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Research Article

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Spectrofluorimetric study of 1-naphthoic acid in micellar surfactant solution

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ABSTRACT

This study focuses on the spectrofluorimetric behaviour of a pharmaceutically and analytically important molecule 1-naphthoic acid in the presence of various surfactant solutions. Micellar solubilization is a powerful alternative for dissolving hydrophobic compounds in aqueous environment. Fluorescence and absorption spectroscopy are the two techniques used to monitor the micellar solubilization studies of 1-naphthoic acid. The influence of surfactant, concentration and working experimental conditions on the fluorescence spectra of 1-naphthoic acid 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-naphthoic acid 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-Naphthoic acid, Fluorescence, Solubilization

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INTRODUCTION

Today, fluorescence spectroscopy is an important tool of investigation in many areas in analytical sciences. During the past 35 years there has been a remarkable growth in the use of fluorescence in the biological sciences [1]. Fluorescence spectroscopy and time-resolved fluorescence are considered to be primarily research tools in biochemistry and biophysics [2]. This emphasis has changed, and the use of fluorescence has expanded. Fluorescence is now a dominant methodology used extensively in biotechnology, flow cytometry, medical diagnostics, DNA sequencing, forensics, and genetic analysis, to name a few. Fluorescence detection is highly sensitive, and there is no longer the need for the expense and difficulties of handling radioactive tracers for most biochemical measurements. There has been dramatic growth in the use of fluorescence for cellular and molecular imaging. Fluorescence imaging can reveal the localization and measurements of intracellular molecules, sometimes at the level of single-molecule detection [3-4].

Micelles are dynamic microheterogeneous structure containing surfactant molecules and constitute an important research subject [5-6]. It is possible within their internal environment to include some compounds that are insoluble in water, to perturb their kinetics of many photophysical processes and to provide structural mimics of biological membrans [7]. Surfactants because of their ability to solubilize the membrane proteins are extremely important in simulating the complex environmental condition present in larger bioaggregates such as biological membranes [8]. 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. Surfactants

play a vital role in various drug delivery. They are pharmaceutically acceptable cosolvents and are employed to increase the solubility of compounds.

1-Naphthoic acid is an important pharmaceutically and analytically molecule. It is used as an intermediate for the synthesis of pharmaceuticals, photochemicals, plant growth hormones, dyes and other organic compounds. The present study includes a study on the influence of various nonionic, anionic and cationic surfactants on the fluorescence and absorption spectra of 1-naphthoic acid. The results have been interpreted from the calculations of molar extinction coefficient, empirical fluorescence coefficient, quantum yields of 1-naphthoic acid fluorescence in various micellar media and Stokes' shift calculations at various concentration of 1-naphthoic acid.

EXPERIMENTAL SECTION

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 1-naphthoic acid(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 1-naphthoic acidat $1 \text{ X } 10^{-5}$ M. All the surfactants used were either of sigma (USA) or BDH product. The following surfactants were employed.

(A) Nonionic: Polyoxyethylene tertoctyl phenol (TX-100), Polyoxyethylene sorbitan monolauriate (Tween-80) and Polyoxyethylene sorbitan monopalmitate (Tween-40)
(B) Cationic: Cetyltrimethyl ammonium Bromide (CTAB), Cetylpyridinium chloride (CPC) and Cetylpyridinium bromide (CPB)
(C) 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 1-naphthoic acid showed maximum excitation peak at 295 nm while the emission spectrum showed a peak at 370 nm as shown in fig. 1.

