provides a hydrophobic environment of lower polarity than chitosan alone to the aqueous curcumin. The chitosan-CTAB complex acts as a barrier between curcumin and water, thereby wrapping the curcumin molecules inside its hydrophobic core.

The UV-visible absorption spectra of 2.5x 10^{-5} mol dm^{-3} aqueous curcumin induced by chitosan in presence of 1.0x 10^{-3} mol dm^{-3} TW80 at *p*H 7.40 and 298 (± 0.1) K have been shown in the **Fig. III.C.30**. The intensity of 420 nm band increases significantly with corresponding increase in the concentration of chitosan in presence of TW80 in a similar way as was observed in the presence of CTAB. The binding constant of curcumin-nonionic surfactant-chitosan system has been determined by monitoring the change in absorbance values of the aqueous curcumin at progressively increasing concentration of chitosan, in fixed concentration of TW80. In chitosan-TW80 system the positively charged polymer interacts with TW80 by electrostatic means.[83] The electronegative oxygen atoms of the PEO chains of TW80 might associates with the electropositive chitosan chains. The excess polymer chains left after association with TW80 may form a transient network which is also available to interact with curcumin. As a result, the hydrophobic interaction of curcumin with chitosan in the presence of TW80 is more pronounced than that in the presence of CTAB.

As shown in the **Fig. III.C.31**, the FI of the aqueous buffered curcumin (2.5x 10^{-5} mol dm^{-3}) increases effectively with increasing concentration of chitosan, with a blue shift from 550 nm to 490 nm, in the presence of 1.0x 10^{-3} mol dm^{-3} of TW80. The blue shift observed for aqueous curcumin in chitosan-TW80 system (~ 60 nm) is larger than that observed for aqueous curcumin in chitosan-CTAB system (~ 50 nm). This large blue shift may be due to the more hydrophobic microenvironment of chitosan-TW80 system than that of chitosan-CTAB system.

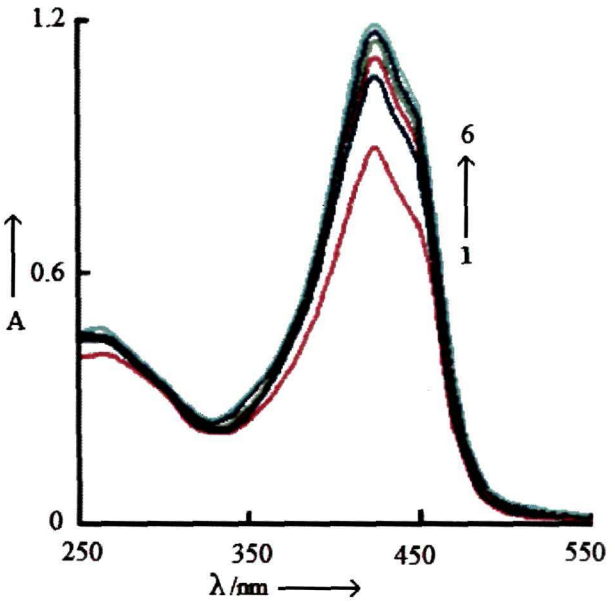


Fig. III.C.30: UV-visible absorption spectra of curcumin (2.5x 10^{-5} mol dm^{-3}) at various concentrations of chitosan in presence of 1.0x 10^{-3} mol dm^{-3} of TW80 at *p*H 7.40 and 298 (±0.1) K: [chitosan] / 10^{-6} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 14.0.

