

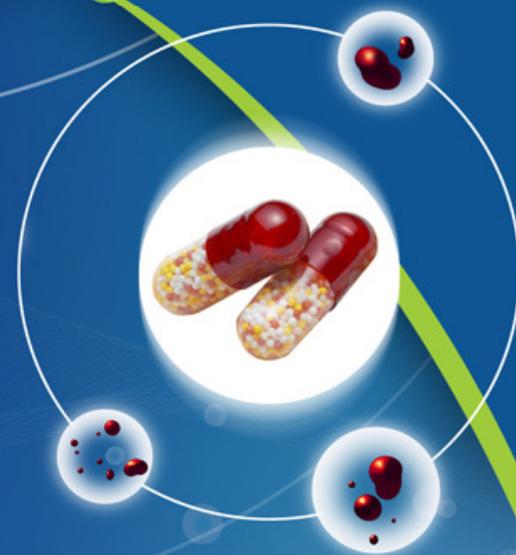


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Research Article

MICELLER SOLUBILIZATION OF 1-NAPHTHOL BY SPECTROFLUORIMETRY

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ABSTRACT

1-Naphthol is widely used chemical in industry biomedical and forensic sciences. 1-naphthol is precursor to a variety of insecticides including carbaryl and pharmaceuticals nadolol. Micellar solubilization of 1-naphthol in nonionic 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 1-naphthol 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 1-naphthol molecules have been solubilized. 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, 1-Naphthol, Fluorescence, Solubilization

INTRODUCTION

Fluorescence spectroscopy is an important tool of investigation in many areas in analytical sciences, its advantage is extremely high sensitivity and selectivity even single molecule can be detected and it achieves a high spatial resolution and time resolution in combination with microscopic techniques as laser techniques, respectively [1]. In material sciences, this is used to study structure and dynamics of surfaces, particularly in this area of biochemistry and molecular genetics, fluorescence spectroscopy has become a dominating technique.

Together with the latest imaging techniques, fluorescence spectroscopy allows a real time observation of the dynamics of intact biological system with an unprecedented resolution [2].

The formation of colloidal sized clusters in solutions, known as micelles are of particular significance in pharmacy because of their ability to increase the solubility of sparingly soluble substances in water. The most striking feature of micelles is the ability to solubilize a variety of compounds in its different regions [3]. 1-Naphthol is widely used chemical in industry biomedical and forensic sciences. 1-naphthol is precursor to a variety of insecticides including carbaryl and pharmaceuticals nadolol. A rapid and automated method based on coupled-column liquid chromatography (LC-LC) with fluorescence detection has been developed for the determination of 1-naphthol in human

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urine[4]. A simple multidimensional system for direct injection of large volumes has been developed for the determination of three naphthalene-derivative pesticides [2-(1-naphthyl) acetamide (NAD), 1-naphthyl methylcarbamate (carbaryl) and 1-naphthol] in water using fluorescence detection[5]. The excited state proton transfer (ESPT) behavior of excited singlet acids like 1-naphthol in lipid bilayer membranes has been extensively studied [6-9].

N. Tanaka et al [10]. have studied changes in co-ordination number of Co^{+2} ion and fluorescence spectrum of 1-naphthol during the sol-gel reaction of TEOS, and concluded that under the sol gel transition 1-naphthol forms the contact ion pair and separate ion pair with six coordinated Co^{+2} . A fully automated method based on on-line solid phase extraction (SPE) then liquid chromatography with diode array and fluorescence detection has been developed for the trace level determination of carbaryl and 1-naphthol at ppt level in environmental water samples by Hidalgo and Coworkers[11]. The characterization of 1-naphthol bonded to polyurethane foam (1-Nap-PUF) and the sorption behaviour of Ni^{+2} and Cu^{+2} on 1-Nap-PUF have been investigated by Noawed and Shaahat [12]. Pappayee and Mishra [13]. have evaluated of 1-naphthol as a convenient fluorescent probe for monitoring ethanol-induced interdigitation in lipid bilayer membrane.

The present study includes a study on the influence of various nonionic, anionic and cationic surfactants on the fluorescence and absorption spectra of 1-naphthol. The results have been interpreted from the calculations of molar extinction coefficient, empirical fluorescence coefficient, quantum yields of 1-naphthol fluorescence in various micellar media and Stokes' shift calculations at various concentration of 1-naphthol .