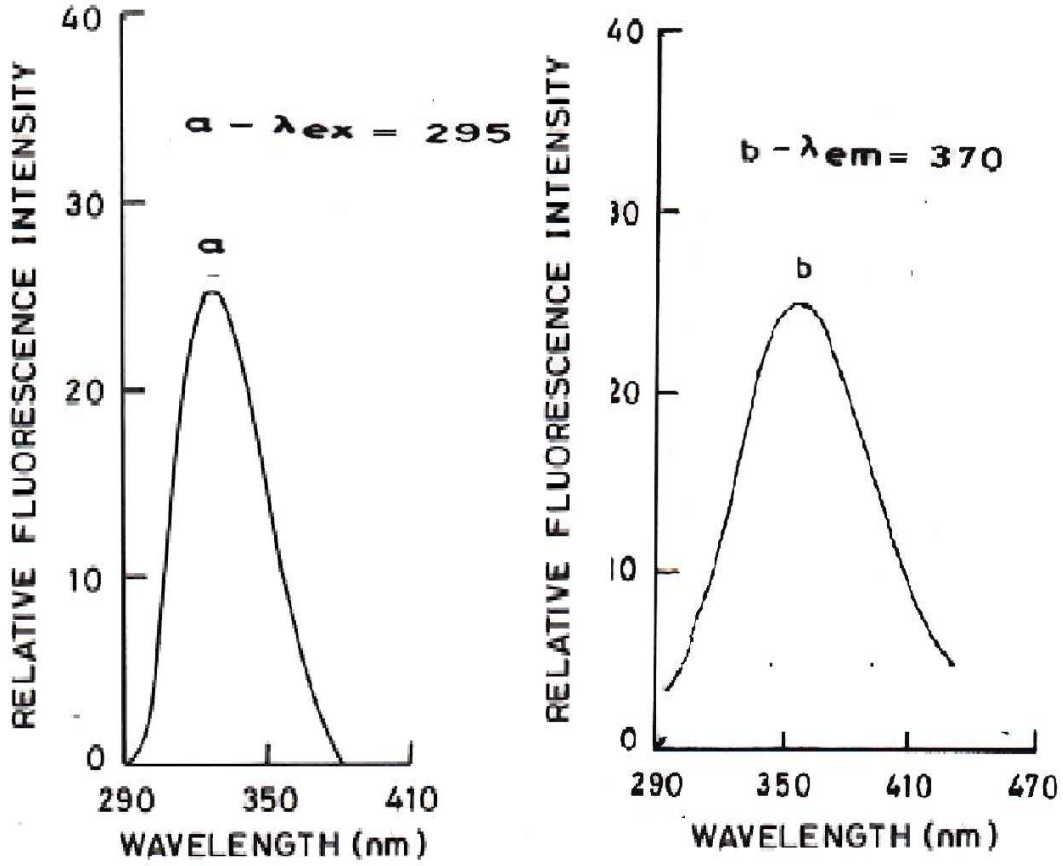

Fig.1: Excitation and emission spectra of 1-naphthoic acid

On addition of the nonionic surfactants caused an enhancement in the fluorescence intensity with 5–15 nm gradual red shift. Among these surfactants TX-100 exerted maximum effect. The changes in fluorescence intensity of 1-naphthoic acid on addition of TX-100 are showed in Fig.2.

On addition of any of the anionic surfactant, initially the fluorescence intensity decreased. The further addition of the surfactant showed enhancement in the fluorescence intensity of 1-naphthoic acid. On addition of the cationic surfactant, initially it caused a enhancement in fluorescence intensity while its further addition showed a gradual decrease in the fluorescence intensity with a 5 nm gradual blue shift. The changes observed in fluorescence emission intensity in presence of surfactants is as given in table 1.

Table 1: Fluorescence intensity (FI) of the 1-naphthoic acid ($1X10^{-5}$M) in the absence and presence of surfactants
λ_{ex}= 295 nm, λ_{em}= 370 nm , P.M. Gain = 2, Sensitivity Range = 0.1

S. No.	Name of Surfactant	Fluorescence intensity(FI) in the absence of surfactant	Concentration of surfactant used(%)	Maximum Fluorescence intensity(FI) in the presence of surfactant
1	TX-100	24	0.7	44
2	Tween -80	24	0.7	36
3	Tween – 40	24	0.7	32
4	DBSS	24	0.7	33
5	SLS	24	0.7	30
6	DSSS	24	0.7	29
7	CTAB	24	0.7	12
8	CPB	24	0.7	19
9	CPC	24	0.7	14

The absorbance of 1-naphthoic acid was found to be maximum at 280 nm. The effect of all the three classes of surfactants on absorption spectra showed a similar trend to that of fluorescence spectra. The fluorescence quantum

yield values obtained showed parallel trends to fluorescence intensity. Molar extinction coefficient values showed maximum effect in nonionic surfactants. The result observed for molar extinction coefficient (ε) and quantum yield (Φ_f) for 1-naphthoic acid on addition of TX -100 are as given in table 2.