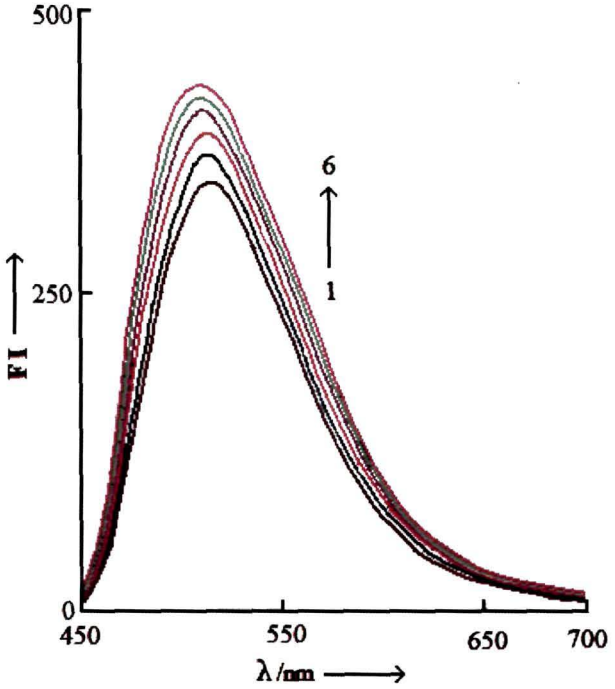


Fig. III.C.31: Fluorescence spectra of curcumin (2.5x 10^{-5} M) at various concentrations of chitosan in presence of 1.0x 10^{-3} mol dm^{-3} of TW80 at *p*H 7.40 and 298 (±0.1) K: [chitosan] / 10^{-6} mol dm^{-3} = (1) 0.0, (2) 2.0, (3) 4.0, (4) 8.0, (5)12.0 and (6) 14.0.

b. Determination of binding constants

The binding process of curcumin (Cur) with chitosan can be described by the following equilibrium,

$$Cur + chitosan \overset{K_S}{\rightleftharpoons} [complex] \qquad \text{III.C(16)}$$

The equilibrium constant K_s for the above equilibrium can be written as,

$$K_s = \frac{[complex]}{[chitosan][Cur]} \qquad \text{III.C(17)}$$

Assuming 1:1 complex formation between chitosan and curcumin, linear plot has been made by following the absorbance changes at a suitable wavelength, as a function of reciprocal concentration of chitosan according to the equation, the modified Benesi-Hildebrand equation {Eq. III.C(18)} given below,[67-69]

$$\frac{1}{\Delta A} = \left[\frac{1}{K_S \Delta\varepsilon[Cur]}\left(\frac{1}{[chitosan]}\right) + \frac{1}{\Delta\varepsilon[Cur]}\right. \qquad \text{III.C(18)}$$

here, ΔA and $\Delta\varepsilon$ correspond to the change in the absorbance and the molar extinction coefficient at the wavelength of the study (at 422 nm), respectively. [chitosan] and [Cur] corresponds to the equlibrium concentrations of chitosan and curcumin, respectively.

The binding constants can be estimated by following the fluorescence changes also. The FI of curcumin increases significantly in presence of chitosan. The changes in FI at 420 nm due to curcumin were followed as a function of concentration of chitosan according to Eq. III.C(19) to estimate the binding constant, K_s,[69,83]

$$\frac{1}{F - F_o} = \frac{1}{F_{complex} - F_o} + \frac{1}{F_{complex} - F_o}\left(\frac{1}{K_S[citosan]}\right) \qquad \text{III.C(19)}$$

here, F_o and F are the respective FI from curcumin at a suitable wavelength in of 540-550 nm in the absence and presence of chitosan.

In absorption method, the binding constants have been estimated following the changes in absorption intensity at λ_{max} due to curcumin at various concentrations of chitosan, and keeping curcumin concentration at 2.5x 10^{-5} mol dm^{-3} and fitting the data to Eq. III.C(18). In fluorescence method, the binding constants have been estimated following the changes in FI at $\lambda_{em\cdot max}$ due to curcumin at various concentrations of chitosan, and keeping curcumin concentration at 2.5x 10^{-5} mol dm^{-3} and fitting the data to Eq. III.C(19). From the results obtained {**Table III.C(4)**} it has been observed that binding constant of chitosan-curcumin binding increases in the order: chitosan < chitosan-CTAB < chitosan-TW80. The binding constants determined by the two methods are comparable.

