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Analysis of Spectral Behaviour of 2,3-Diaminonaphthalene in Micellar Surfactant Solution by Spectrofuoremetry

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ABSTRACT

2,3-Diaminonaphthalene(DAN) is widely used chemical in biomedical and forensic sciences. Micellar solubilization of 2,3-diaminonaphthalene in non-ionic and ionic surfactants heteromicroenvironment is monitored by fluorescence and absorption spectral techniques has been reported by the authors. The influence of surfactant, concentration and working experimental conditions on the fluorescence spectra of 2,3-diaminonaphthalene is thoroughly evaluated and discussed. The increase in fluorescence intensity in micellar media can be attributed to the increase in quantum efficiency suggests that the suspended hydrophobic 2,3-diaminonaphthalene molecules have been solubilised. The solubilizing action has been supplemented and confirmed by few theoretically calculated spectral parameters like, empirical fluorescence coefficient (k_f), quantum yield (ϕ_f), molar extinction coefficient (ε) and Stokes' shift values.

Keywords: Surfactants, 2,3-Diaminonaphthalene , Fluorescence, Solubilization.

INTRODUCTION

Fluorescence is a powerful tool for investigating the structure and dynamics of matter or living systems at a molecular or supramolecuar level. Polymers, solutions of surfactants, solid surfaces, biological membranes, proteins, nucleic acids and living cells are well-known examples of systems in which estimates of local parameters such as polarity, fluidity, order, molecular mobility and electrical potential is possible by means of fluorescent molecules playing the role of probes. The high sensitivity of fluorimetric methods in conjunction with the specificity of the response of probes to their microenvironment contribute towards the success of this approach[1-5]. The high sensitivity of fluorescence analysis has largely justified the use of fluorescence technique for many determinations. Lower limits of detectability for many methods lie in the sub parts per million (ppm) to parts per billion (ppb) range. Similarly the great selectivity of the fluorescence analysis has been good, variation in excitation and/or analytical wavelength has allowed simultaneous determination of component in many mixtures. Micelles are biologically important aggregates that are formed in aqueous solution by surfactants, which are compounds possessing a water soluble moiety (often an ionic group) and a water insoluble portion (a long hydrocarbon chain). Micelles are spherical aggregates of 20-200 molecules, containing hydrocarbon interiors and ionic surfaces[6-8]. It is possible within their internal environment to include some compounds that are insoluble in water, to perturb their kinetics of many photo physical processes and to provide structural mimics of

biological membrane[9]. Surfactants because of their ability to solubilize the membrane proteins are extremely important in simulating the complex environmental condition present in larger bio aggregates such as biological membranes[10]. Micellar effects on reactivity and equilibrium have been exploited to modify and improve a variety of important analytical methods. Work in the area of micellar, reverse micellar, monolayer and metal chelating nanoparticle environment are of growing importance to modify and improve the sensing capability of flurosensors. The most striking feature of micelles is the ability to solubilize a variety of compounds in its different regions[11]. Surfactants also play a vital role in various drug delivery. They are pharmaceutically acceptable co solvents and are employed to increase the solubility of compounds. 2,3-Diaminonaphthalene is widely used chemical in biomedical and forensic sciences and also known as DAN. It is an important pharmaceutically and analytically molecule. 2,3-Diaminonaphthalene used for determination of selenium. Improved molecular fluorescence method for the determination of selenium in biological samples developed by Harrison et al.[12]. 2,3-Diaminonaphthalene (DAN) also used for the detection of nitric oxide. Many methods for determination of nitrite and nitrate in cell culture medium has been developed[13-15]. These method is based on pre-column derivatisation of nitrite with 2,3-diaminonaphthalene under acidic conditions forms a fluorescent product, 1-(H)-naphthotriazole.

