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FLUORESCENCE SPECTROMETRIC STUDY OF MERCUROCHROME DYE - SURFACTANT INTERACTIONS

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ABSTRACT

The fluorescence properties of an anionic dye, mercurochrome (of xanthene series) solubilized in the surfactant micelles in aqueous media is studies with the help of fluorescence spectroscopy. The fluorescence peak height at 530 nm decreases on increasing the concentration of surfactant reaching a limiting value. At room temperature emission of mercurochrome in surfactant micelles shows a significant, red shifts compared with that in pure water. Quantum yield measurements were also made at different concentration of the surfactants, using anthracene as the standards. Stokes shift was also measured at different concentration of the solutions. The decrease in flouroscence intensity is due to interaction between the surfactant micelles and the dye molecules which cause the aggregationof monomeric form of the dye molecules into its dimeric or polymeric form. The result has been attributed to micelle formation action of surfactants and the dye surfactants interactions.

Key words: Fluorescence, mercurochrome, aggregation and micellar media.

INTRODUCTION

The dye molecules have tendency to undergo self-aggregation on the interaction of surfactants into dimmers or higher polymeric forms[1]. The efficiency of fluorescence and absorption characteristics of the dye are affected by its aggregation[2]. The interaction of oppositely charged dyes and surfactants show spectral changes below CMC, which have been attributed to the suspension of the dye-surfactant salts, formation of dye-n-mers, dye-surfactant aggregation charge transfer complex or merely formation of complexes of indefinite composition[3].

The present paper deals with the influence of various surfactant micelles on mercurochrome axanthene dye. This dye has application as an anticeptic and as a biological stain .Preparations stained with this dye stained with this dye do not fade even when exposed to strong sunlight for very prolonged periods of time[4].

EXPERIMENTAL

A Perkin- Elmer 204 A fluorescence spectrophotometer was used.

All experiments were carried out at rom temperature. The sotck solution of analytical pure grade mercurochrome(sigma) was prepared in doubled distilled water. The concentration of dye was kept at 10^{-6} M for fluorescence measurements .

The surfactants employed for the study are as follows:-

(A) Non- ionic surfactants

(i) TX-100: polyoxethylene ter- octyl phenol (Eq. 10)
(ii) Brij-35 polyoxyethylene (23) lauryl ether
(iii) Tween-20: polyoxyethylene sorbitain monolaurate
(iv) Tween-40: polyoxyethylene sorbitain monopalmitate

(B) Anionic surfactants

i. DSSS: Dictyl sodium sulpho succinate
ii. Aerosol-OT

(C) Cationic surfactants

i. CPC: Cetylpyridinium chloride
ii. CDBAC: Cetyldimethyl benzyl ammonium chloride.

All surfactants were Sigma product except Brij - 35 (BDH) product and were used as such.

RESULT S AND DISCUSSION

Mercurochrome in aqueous solution shows a maximum emission wave length at 530 nm and maximum excitation wave length at 505nm.

On addition of non ionic surfactants the emission peak showed a gradual red- shift of 30nm. The fluorescence intensity of mercurochrome first increased the little and then at the shifted wavelength decreased gradually to almost zero and the solution became colourless at higher concentration of the surfactants. Table - 1 incorporates the results obtained.

The addition of anionic surfactants to the dye solution caused deacrease in fluorescene intencity with Aerosol -OT and DSSS with a red shift of 10 nm in the emission peak position. The changes obtained in the flouorescene spectra with anionic surfactants are given in Table - 2. Both the cationic surfactants used initially a gradually decrease in flouorence intensity of the dye to almost zero which was followed by a shift in the em. At the shift λ_{em}, a large enhancement in flourence intensity which reached a limiting value. Changes in flourence intensity at λem on changing the concentration of cationic surfactants are given in Table - 3.

The variations occurring in the relative flourence intensity of the dye on changing the concentration of TX-100, DSSS and CDBAC are represented graphically in Fig. -1.