The energy efficiency of the chitosan-curcumin system has been studied by monitoring the change in the binding constant, K_s values as a function of temperature in the temperature range between 298 and 313 K. ΔG^o has been determined from the following equation,

$$\Delta G^o = -RT \ln K_s \qquad \text{III.C(20)}$$

The ΔG^o value has been obtained as –5.64 kJ mol^{-1} at 298 (±0.1) K. ΔH^o and ΔS^o have been determined using the van't-Hoff equation. It has been found that K_s values significantly decreases with increasing temperature. The van't-Hoff plot for the interaction of curcumin with chitosan at *p*H 7.40 is shown in **Fig. III.C.32**. The values ΔH^o and ΔS^o have been determined as –21.52 kJ mol^{-1} and 23.08 J $mol^{-1}K^{-1}$ at 298 (±0.1) K. The ΔH^o values for the transfer of curcumin from aqueous phase to chitosan rich colloidal phase were larger than the total free energy change, ΔG^o, indicates that the process is mainly enthalpy driven, although there is a contribution of small positive entropy changes. Thus, the strong interactions between curcumin and chitosan are driven by both hydrophobic force and hydrogen bond formation between the hydroxyl group of the glucosamine chains of chitosan and curcumin. And the rest of curcumin free in solution as anionic curcumin interacts with the cationic polymer.

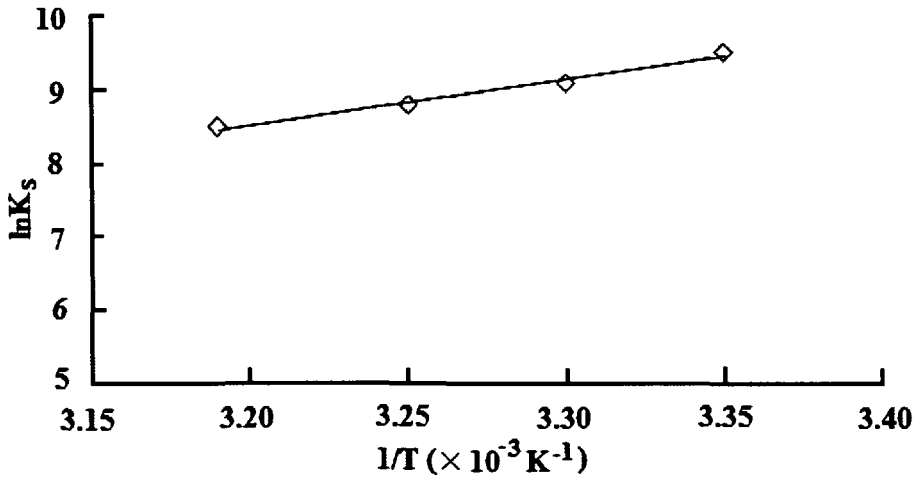


Fig. III.C.32: The van't- Hoff plot for the interaction of curcumin with chitosan at *p*H 7.40