MATERIALS AND METHODS

MATERIALS

Analytically pure 1-naphthol was a Merck sample. The following surfactants were

employed : (A) Nonionic (i) TX-100 : Polyoxyethylene tert-octyl phenyl ether (ii) Tween-80 : Polyoxyethylene sorbitain monooleate (iii) Tween-20 : Polyoxyethylene sorbitain monolaurate (B) Anionic (i) SLS : Sodium lauryl sulphate (ii) DBSS : Dodecylbenzyl sodium sulphonate (iii) DSSS : Dioctyl sodium sulphosuccinate (C) Cationic (i)CPC: Cetylpyridinium chloride (ii) CTAB : Cetyltrimethyl ammonium bromide (iii) MTAB : Myristyltrimethyl ammonium bromide. All the surfactants were either of Sigma (USA) or BDH (UK) products.

METHODS

The stock solution of 1-naphthol was prepared in distilled methanol. All the experiments were performed around 23-25 C in aqueous medium containing 1% (v/v) methanol keeping the final concentration of 1-naphthol at 3×10^{-5} M for fluorescence studies. For absorption studies the concentration of 1-naphthol was kept at 1×10^{-4} M throughout the experiments.

All the fluorimetric experiments were carried out with Perkin Elmer Fluorescence Spectrophotometer (Model No. 204 A) with a synchronized strip chart recorder (Model no. 056). A Xenon lamp was used as a light source. For recording the fluorescence excitation and emission spectra, its slit width was kept at 10 nm and a cell of 1 cm path length was used. The absorption measurements were made with Hewlet Packard (HP) 8452, and diode array spectrophotometer respectively.

The purity of the surfactants was checked by determining their CMC values the help of surface tension measurements, employing drop-weight method. The values obtained coincided with the recorded values. The absolute fluorescence quantum yield (ϕ_f) of 1-naphthol was calculated relative to anthracene solution as standard. Fluorescence emission of anthracene is in the same range as that of 1-naphthol . Approximate corrections were made to compensate for different absorption of the compound and the 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 data have been reported as its logarithm ($\log \epsilon$). The Stokes' shift data have also been calculated and are expressed in nanometers.

RESULTS AND DISCUSSION

The metholic solution of 1-naphthol showed maximum excitation peak at 340 nm and the maximum emission peak at 360 nm as shown in fig. 1

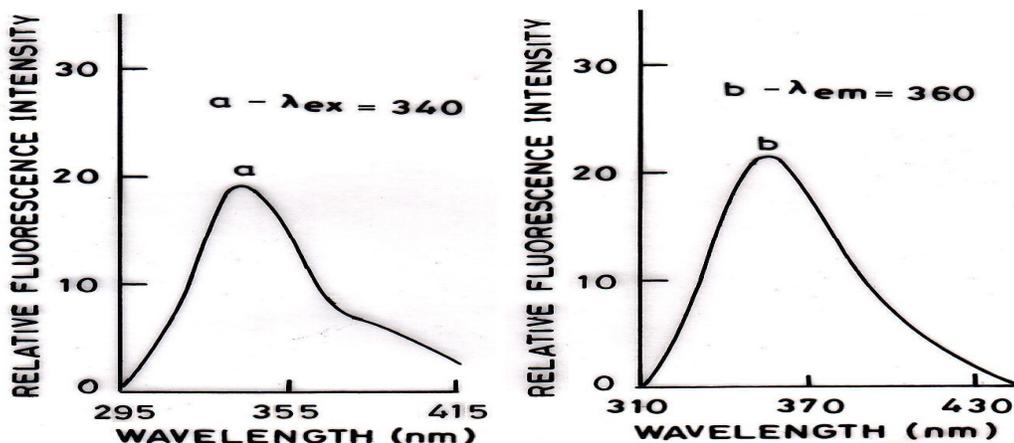


Fig.1 Excitation and emission spectra of 1-naphthol

All the nonionic surfactants, on addition to 1-naphthol solution caused a continuous enhancement in its fluorescence emission intensity with increasing concentration. Among them TX-100 exerted the maximum effect accompanied without any shift in λ_{em} . The changes in the fluorescence spectra of 1-naphthol on addition of tween-80 and TX-

100 are shown in Fig. 2. All the anionic surfactants, caused increase in the intensity of the emission peak on addition of the surfactants with 5-10 nm red shift. Effect of solvent (methanol) was also studied upto 100% (v/v) methanol, the fluorescent intensity increased gradually