The present study includes a study on the influence of various nonionic, anionic and cationic surfactants on the fluorescence and absorption spectra of 2,3-diaminonaphthalene . The results have been interpreted from the calculations of molar extinction coefficient, empirical fluorescence coefficient, quantum yields of 2,3-diaminonaphthalene fluorescence in various micellar media and Stokes' shift calculations at various concentration of 2,3-diaminonaphthalene**.**

MATERIALS AND METHODS

All the fluorimetric and absorption experiments were carried out with Perkin- Elmer fluorescence spectrophotometer model no. 204 A with a synchronized model no. 056 strip chart recorder and Hewlet Packard (HP) 8452 A diode array spectrophotometer, respectively. The stock solution of analytically pure 2,3-diaminonaphthalene (Sigma Chemicals) was prepared in distilled methanol. All the experiments were made at room temperature (23^0-25^0C) and 1% methanolic medium keeping the final concentration of 2,3-diaminonaphthalene at 1 X 10^{-5} M. All the surfactants used were either of sigma (USA) or BDH product.

The following surfactants were employed.
1. Nonionic: Polyoxyethylene tertoctyl phenol (TX-100), Polyoxyethylene sorbitan monolauriate (Tween-80) and Polyoxyethylene sorbitan monopalmitate (Tween-40)
2. Cationic: Cetyltrimethyl ammonium Bromide (CTAB), Cetylpyridinium chloride (CPC) and Cetylpyridinium bromide (CPB)
3. Anionic: Dodecylbenzene sodium sulphonate (DBSS), Dioctylsodium sulphosuccinate (DSSS) and Sodiumlauryl sulphate (SLS)

The purity of surfactant was checked by determining their CMC values with the help of surface tension measurement, employing drop weight method. The absolute fluorescence quantum yield (Φ_f) of the compound was calculated relative to anthracene solution as standard. Each time the total intensity of fluorescence emission was measured for the standard and the sample from the area of the fluorescence spectrum recorded over the whole range of emission under identical conditions, Molar extinction coefficient (ε) data have been reported in term of its logarithm log ε, the Stokes' shift data been calculated in different micellar media and are expressed in term of nanometers.

RESULTS AND DISCUSSION

The metholic solution of 2,3-diaminonaphthalene showed maximum excitation peak at 370 nm and the maximum emission peak at 410 nm. All the non-ionic surfactants, on addition to 2,3-diaminonaphthalene solution caused a continuous enhancement in its fluorescence emission intensity with increasing concentration. Among them TX-100 exerted the maximum effect accompanied with 5-10 nm red shift in λ_{em}. The changes in the fluorescence spectra of 2,3-diaminonaphthalene on addition of TX-100 are shown in fig. 1. All the anionic surfactants, caused initially decrease and then increase in the intensity of the emission peak on addition of the surfactants with 5 nm red shift. While on addition of cationic surfactant fluorescence intensity quenched. Effect of solvent (methanol) was also studied upto 100% (v/v) methanol, the fluorescent intensity increased gradually. Fluorescent intensity of 2,3-diaminonaphthalene in presence and absence of the non-ionic surfactants are given in Table 1 .

Table1: Effect of non-ionic surfactants on the fluorescence intensity (F.I.) of 2,3-diaminonaphthalene

S. No.	% of Tween-40	F.I.	% of Tween-80	F.I.	% of TX-100	F.I.
1.	0.000	18	0.000	18	0.000	18
2.	0.01	21	0.01	24	0.01	33
3.	0.1	25	0.1	28	0.1	43
4	0.7	30	0.7	39	0.7	55