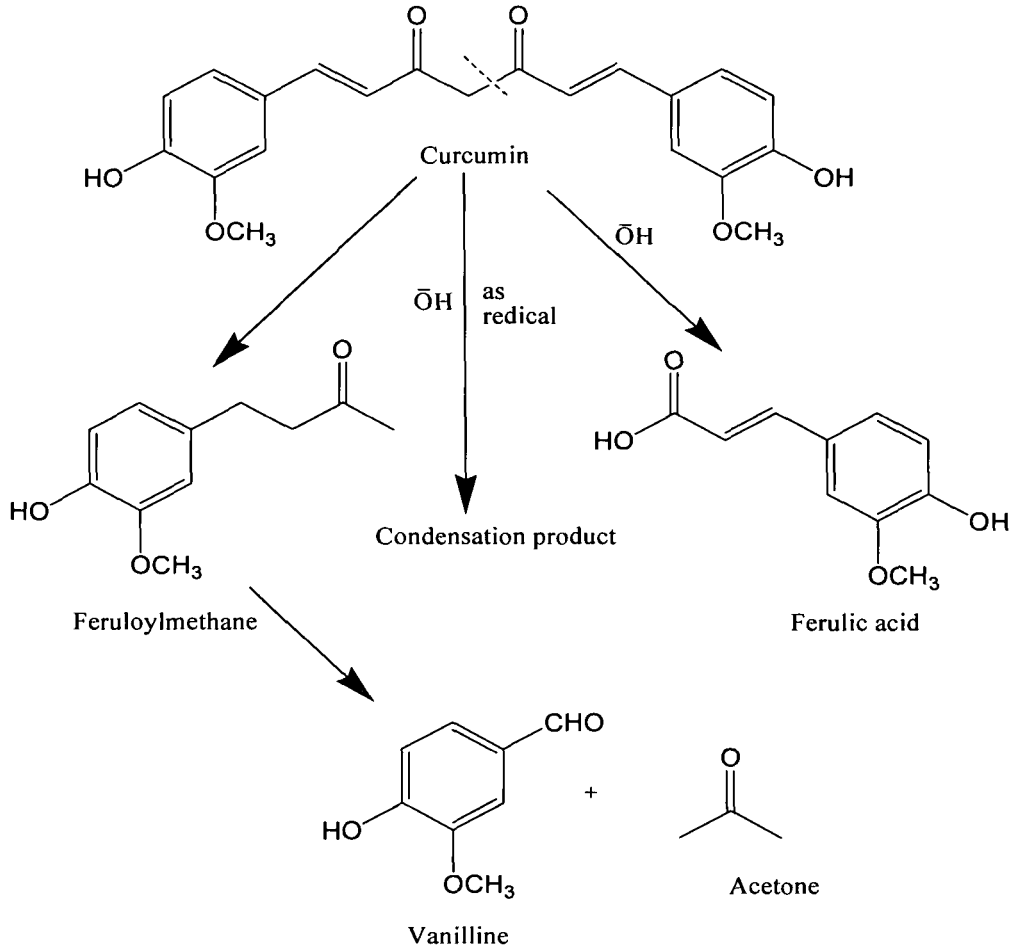
a. Kinetic study

Deprotonation of curcumin occurs in phosphate buffer medium at *p*H 7.40 or above.[84] Curcumin is initially deprotonated and then hydrolysed resulting in *trans*-6-(4'-hydoxy-3'-methoxypenyl)-2,4-dioxo-5-hexenal.[84] The hydrolysed product then further degreded to smaller molecular components such as vanillin, feruloyl methane, and ferulic acid (**Fig. III.C.33**).[84] The contribution from these molecules to the absorption maximum of 425 nm of curcumin in aqueous buffer medium is negligible.[56] More than 90% of curcumin decomposed rapidly in buffer systems at physiological *p*H (*p*H 7.40) conditions.[84]

The rate constant (k_t) of alkaline decomposition of curcumin in buffered medium in absence and in presence of surfactant ant chitosan have been determined by using the following equation developed by Sengupta *et al.* for pseudo first order rate,[85]

$$\ln(d_t - d_\alpha) = -kt + \ln(d_o - d_\alpha) \qquad \text{III.C(21)}$$

where d_o, d_t, d_α are the absorbances at absorption maximum of the aqueous dye solution at start, at time t, and at infinite time respectively.



Scheme III.C.1: The chemical structure of products obtained from the degradation of curcumin in phosphate buffer at *p*H 7.20.[85]

For the kinetic study of degradation of curcumin, the absorbance changes of aqueous curcumin solutions in presence and absence of chitosan have been monitored as a function of time. Since, the maximum absorption occurred at 422 nm in presence of chitosan, the studies have been carried out monitoring curcumin concentration at λ_{max} 422 nm. As shown in **Fig. III.C.33** there is a substantial decrease in the UV-visible absorption curve of curcumin as a function of time at *p*H 7.40 (phosphate buffer). However, in presence 1.0x 10^{-5} mol dm^{-3} of chitosan the degradation of curcumin has been suppressed to a larger extent as the decrease in absorption maxima is negligible compared to the original value. The linearity of the time dependent degradation of curcumin shows that the reaction is of pseudo first order. As shown in inset of **Fig. III.C.33** the linear curves have been obtained with acceptable squared correlation coefficients. The rate constant for the degradation of curcumin in phosphate buffer medium has been obtained as 0.20 min^{-1} at

