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ORIGINAL ARTICLE

Fluorescence spectrometric study of eosin yellow dye–surfactant interactions

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Abstract The spectrofluorimetric behavior of an analytically important molecule eosin yellow was studied in the presence of various surfactant solutions. The relatively weak fluorescence of eosin yellow was significantly enhanced in micellar media formed by cationic and anionic (DBSS) surfactants. The influence of the surfactant structures, concentrations and working experimental conditions on the fluorescence spectra of eosin yellow was thoroughly evaluated and discussed. The solubilizing action of the surfactant has been supplemented by the theoretically calculated spectral parameters like, empirical fluorescence coefficient, quantum yield, molar extinction coefficient and Stokes' shift.

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1. Introduction

Analytical methods which rely on the use of surfactants are becoming more and more numerous, since addition of surfactants provides an increase in selectivity and sensitivity (Peris-Cardells et al., 1993; Beltrán et al., 1995). Eosin (yellowish)-Tetrabromo fluorescein sodium salt is an acid xanthene (natural anionic) dye. A comparative photophysical study of rose bengal, eosin yellow and their monomethyl and dimethyl derivatives shows that aggregates of these dyes are probably non-emissive (Delvalle et al., 1993). Dye sensitized chemiluminescence of luminol and related cyclic hydrazides shows that this emission can be initiated by triplet states of methylene blue and eosin yellow (Klimov et al., 1992). Lu et al. (2003) found that fluorescein, eosin yellow and uranine have evidence of a chemiluminescence enhancing of the $Cu^{II}(H_2O_2)$ and Co^{II}-(H_2O_2) systems. Eosin yellow provides example of direct measurement of elementary processes like singlet excited state absorption of the excited singlet state (Penzkofer et al., 1993). Color removal from effluent is one of the most difficult requirements faced by the textile finishing, dye manufacturing, and pulp and paper industries. These industries are major consumers of water and, therefore, cause water pollution. Most of these dyes are harmful when brought in contact with living tissues for a long time. The discharge of such dyes to the river stream without proper treatment causes irreparable damage to the crops and living beings, both aquatic and terrestrial (Purkait et al., 2005).

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Separation of Congo red by surfactant mediated cloud point extraction, removal of dye from wastewater using micellar enhanced ultrafiltration and regeneration of surfactant and resistance in series model for micellar enhanced ultrafiltration of eosin dye have been studied (Purkait et al., 2004,,). The photophysical and photo catalytic parameters of sulfo and tetrabromo sulfo derivatives of fluorescein have also been studied (Ponyaev et al., 2001). Seret and Vorst (1990) have studied solubility properties of eosin yellow and rose bengal triplet state in sodium dodecyl sulphate micellar solutions.

From an analytical view point, the use of surfactants increases the solubility of organic substances in water, through shallow or deep penetration of the micelles or simply by surface adsorption (Pal and Jana, 1994), and can also catalyze specific reactions by modification of the micro-environment in which these reactions take place (Sicilia et al., 1994). Surfactants at concentrations higher than the critical micelle concentration (CMC) has been extensively used in the application of spectroscopic (ultra-violet, fluorescence, phosphorescence, atomic spectroscopy), electroanalytical and separation methods to sparingly soluble analytes (Neal and Villegas, 1995; Khaledi and Rodgers, 1990).

Eosin has been used as a groundwater migration tracer by capillary electrophoresis/laser-induced fluorescence using a multi wavelength laser (Brumley and Farley, 2003). The decomposition of eosin (yellow) under UV–visible light irradiation in the presence of CeO_2–$CeTi_2O_6$ films shows the presence of photoactivity in these films (Verma et al., 2007). Modification of the properties of NaDS micellar solutions by adding electrolytes and nonelectrolytes: investigations with decyl eosin as a p*K*a probed by Loginova et al. (2001).

The staining of eosin with haematoxylin have been used in structure determination of grasshopper and mammalian testis as well as supporting structure determination of destruction of dental tissues (Espada et al., 1993).

This paper includes study of the influence of various nonionic, anionic and cationic surfactants on the fluorescence and absorption spectra of eosin yellow. The optimum solubilization showing dye–surfactant interaction can be utilized as separation of dyes from waste dye-stuffs of different textile, paper and pulp industries. The results have been interpreted from the calculation of molar extinction coefficient, empirical fluorescence coefficient and quantum yield of eosin yellow fluorescence in various micellar media. Stokes' shift calculation at various concentration of eosin yellow is also supportive.

2. Experimental

2.1. Materials and method

Fluorimetric studies were carried out with a Perkin Elmer spectrophotometer 204 A. The slit width was kept at 10 nm throughout for excitation as well as emission spectra. Absorption spectra of eosin yellow were taken on a chemito UV–VIS 2600 double beam spectrophotometer.