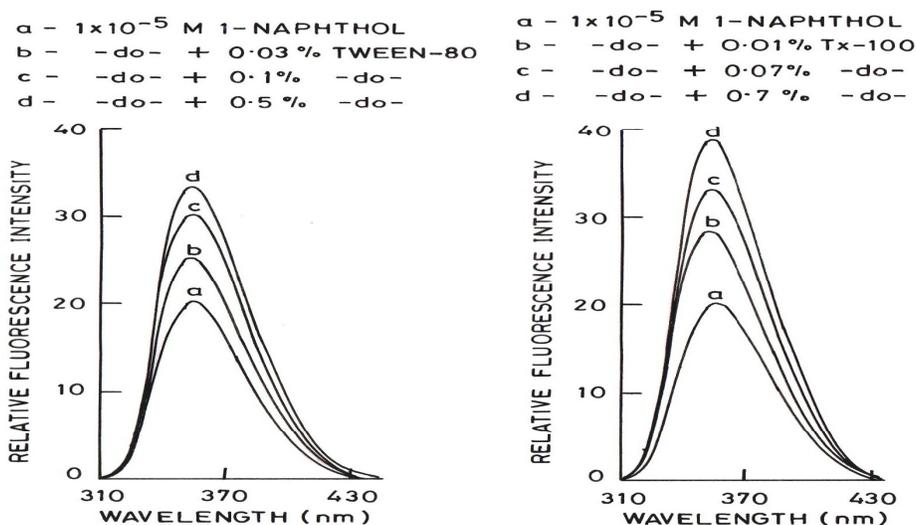


Fig:2 Fluorescence emission spectra in presence of nonionic surfactants tween-80 and TX-100

Fluorescent intensity of 1-naphthol in presence and absence of the surfactants are given in Table 1 and 2.

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

S. No.	% of Tween-40	F.I.	% of Tween-80	F.I.	% of TX-100	F.I.
1.	0.000	20	0.000	20	0.000	20
2.	0.01	27	0.01	24	0.01	28
3.	0.1	32	0.1	28	0.1	35
4.	0.7	35	0.7	33	0.7	39

Table 2: Effect of anionic surfactants on the fluorescence intensity (F.I.) of 1-naphthol

S. No.	% of DBSS (w/v)	F.I.	% of SLS (w/v)	F.I.	% of DSSS (w/v)	F.I.
1.	0.000	20	0.000	20	0.000	20
2.	0.01	25	0.01	24	0.01	24
3.	0.1	31	0.1	29	0.1	29
4.	0.7	38	0.7	33	0.7	31

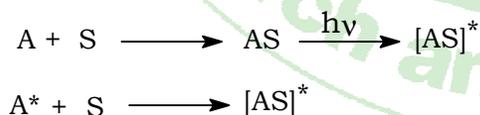
There appeared an absorption peak at 330 nm. All the nonionic, anionic and cationic surfactants show almost parallelism with fluorescence spectra. The calculated fluorescence quantum yield data (ϕ_f) of the surfactant added 1-naphthol solution showed parallelism with changes in fluorescence intensity. Quantum yield values obtained show increasing trend with nonionic surfactants while with anionic surfactants, (ϕ_f) values

initially decreased and then increased. Highest (ϕ_f) values obtained are for TX-100 added 1-naphthol solution. The molar extinction coefficient ($\log \epsilon$) 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 1-naphthol solution illustrated in Tables 3.

Table 3: Stokes' shift data values of 1-naphthol

S.No.	Concentration of compound	F.I.	λ_{ex} (nm)	λ_{em} (nm)	Stokes' Shift (cm ⁻¹)
1.	1 x 10 ⁻⁵ M	20	340	360	1633
2.	3 x 10 ⁻⁵ M	21	340	360	1633
3.	5 x 10 ⁻⁵ M	23	340	360	1633
4.	7 x 10 ⁻⁵ M	25	338	365	2014
5.	1 x 10 ⁻⁴ M	27	338	365	2188
6.	3 x 10 ⁻⁴ M	30	338	365	2188
7.	5 x 10 ⁻⁴ M	31	338	365	2188
8.	1 x 10 ⁻³ M	33	336	365	2364

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 1-naphthol was obtained with TX-100, which has also been supported by absorbance values and $\log \epsilon$ values. The enhancement of fluorescence of 1-naphthol 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 fluorescencer [14]. Thus the increased (ϕ_f) values showed that the micelles have been possibly adsorbed on to the dispersed microcrystals of 1-naphthol. The molecules of 1-naphthol have been subsequently solubilized by incorporation into the interior nonpolar core of the micelles. Sufficiently large values of molar extinction coefficient ($\log \epsilon$) is assigned to the π - π^* transitions. The large magnitude of Stokes' shift of 1-naphthol are due to hydrogen-bond formation, between solute and solvent in ground state. This bond breaks following excitation to S_1 but reforms following proton transfer [15]. The hydrogen bonded excited state can be produced via two routes as shown by following scheme in which S represents the solvent molecule and A represents the fluorophore [16].



The absorption spectra of 1-naphthol 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.

CONCLUSION

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 1-naphthol 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 photophysical data, present kind of study finds application in biochemical and agro-chemical analyses. 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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