*p*H 7.40. In presence of chitosan (1.0x 10^{-5} mol dm^{-3}), the rate constant has been obtained as 0.076 min^{-1}. Thus, the degradation occurs approximately 3 times slower in presence of 1.0x10^{-5} mol dm^{-3} chitosan. We can say that the degradation of curcumin is suppressed by chitosan (1.0x 10^{-5} mol dm^{-3}) with a yield of 62 ± 5%. The yield can be defined as: Yield of suppression = [$rate_{buffer}$– $rate_{chitosan}/rate_{buffer}$] x 100% for aqueous chitosan system.[58] But, in chitosan-CTAB system, the rate constant of degradation of curcumin has been obtained as 0.019 min^{-1} and thus the yield of suppression of degradation is 90.5 ± 5%. Moreover, the rate constant of degradation of curcumin in chitosan-TW80 system is obtained as 0.011 min^{-1} with an impressive yield of 94.5 ± 5%. The above observations strongly indicate that, chitosan can diminish the degradation process of curcumin at physiological *p*H condition (*p*H = 7.40) more effectively in presence of the surfactants. The yield of suppression of curcumin by chitosan is however less than that by Human Serum Albumin and fibrinogen as observed in an earlier report.[58] The suppression is better in presence of the nonionic surfactant than the cationic surfactant again indicating a contribution from the interactions of the polymer chain with the polyoxyethelene groups of the nonionic surfactant.

Table III.C(4): Rate of degradation of curcumin in aqueous buffer (*p*H 7.40) and in chitosan- surfactant systems, yield of suppression of degradation by chitosan, and the curcumin-chitosan association constants.

Surfactant	**Polymer**	**Rate of degradation min^{-1}**	***Yield of suppression (±5%)**	**[a]K_s (absorption method) dm^3 mol^{-1}**	**[a]K_s (fluorescence method) dm^3 mol^{-1}**
-	-	0.20	-	-	-
-	Chitosan	0.076	62%	2.01x 10^4	2.24x 10^4
CTAB	Chitosan	0.019	90.5%	2.10x 10^5	2.14x 10^5
TW80	Chitosan	0.011	94.5%	3.32x 10^5	3.39x 10^5

[a]Experimental error limit ±5%.

*Yield of suppression = [($rate_{buffer}$-$rate_{chitosan}$) / $rate_{buffer}$]x 100% for aqueous chitosan system, Yield of suppression = [($rate_{buffer}$-$rate_{chitosan\text{-}surfactant}$) / $rate_{buffer}$ x 100%] for aqueous chitosan-surfactant system.[58]