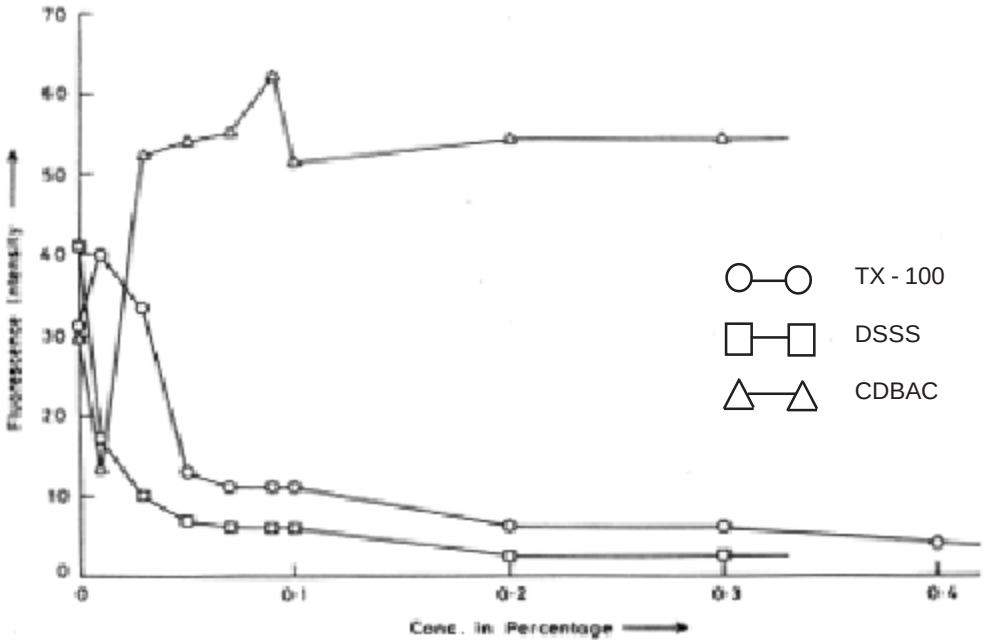

Fig. - 1 : Effect of the addition of non-ionic surfactants on the fluorescence emission of 1 x 10^{-6} M, mercurochrome solution

Table - 1 : Effect of Nonionic surfactants on the fluorescence intensity (F.I.) of mercurochrome

λex = 505 nm, λem = 530 nm, PM Gain = 1, Sensivity range = 0.3

% of solution	Conc. of surfactant	TX-100		Brij-35		Tween-20		Tween-40	
		F.I.	λem	F.I.	λem	F.I.	lem	F.I.	λem
0.1	0.000	30-31	530	30-31	530	30-31	530	30-31	530
0.1	0.001	32-33	530	35	530	30-31	530	35-36	530
0.1	0.003	40	530	40-41	530	54	530	76	530
0.1	0.005	43	530	41	530	56	530	46-47	530
0.1	0.007	49	530	43	530	44	530	74	530
0.1	0.01	40	530	47-48	530	49	530	40-41	530
0.1	0.03	33	530	53	530	28	530	47-48	530
0.1	0.05	13	535	9	535	31	530	54	530
0.1	0.07	11	535	5	550	33	530	34-35	530
0.1	0.09	11-12	555	5	550	30	530	46-47	530
0.1	0.1	4	555	4	555	27	535	5	555
0.1	0.3	4	555	3	555	14	540	3-4	560
0.1	0.5	4	555	3	555	5	550	3-4	560
0.1	0.7	4	555	3	555	10	550	3-4	560
0.1	0.9	4	555	3	555	10	550	3-4	560

Table - 2 : Effect of Anionic surfactants on the flurescence intensity (F.I.) of mercurochrome

λex = 505 nm, λem = 530 nm, PM Gain = 1, Sensivity range = 0.1

% of sol.	conc. of surfactant	Aerosol-OT		DSSS	
		F.I.	λem	F.I.	λem
0.1	0.000	30-31	530	41-42	530
0.1	0.001	33	530	42-43	530
0.1	0.003	28-29	530	53	530
0.1	0.005	27	530	46	530
0.1	0.007	27-28	530	22-23	530
0.1	0.009	22	530	16-17	530
0.1	0.01	5	540	15	540
0.1	0.03	3	540	9-10	535
0.1	0.05	5	540	7	535
0.1	0.07	4	540	6-7	540
0.1	0.09	3	540	6	540
0.1	0.1	2	540	5-6	540
0.1	0.3	1	540	3	540

The fluorophore is fluorescein in the mercurochrome dye which is disodium salt of dibromo hydro oxy mercurifluorescein. The fluorophore exists in two forms, one is more stable quinonid structure (A) which is coloured and gives intense flourence while the other is colourless lactone form (B) which is non- flourerencent as give in Fig. - 2.

The initial enhancement in the fluoresent intencityof the dye of the dye on adding nonionic surfactant is due to the interaction of the hyudro phallic part of the surfactant with the polymeric part of of the surfactant with the polymeric part of the surfactant with the polymeric part of the surfactant with the polymeric dye molecules which results breaking them yo monomeric form. At higher concentrations of the surfactants the quoinoid form of the fluorophore changedinto lactone form which is colourless and emission intensity became almost zero . It is well known [5] that all solvent media like ketone ,ether and esters having oxygen cause the structural change. Similar effects are observed due to the presence of poly oxythylene groups in the surfactants.