The stock solution of analytically pure eosin yellow (Sd fine chemicals) was prepared in double distilled water. All the experiments were made at room temperature (23–25 °C) and were performed in aqueous medium keeping the final concentration of eosin yellow at 10^{-6} M. All the surfactants used were either of sigma (USA) or BDH products.

(A) Nonionic
Polyoxyethylene 23 lauryl ether (Brij-35)
Polyoxyethylene sorbitan monopalmitate (Tween-40)
Polyoxyethylene tertoctyl phenol (Eq-10) (Tx-100)
(B) Anionic
Dodecylbenzene sodium sulphonate (DBSS)
Sodiumlauryl sulphate (SLS)
Dioctylsodium sulphosuccinate (DSSS)
(C) Cationic
Cetyltrimethyl ammonium Bromide (CTAB)
Cetylpyridinium chloride (CPC)
Myrstyltrimethyl ammonium bromide (MTAB)

The purity of surfactants was checked by determining their CMC values with the help of surface tension measurements, employing drop weight method. The absolute fluorescence quantum yield of the compound was calculated relative to anthracene solution used as a standard. Each time the total intensity of fluorescence emission was measured for the standard and the sample from the area of fluorescence spectrum recorded over the whole range of emission under identical conditions.

3. Results and discussion

The aqueous solution of eosin yellow showed maximum excitation peak at 510 nm while the emission spectrum showed a peak at 535 nm. The cationic surfactants caused an enhancement in the fluorescence intensity with 15–20 nm gradual red shifts. Among these surfactants CTAB exerted maximum effect. The changes in fluorescence intensity of eosin yellow on

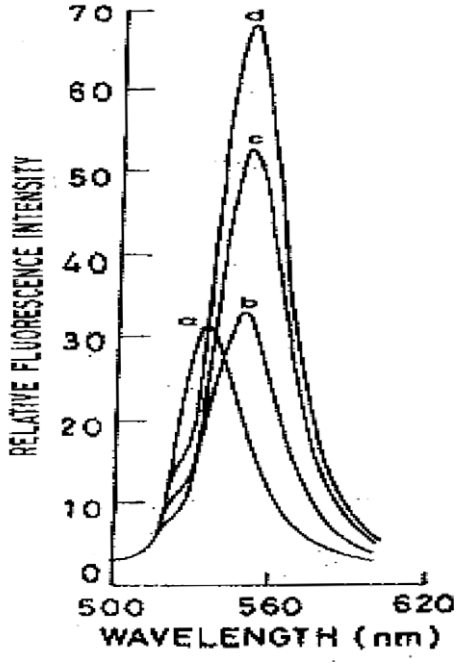

Figure 1 The changes in the fluorescence intensity of eosin yellow on adding different concentrations of CTAB are given: (a) 1×10^{-6} M eosin yellow; (b) 1×10^{-6} M eosin yellow + 0.05% CTAB; (c) 1×10^{-6} M eosin yellow + 0.3% CTAB and (d) 1×10^{-6} M eosin yellow + 0.5% CTAB.

addition of CTAB are shown in Fig. 1. On addition of a cationic surfactant red shift occurs at maximum. This may be attributed to the difference in solvation energy of the solute in the ground state and the excited state.

On addition of the nonionic surfactants like Brij-35 and Tween-40, fluorescence intensity decreased with 5–10 nm blue shift while for TX-100 fluorescence intensity reached maximum initially and then it decreased with the increase in concentration of the surfactant accompanied by red shift of 15–20 nm was observed while on addition of anionic surfactants like DBSS, fluorescence intensity increased with a red shift of 5 nm. For SLS and DSSS, initially fluorescence intensity reduced to a very low value accompanied by 15 nm blue shift and then it was gradually increased with the concentration of the surfactant. The changes in fluorescence intensity of eosin yellow on addition of DBSS are shown in Fig. 2.