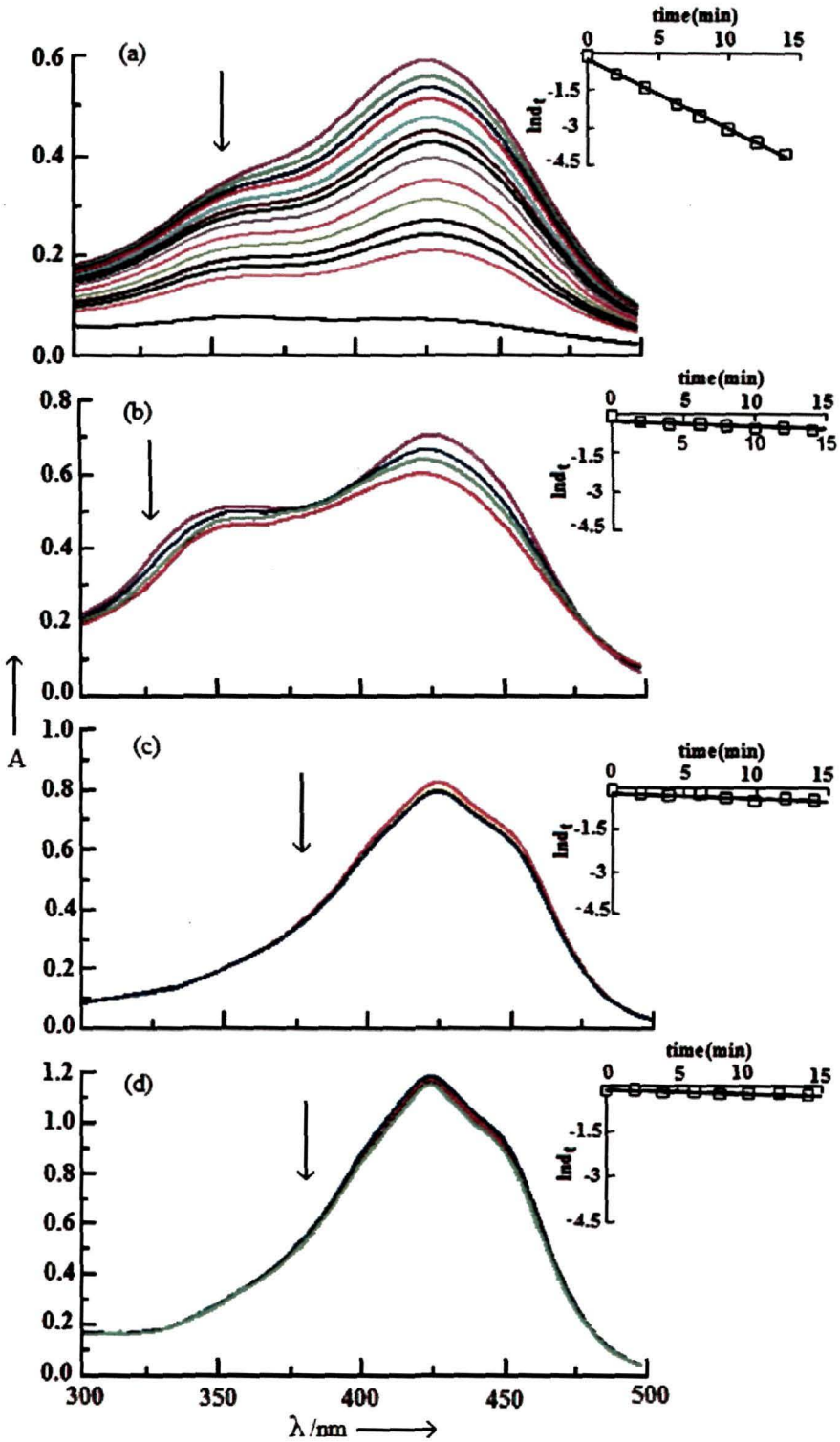


Fig. III.C.33: UV-vis absorption spectra of curcumin (2.5x 10^{-5} M mol dm^{-3}) in (a) *p*H 7.40 (phosphate buffer), (b) 1.0x 10^{-5} mol dm^{-3} chitosan alone, (c) 1.0x 10^{-5} mol dm^{-3} chitosan in presence of 1.5x 10^{-3} mol dm^{-3} CTAB, (d) 1.0x 10^{-5} mol dm^{-3} chitosan in presence of 1.0x 10^{-3} mol dm^{-3} TW80. The rate of degradation is determined from the initial slope of the best-fit linear curve.

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CHAPTER-IV

IV: Conclusion:

The present study of spectral characteristic of dyes in the environment of aqueous mixed polymer-surfactant systems and their thermodynamics revealed some interesting novel information regarding the polymer-surfactant interactions as well as dye-surfactant interactions and dye-polymer interactions, which have been summarized in the conclusion below:

IV.A.1: *Acid-base equilibrium of phenol red in aqueous polymer-surfactant medium*

- The spectrophotometric investigations on the acid-base equilibrium of PR revealed that the association of PR is stronger with the SDS-nonionic polymer mixtures than with SDS alone. In case of PEG-SDS, the association with the increase in molecular weight of the polymers due to hydrophobic interaction. The strength of the association increases in the order: PEG 200< PEG 400<PEG 600<PVA.
- In case of Tris buffer system there is a partition of the buffer components between the aqueous phase and micellar pseudophase which shield the polar head group region of the SDS micelles bound to PVA and PEGs. As a result, the association of PR with SDS-PVA and SDS-PEG system is greater in Tris buffer medium than in phosphate buffer medium of the same *p*H.
- The partition equilibrium method can be used to study the interaction of PR with aqueous SDS-nonionic polymer systems to determine simultaneously the association constants of the dye with SDS-nonionic polymer combined systems and the CAC of the surfactant in presence of the polymers. The interactions of the dye with the SDS-PVA and SDS-PEG systems are found to be endothermic and driven by entropy.