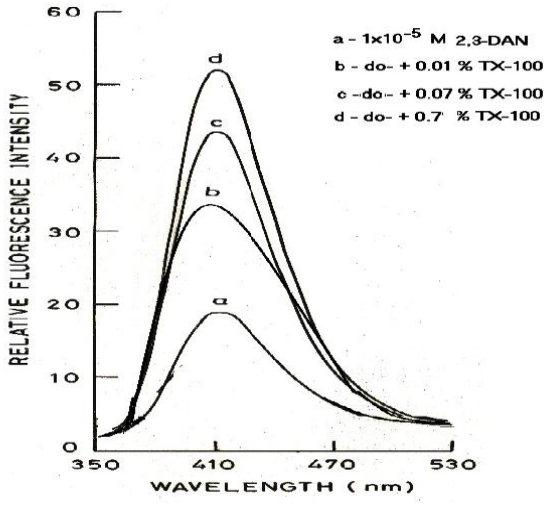

Fig.1: Fluorescence emission spectra in presence of nonionic surfactant TX-100

There appeared an absorption peak at 330 nm. All the non-ionic, anionic and cationic surfactants show almost parallelism with fluorescence spectra. The calculated fluorescence quantum yield data (ϕ_f) of the surfactant added 2,3-diaminonaphthalene solution showed parallelism with changes in fluorescence intensity. Quantum yield values obtained show increasing trend with non-ionic surfactants while with anionic surfactants, (ϕ_f) values initially decreased and then increased. Highest (ϕ_f) values obtained are for TX-100 added 2,3-diaminonaphthalene solution. The molar extinction coefficient ($\log \varepsilon$) values showed a gradual increase on raising the concentration of nonionic surfactants. The calculated Stokes' shift values show that it becomes larger for high concentration of 2,3-diaminonaphthalene solution illustrated in table 2 .

Table 2: Stokes' shift data values of 2,3-diaminonaphthalene

S. No.	Concentration of compound	F.I.	λ_{ex} (nm)	λ_{em} (nm)	Stokes' Shift (cm^{-1})
1.	1×10^{-5} M	18	370	410	2632
2.	3×10^{-5} M	20	370	410	2632
3.	5×10^{-5} M	22	368	410	2732
4.	7×10^{-5} M	25	368	415	3033
5.	1×10^{-4} M	27	368	415	3033
6.	3×10^{-4} M	33	366	415	3226

The results obtained can be explained on the basis of solubilization by the micelles present in the surfactant solution at or marginally above CMC. The maximum fluorescence emission intensity enhancement of 2,3-diaminonaphthalene was obtained with TX-100, which has also been supported by absorbance values and $\log \varepsilon$ values. The enhancement of fluorescence of 2,3-diaminonaphthalene in TX-100 micellar media can be attributed to the increase in quantum efficiency of fluorescence. Furthermore, the quantum yield of fluorescence is higher in nonpolar medium because of the lesser effect of other deactivation processes which compete with fluorescence[16,17]. Thus the increased (ϕ_f) values showed that the micelles have been possibly adsorbed on to the dispersed microcrystals of 2,3-diaminonaphthalene. The molecules of 2,3-diaminonaphthalene have been subsequently solubilised by incorporation into the interior nonpolar core of the micelles. Sufficiently large values of molar extinction coefficient ($\log \varepsilon$) is assigned to the π-π* transitions .The large magnitude of Stokes' shift of 2,3-diaminonaphthalene are due to hydrogen-bond formation, between solute and solvent in ground state[18-20]. Quenching can also be caused by non-radiation loss of energy from the excited molecules. Fluorescence quenching was also observed by the addition of cationic surfactants, which may be attributed to the electrostatic preferential interaction between the polar substituent of 2,3-diaminonaphthalene molecules where it loses the coplanarity. The quenching may also be due to interaction between the π-electron system of the excited state fluorophore and quencher molecule due to the presence of nucleophilic pyridine ring in the structure which make it act as a quencher via hydrogen bond between the proton donor and acceptor. This will result in delocalization of the π-electrons of the excited state and hence loss of fluorescence [21]. The absorption spectra of 2,3-diaminonaphthalene are very less affected on adding surfactants as compared to fluorescence spectra. This may be due to the fact that absorption is less sensitive to its environment as compared to fluorescence.

APPLICATIONS

This study finds application in biochemical and forensic l analyses. Hence, micellar solubilization finds an extensive application in biochemical and biomedical fields.

CONCLUSIONS

The present analysis and interpretation suggests that experimental results observed and the theoretically calculated spectral data are found to be in good agreement. During micellar solubilization of 2,3-diaminonaphthalene the incorporation of solute influences the balance of favourable and unfavourable forces guiding micellization and structural changes occurring due to aggregation, dissociation and hydrogen bonding. Aside from the presentation of the spectral and photo physical data, present kind of study finds application in biochemical and forensic analysis. Hence, micellar solubilization finds an

extensive application in biochemical and biomedical fields. The present analysis is an effort to mimic this at laboratory level.

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