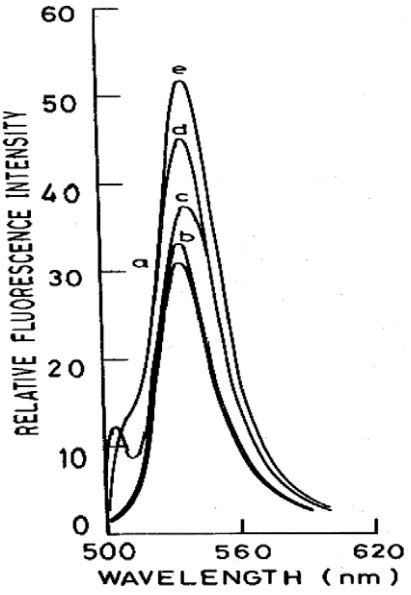

Figure 2 The changes in the fluorescence intensity of eosin yellow on adding different concentration of DBSS are given: (a) 1×10^{-6} M eosin yellow; (b) 1×10^{-6} M eosin yellow + 0.003% DBSS; (c) 1×10^{-6} M eosin yellow + 0.005% DBSS; (d) 1×10^{-6} M eosin yellow + 0.07% DBSS and (e) 1×10^{-6} M eosin yellow + 0.1% DBSS.

The changes observed in fluorescence emission intensity in presence of surfactants are as given in Tables 1–3.

The absorption spectrum gave peak at 505 nm. On addition of any of the nonionic surfactants, a continuous decrease in absorbance was observed with 5 nm blue shift in peak position. Among anionic surfactants, DBSS showed a gradual enhancement in the absorbance without any shift while for SLS and DSSS, initially absorbance reached a lowest value with 15 nm blue shift and then gradually increased.

For cationics absorbance spectra enhanced without any shift in peak position. Molar extinction coefficient ($\log \varepsilon$) calculations showed a gradual increase in $\log \varepsilon$ values with the increase in cationic surfactant concentration. It was due to the strong $\pi \rightarrow \pi^*$ transitions, while on increasing concentration of cationic surfactant $n \rightarrow \pi^*$ transition decreased. With nonionic surfactants as the concentration increased, the ($\log \varepsilon$) values decreased gradually, with anionic surfactants, the ($\log \varepsilon$) values initially decreased and then increased.

The molar extinction coefficient $\log \varepsilon$ values of the solubilizate molecule in different micellar media follow the same trend as their emission intensity. Hence it proves the well known fact that fluorescence intensity of a fluorophore is directly related to its molar extinction coefficient ($\log \varepsilon$) (Guilbault, 1993). The empirical fluorescence coefficient (k_f) values showed a similar trend to the fluorescence emission intensity.

The value of k_f confirms this observation and attributes to the increased sensitivity of fluorimetric analysis of the organic molecule by solubilization. This was attributed to the fact that surfactants offer protective microenvironment, leading to enhanced fluorescence of the guest molecule (solubilizate) by shielding the excited state from non-radiative decay that normally occurs in bulk aqueous solution. The empirical fluorescence coefficient (k_f) is the ratio of fluorescence intensity and the concentration of the fluorescent molecule and it was determined by the formula given below (Aithal et al., 2005)

$$K_f = \frac{I_f}{C}$$

where I_f = Fluorescence intensity C = Concentration in moles/litre.

The fluorescence quantum yield (ϕ_f) values of eosin yellow have been determined in aqueous medium at different concentrations of aqueous surfactant solution added to it. For nonionic surfactants added solutions the quantum yield ϕ_f) values decreased. With anionic surfactants like DBSS, the ϕ_f

Table 1 Effect of nonionic surfactants on the fluorescence intensity (FI) of eosin yellow.

S. No.	% of Brij-35	FI	λ_{em} (nm)	% of Tween-40 (w/v)	FI	λ_{em} (nm)	% of TX-100 (w/v)	FI	λ_{em} (nm)
1	0.000	29	535	0.000	31	535	0.000	30	535
2	0.003	22	535	0.003	29	540	0.003	64	535
3	0.005	11	535	0.005	29	538	0.005	41	535
4	0.007	10	520	0.007	26	538	0.007	35	535
5	0.01	10	520	0.01	24	538	0.01	34	535
6	0.03	9	520	0.03	14	538	0.03	33	535
7	0.05	8	520	0.05	12	535	0.05	25	535
8	0.07	7	520	0.07	12	535	0.07	18	555
9	0.1	7	520	0.1	11	530	0.1	16	555
10	0.3	6	515	0.3	8	515	0.3	10	550
11	0.5	5	515	0.5	4	515	0.5	8	550

λ_{ex} = 510 nm; λ_{em} = 535 nm; PM gain = 2; sensitivity = 0.3.

Table 2 Effect of anionic surfactants on the fluorescence intensity (FI) of eosin yellow.