IV.A.2: *Acid-base equilibrium of neutral red in aqueous polymer-surfactant medium*

- Both the electrically neutral base form and the cationic conjugate acid form of NR are significantly associated with nonionic micelles bound to nonionic polymers in a well buffered medium, although the base form binds preferentially over the acid form of the dye. The influence of the nonionic surfactants on the dye is greater than that of the nonionic polymers.
- The partition equilibrium method can be applied to predict the pK_a NR in aqueous solutions of nonionic micelles as well as in aqueous solutions of non-ionic micelles bound to nonionic polymers. The method can also be applied to determine the

association constants of NR with Tween-PVA and Tween-PEG systems, and the CAC of the surfactant in aqueous systems containing both the polymer and the surfactant. The CAC of the surfactants in presence of the polymers increases in the order: PVA < PEG 600 < PEG 400 < PEG 200, suggesting that the surfactant-polymer aggregation decreases as the molecular weight of the polymer decreases.

- The association of NR with the nonionic surfactant micelles in absence as well as in the presence of the nonionic polymers is found to be endothermic and driven by entropy. The interaction is weaker with low molecular weight of polymer and with lower hydrophobicity of surfactant.
- The apparent pK_a of the dye decreases in the aqueous nonionic surfactant-polymer system due to a preferential binding of the neutral base form of the dye to the nonionic micelle-polymer systems. The overall acid dissociation of the dye increases with increase in the chain length, *i.e.,* hydrophobicity of the surfactant and the polymers.

IV.B: ***Monomer-dimer equlibrium of methylene blue in aqueous polymer-surfactant medium***

- The dimerization of MB in water is about 10 times greater than that in SDS micellar medium but is comparable to that in aqueous PVA-SDS system.
- There is a competition between MB and SDS for binding site on PVA where SDS exhibits stronger binding to PVA. When surfactant concentration exceeds the CAC and surfactant aggregates are formed, the dye is incorporated in its monomeric form into the hydrophobic SDS-PVA complexes.
- The aggregation of MB in PVA-SDS system was found to be exothermic. The presence of SDS facilitates dimerization of MB below the CAC but the dye prefers the monomeric form in the presence of the hydrophobic PVA-SDS complex above the CAC.

IV.C.1: ***Interaction of curcumin with submicellar surfactants in absence and in presence of polymers***

- The dye-surfactant complex formation between curcumin and alkyltrimethylammonium surfactants increases with increase in the surfactant chain length.
- The interaction takes place in acidic and neutral *p*H and the strength of the interaction decreases with *p*H variation in the order of *p*H: 5.00 > 7.00 > 2.00.
- A dye-surfactant complex is formed between curcumin and submicellar anionic surfactants also.
- The complex formation may involve electrostatic interaction between the head groups of the surfactants and the β-diketo moiety of curcumin in the diketo tautomeric form of the dye.
- In the case of SDBS, there is an indication also of an interaction through the benzene ring of SDBS with curcumin.
- At higher surfactant concentrations, the di-keto curcumin converts rapidly to the keto-enol form to retain its conjugation.
- The strength of the curcumin-anionic surfactant binding in the submicellar concentrations decreases on changing the surfactant in the order SDS > SDBS > SDSN, but the order was SDS > SDSN > SDBS at *p*H 5.00 and 2.00. With a particular surfactant, on varying the *p*H, the K_c increased in the order of *p*H: 2.00 < 7.00 < 5.00.
- The structural alteration of curcumin in both submicellar anionic and cationic surfactants is absent in presence of a nonionic polymer. Here curcumin predominantly binds with the nonionic polymer in its keto-enol form.
- Finally, the observed stabilization of the diketo form may be utilized for enhancing the antioxidant property of curcumin.