Table - 3 : Effect of cationic surfactants on the flurescence intensity (F.I.) of mercurochrome λex = 505 nm, λem = 530 nm, PM Gain = 1, Sensivity range = 0.1

% of sol.	conc. of surfactant	CPC F.I.	CPC λem	CTAB F.I.	CTAB λem
0.1	0.000	43	530	30-31	530
0.1	0.001	23	525	26-27	525
0.1	0.003	5	525	37	530
0.1	0.005	5	510	36	530
0.1	0.007	4	510	38-39	530
0.1	0.009	4	510	32	530
0.1	0.01	4-5	510	28	530
0.1	0.03	19	545	12	525
0.1	0.05	34	545	9	525
0.1	0.07	44	545	2	540
0.1	0.09	43	540	2	540-45
0.1	0.1	38	540	3	545
0.1	0.3	40	540	8	525

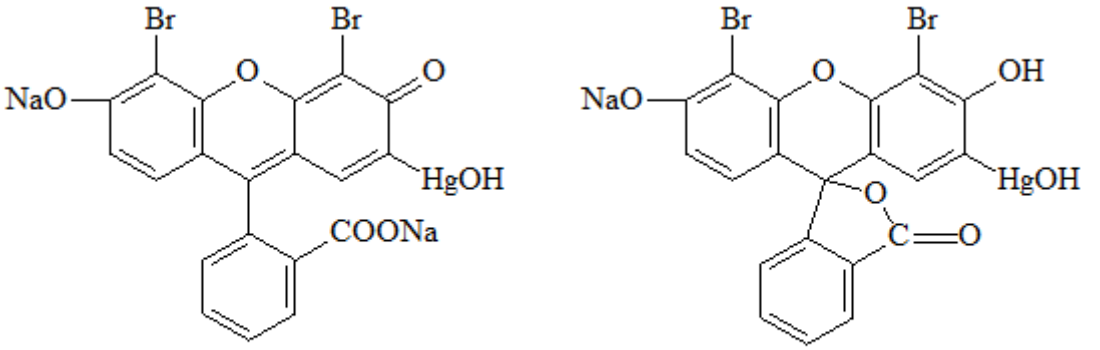

Fig. - 2

Table - 4 : Fluorescence quantum yield of TX-100 aded mercurochrome solution

S. No.	% of the dye solution	Conc. of TX-100 used in %	λem (nm)	ϕr Anthracene	ϕr Mercurochrome
1.	0.1	0.000	530	0.264	0.326
2.	0.1	0.001	530	0.54	0.19
3.	0.1	0.003	530	0.59	0.27
4.	0.1	0.05	530	0.73	0.09

Table - 5 : Stokes' shift data for mercurochrome at room temperature

S. No.	Conc. of Dye	Fl.	λex	λem	PM gain	Stokes' shift
1.	$1x10^{-6}$	25	505	530	1	934.0556
2.	$3x10^{-6}$	35	505	530	1	934.0556
3.	$5x10^{-6}$	55	505	530	1	934.0556
4.	$7x10^{-6}$	66-67	505	530	1	934.0556
5.	$9x10^{-5}$	66-67	505	530	1	934.0556
6.	$1x10^{-5}$	61	500	530	1	1132.0754
7.	$3x10^{-5}$	59-60	500	550	1	1818.1818
8.	$5x10^{-5}$	43	470	540	1	2758.0772
9.	$7x10^{-5}$	29	465	545	1	3156.7524
10	$1x10^{-4}$	41-42	525	550	2	865.800

The dye being anionic in nature, no interactions could be expected with anionic surfactants. But DBS and Aerosol-OT are bidentate with bulky size, were able to cause a change in geometry of the dye molecules, wherein, it lost the coplanarity and hence a decrease in lem peak height was obtained. The red-shift indicates characteristic bond formation between the bromine atoms of the dye molecules and the surfactant in the vicinity of the CMC of the surfactant.

The interaction between the anionic dye and the cationic surfactant leads to an initial charge neutralization, *i.e.*, dye-surfactant ion pair formation which further induces protonation of the system[6]. Such ion pair or sait or complex formation of pre-micelles. The quantum yield data obtained with different surfactants are found to be in good agreement with the experimental observations. The calculations obtained with TX-100 are given in Table -4. the Stokes' shift indicates the energy dissipated in bringing about ionization during the life time of excited state before return to the ground state[8]. the abnormally high values of Stokes' shift so sbtained may be interpreted in terms of an interpreted in terms of an intramolecular proton transfer in the excited state causing isomerization of the dye molecule. The calculated data are given in Table - 5.

Conclusion

From the present study it can be concluded that the dye-surfactant interactions resemble the blended electrostatic-hydrophobic effect that pertains to several biologically important processes. Particularly in medicinal chemistry. The flurescence spectral variations observed for mercurochrome dye at concentrations of the surfactants slightly below CMC which were hitherto attributed to self-aggregation of dyes may actually be due to change in microenvironment of the flurophore of the dye on incorporation into premicelles.

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