S. No.	% of DBSS (w/v)	FI	λ_{em} (nm)	% of SLS (w/v)	FI	λ_{em} (nm)	% of DSSS (w/v)	FI	λ_{em} (nm)
1	0.000	32	535	0.000	31	535	0.000	31	535
2	0.003	34	535	0.003	9	520	0.003	9	520
3	0.005	38	540	0.005	9	520	0.005	8	520
4	0.007	40	535	0.007	11	520	0.007	8	520
5	0.01	41	535	0.01	12	520	0.01	10	520
6	0.03	42	535	0.03	12	520	0.03	10	520
7	0.05	44	535	0.05	13	520	0.05	12	520
8	0.07	46	535	0.07	15	520	0.07	12	520
9	0.1	53	535	0.1	17	520	0.1	14	520
10	0.3	53	535	0.3	35	520	0.3	19	520
11	0.5	54	535	0.5	47	520	0.5	21	515

λ_{ex} = 510 nm; λ_{em} = 535 nm; PM gain = 2; sensitivity = 0.3.

Table 3 Effect of cationic surfactants on the fluorescence intensity (FI) of eosin yellow.

S. No.	% of CTAB (w/v)	FI	λ_{em} (nm)	% of CPC (w/v)	FI	λ_{em} (nm)	% of MTAB (w/v)	FI	λ_{em} (nm)
1	0.000	31	535	0.000	31	535	0.000	31	535
2	0.003	31	520	0.003	31	520	0.003	31	520
3	0.005	32	520	0.005	31	520	0.005	31	520
4	0.007	32	520	0.007	25	520	0.007	32	520
5	0.01	32	520	0.01	19	520	0.01	33	520
6	0.03	32	520	0.03	18	550	0.03	34	520
7	0.05	33	545	0.05	40	550	0.05	34	520
8	0.07	43	545	0.07	59	550	0.07	34	550
9	0.1	41	545	0.1	68	550	0.1	35	550
10	0.3	53	545	0.3	80	545	0.3	36	550
11	0.5	68	545	0.5	83	545	0.5	38	550
12							0.7	43	550

λ_{ex} = 510 nm; λ_{em} = 535 nm; PM gain = 2; sensitivity = 0.3.

Table 4 Empirical fluorescence coefficient (k_f) and quantum yield (ϕ_f) for CTAB.

S. No.	Concentration of CTAB (w/v) in %	Empirical fluorescence coefficient (k_f) $\times 10^4$ per mole	Quantum yield (ϕ_f)
1	0.000	3100	0.427
2	0.05	3300	0.460
3	0.3	5300	0.488
4	0.5	6800	0.582

values increased while for SLS and DSSS, the ϕ_f values were initially decreased and then increased. For cationic surfactants, ϕ_f values were increased. These spectral parameters (fluorescence coefficient and quantum yield) are shown in Table 4.

Stokes' shift value continuously increased as the concentration of eosin yellow increased. The magnitude of Stokes' shift depends on several factors. The large Stokes' shift values for eosin yellow are due to hydrogen bond formation between the solute and the solvent in the ground state. This bond breaks following excitation to S_1 but reforms following proton transfer (Solntsev et al., 1998). When photons from molecules in an excited state are emitted by fluorescence, one of the most important observations was that they are emitted at longer wavelengths (lower frequency) and consequently are less energetic than the photons responsible for the excitation. This difference between the excitation and emission maxima is termed the Stokes' shift.

Stokes' shift is a physical constant of luminescent molecules. It indicates the energy dissipated in bringing about ionization during the lifetime of excited state before return to the ground state.

$$\text{Stokes' shift} = 10^7\left[\frac{1}{\lambda_{ex}} - \frac{1}{\lambda_{em}}\right]$$

where λ_{ex} and λ_{em} are corrected maximum excitation and emission wavelength and are expressed in nanometers. The Stokes' shift is of interest to analytical chemists since the emission wavelength can be greatly shifted by varying the form of the molecule being excited. Electrolytic dissociation in the excited state can also give rise to apparently large Stokes' shift. Several factors influence the magnitude of the Stokes' shift. If the environment is rigid so that little rearrangement is possible then the Stokes shift is expected to be small. The magnitude of the shift depends on factors such as solvent polarity, viscosity and polarisability. It also depends on whether the excited state can undergo any specific interactions such as proton transfer or charge transfer to other molecules or (sometimes) within the same molecule. Where fluorescent materials are used as

Table 5 Stokes' shift data of eosin yellow at room temperature.

S. No.	Concentration of compound (M)	FI	λ_{ex} (nm)	λ_{em} (nm)	PM gain	Sensitivity	Stokes' shift (cm^{-1})
1	1×10^{-6}	18	515	540	3	0.1	898
2	3×10^{-6}	20	515	540	3	0.1	898
3	5×10^{-6}	22	515	540	3	0.1	898
4	7×10^{-6}	37	515	540	3	0.1	898
5	1×10^{-5}	56	518	545	2	0.1	956

detectable labels a large Stokes shift is highly desirable because it makes life easier when optical filters are used to separate exciting light and fluorescence emission. The changes in Stokes' shift on increasing concentration of eosin yellow is given in Table 5.