IV.C.2: ***Interaction of curcumin with surfactants in presence of PVA***

- Curcumin strongly interacts with all the chosen nonionic polymer-surfactant systems. The surfactant-polymer systems, *viz.*, SDS-PVA, CTAB-PVA, TW80-PVA provide hydrophobic environment to the dye.

- The strength of binding increases in the order PVA-SDS < PVA-CTAB < PVA-TW80 in the experimental *p*H of 7.00 indicating the strongest binding of curcumin with nonionic surfactant-polymer aggregates.
- The interaction is mainly hydrophobic and curcumin exists predominantly in the polymer bound micelles.

IV.C.3: ***Interaction of curcumin with chitosan in presence of surfactants***

- Curcumin strongly interacts with chitosan at the physiological *p*H (*p*H = 7.40) of the system and the interaction is more pronounced in presence of surfactants.
- It was observed that the strength of the curcumin binding in chitosan-CTAB system is more than ten times greater compared to that in chitosan alone. The binding is again stronger in chitosan-TW80 system than in chitosan-CTAB system.
- A fraction of the curcumin molecules occupies the hydrophobic interior of chitosan, while the other fraction occupies the cationic centres of the polymer.
- Chitosan suppress the hydrolytic degradation of curcumin with an impressive yield of about 77(±5)%. On the other hand, in presence of CTAB and TW80 the yield is increased up to 90.5(±5)% and 94.5(±5)%, respectively.
- The binding process is driven by both enthalpy and entropy indicating both hydrophobic, electrostatic and hydrogen bond formation between curcumin and chitosan.
- Chitosan can be effectively used together with nonionic TW80 and cationic CTAB surfactant to stabilise curcumin.

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List of publications:

A part of the research work described in the thesis has already been published as mentioned below and the rest is in the process of communication.

(1) "Acid-Base equilibrium of neutral red in aqueous nonionic surfactant-polymer systems", Bornali Boruah, Biren Gohain, Polash M. Saikia, Munindra Borah and Robin K. Dutta, ***J. Mol. Liquids*** 160 (2011) 50-56.

(2) "Spectrophotometric investigation of the monomer–dimer process of C.I. Basic Blue 9 in aqueous polymer-surfactant system", Bornali Boruah, Polash M. Saikia, Robin K. Dutta, ***Dyes and Pigments*** 85 (2010) 16-20.

(3) "Partition equilibrium of phenol red in aqueous polymer-surfactant system: Determination of critical aggregation concentration", Bornali Boruah, Polash M. Saikia, Biren Gohain, Robin K. Dutta, ***J. Mol. Liquids*** 151 (2010) 81-85.

(4) "Binding and stabilisation of curcumin by mixed chitosan-surfactant systems: A spectroscopic study", Bornali Boruah, Polash M. Saikia, Robin K. Dutta, ***J. Photochem. Photobiol. A: Chem.*** 245 (2012) 18-27.

(5) "Premicellar and micelle formation behavior of aqueous anionic surfactants in the presence of triphenylmethane dyes: protonation of dye in ion pair micelles", Biren Gohain, Bornali Boruah, Polash M. Saikia, Robin K. Dutta, ***J. Phys. Org. Chem.*** 22 (2009) 1-9.

Additional:

(6) "Stabilization of diketo tautomer of curcumin by premicellar anionic surfactants: UV-Vis, fluorescence, tensiometric and TD-DFT evidences", Anisha Dutta, Bornali Boruah, Arup K. Manna, Biren Gohain, Polash M. Saikia, Robin K. Dutta, ***Spectrochim. Acta A*** 104 (2013) 150-157.

(7) "Interaction of curcumin with cationic surfactants in submicellar medium: Combined hydrophobic and electrostatic effects" Bornali Boruah, Anisha Dutta, Biren Gohain, Polash M. Saikia, Robin K. Dutta, *communicated.*

(8) Curcumin stabilization in aqueous surfactant-nonionic polymer systems", Bornali Boruah, Polash M. Saikia, Robin K. Dutta, *to be communicated.*

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