Fluorescence intensity of the compound on adding surfactants can be attributed to the increase in the quantum yield. The fluorophore is the fluorescein in the dye molecule, which is disodium salt of dibromo fluorescein. The fluorophore exists in two forms, one is more stable quinoid structure (A) which is coloured and gives intense fluorescence while the other one is colourless lactone form (B) which is non-fluorescent as shown in Fig. 3.

The initial enhancement in the fluorescent intensity of dye eosin yellow on adding TX-100 surfactant was due to the interaction of hydrophilic part of the surfactant with the polymeric part of dye molecules which results in breaking them into monomeric form. This causes an increase in emission intensity initially but at its higher concentration the geometry of the fluorophore in eosin yellow changes to the lactone form which is non-fluorescent. The decrease in emission intensity of eosin yellow on addition of Tween-40 and Brij-35 with a blue shift in λ_{em} may be due to the increase hydrophobicity of the surfactants. The dye being anionic in nature so there should not be any interaction with anionic surfactants. However the DBSS with bulky size was able to cause a change in geometry of dye molecules. Wherein they make the dye more coplanar hence enhance the emission intensity. The interaction between the anionic dye and cationic surfactants leads to an initial charged neutralization; i.e. dye–surfactant ion-pair formation which further induces the protonation of the system. The preferential interaction of cationic surfactants with anionic dye resulted into inactivation of fluorescing sites. Now in its changed conformation it appears to be susceptible to disaggregation on further adding the surfactant. Thus, it causes subsequent micellization and further solubilization hence increase the fluorescence emission intensity.

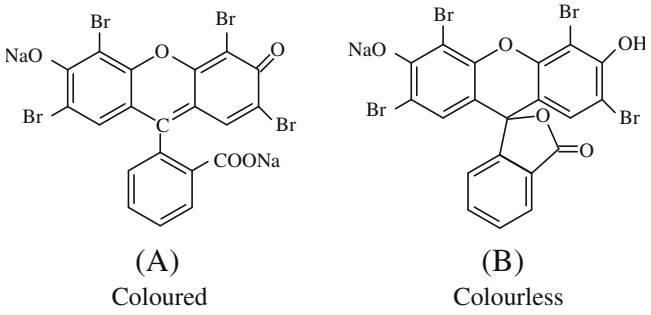

Figure 3 The different form of fluorophore (eosin yellow).

In micellar media many characteristics of organic molecules e.g. absorption and fluorescence spectra are changed drastically. Thus the above observations can be explained by the solubilizing action of surfactant micelles. This process is expected to be most pronounced in the region of critical micelle concentration (CMC) of particular surfactant. During the experiment it was observed that a sudden increase in the fluorescence intensity occurred at particular concentration range of each surfactant, which was in the CMC range of the respective surfactant. In case of ionic surfactant the changes observed were below CMC and this was probably due to the premicellar aggregation in the surfactant micelle.

On adding the surfactants to the aqueous solution of the compound, the surfactant micelles get adsorbed at the interfaces and remove the hydrophobic groups from contact with water, thereby reducing the free energy of the system. But in transferring the hydrophobic groups from solution, to the micelle in the solvent, may experience some loss of freedom confined to the micelle and, in the case of ionic surfactants, from electrostatic repulsion from other similarly charged surfactant molecules in the micelle. These forces increase the free energy of the system and thus oppose micellization.

Whether micellization occurs in a particular case and, if so, at what concentration of monomeric surfactant, therefore depends on the balance between the factors promoting micellization and opposing it. Thus the increase in quantum yield suggests that the surfactants have solubilized the suspended solubilizate molecules (eosin yellow). The higher ϕ_f values in cationic micellar media are because of the lesser effect of other deactivation processes, which compete with fluorescence. Sufficiently large values of $\log\varepsilon$ is assigned to the π–π^* transitions and also confirms the increasing trend of Stokes' shift values. The red shift in the peak wavelength of eosin yellow in micellar media is attributed to the hydrogen bonding capacity of the solubilizate molecule.

4. Conclusion

The present analysis and interpretation suggest that experimental results observed and the theoretically calculated spectral data are found to be in good agreement. This proves the validity of the investigation made. Hence the process of micellization followed by solubilization of the eosin yellow substrate would catalyze its activities which may serve better results in pollution removal in analytical fields and colour stabilization in textile industries. Thus in analytical chemistry, surfactants have been recognized as being very useful for improving analytical methodology, e.g. in chromatography and luminescence spectroscopy.

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