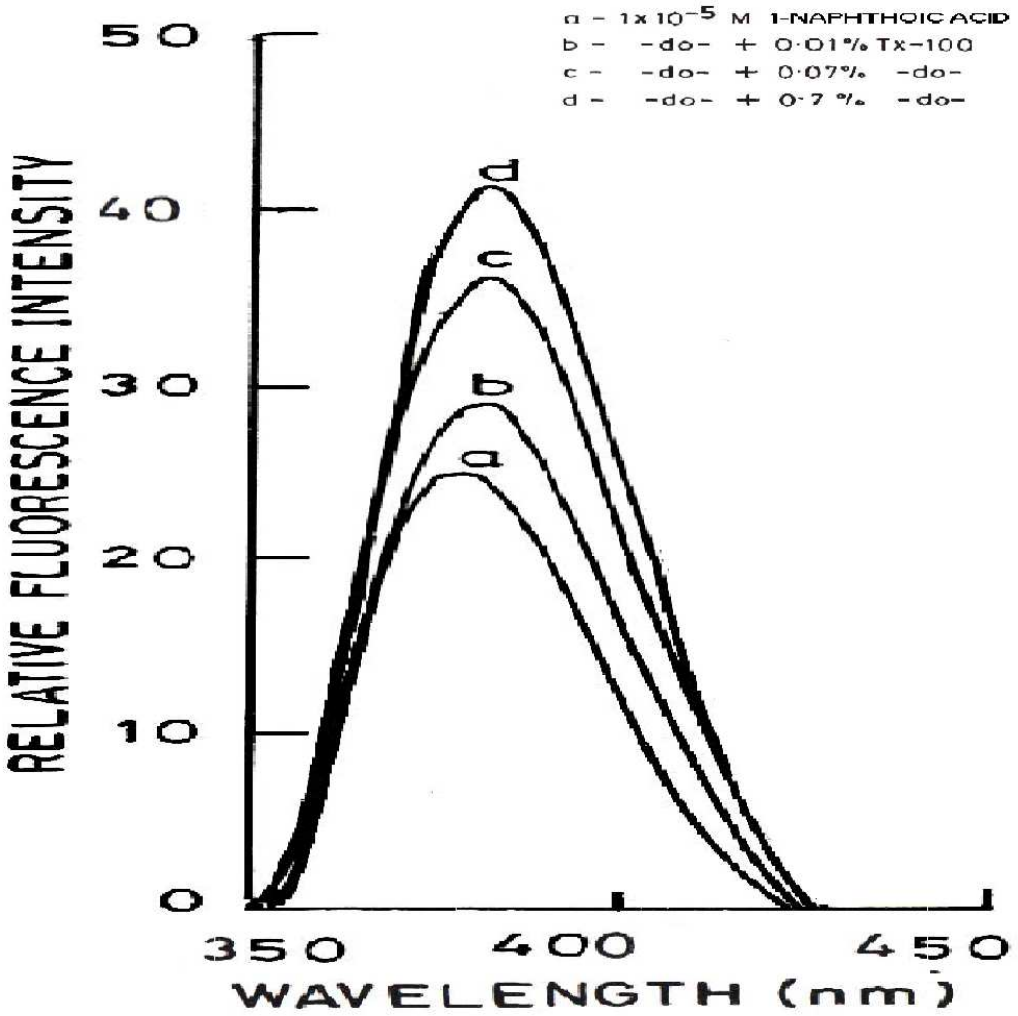

Fig.1 : Effect of surfactant TX-100 on fluorescence intensity of 1-naphthoic acid

Table 2: Molar extinction coefficient(logε) , quantum yield (Φ_f) and empirical fluorescence coefficient (k_f) of 1-naphthoic acidon addition of TX-100

S. No.	TX-100 used (%)	log ε ($dm^{-3}Mol^{-1}cm^{-1}$)	Quantum yield ϕ_f	k_f x10^4 (per mole)
1.	0.000	3.031	0.593	481
2.	0.01	3.112	0.597	503
3.	0.07	3.171	0.645	602
4.	0.7	3.202	0.664	632

Stokes' shift for 1-naphthoic acid at room temperature was increased with its rising concentration. The quantum yield values increased with increasing concentration of the nonionic surfactants and were found to be highest when TX-100 was added to 1-naphthoic acid solution. Enhancement in the fluorescence intensity of the compound on adding surfactant can be attributed to the increase in the quantum efficiency of fluorescence. Furthermore the

quantum yield of fluorescence was higher in nonpolar medium, because of the lesser effect of other deactivation processes which compete with fluorescence [9].

Thus, increase in quantum yield suggest that the surfactants have solubilized the suspended molecule of 1-naphthoic acid in solution. The result show that TX-100 micelles have solubilized 1-naphthoic acidvery efficiently even at its low concentration. To explain its action, an oblate ellipsoid model has been postulated for TX-100 [10-11]. Although a spherical model requires mixing of the hydrophobic part and the hydrophilic part, while the octyl phenyl groups and the polyoxyethylene groups of TX-100 can separate each other and each layer packs well in the oblate ellipsoid model. This model, therefore predicts the hydrophobic and less fluid interior of TX-100 micelles. Kano et al. [12] have found that the interior of the TX-100 is more hydrophobic than those of the ionic micelles. The non polar environment of the TX-100 micelles interior be preferable to incorporate hydrophobic 1-naphthoic acid molecule. The highest solubilizing effect of TX-100 may also be due to the preference of ether linkage in it, while the other nonionic surfactants employed were esters. The higher polarity of the ionic micelles may be ascribed to the loose fluctuating and disorder in structure of these micelles . 1-Naphthoic acid must leave its aggregate and exclude water molecules inside the ionic micelle. These processes should cause slow solubilization. It is assumed that ionic micelles are too hydrophilic to solubilize the hydrophobic 1-naphthoic acidmolecule to larger extent. However, in the case of cationic surfactants fluorescence intensity was quenched. This indicates electrostatic preferential interaction between the π electrons of the solubilizate molecule and cationic head group of the surfactant which may result in change in geometry of the solubilizate molecule where it loses coplanarity leading to decrease in emission intensity.

Absorption spectra of 1-naphthoic acidare very less affected in miceller media as compared to the fluorescence spectra. This may be because absorption is less sensitive to its environment as compared to fluorescence. No major change in the nature of absorption spectrum indicates no structural change due to complex formation or dissociation or hydrogen bonding between 1-naphthoic acid in the ground state and the surfactant. Blue shift obtained in the absorption maxima may be because of the difference in solvation energy of the solubilizate molecule in the ground state and the excited state. The large magnitudes of Stokes' shift of 1-naphthoic acidare due to hydrogen bond formation between solute and solvent in ground state, this bond then breaks following excitations to S_1 state but reforms following proton transfer [13-14]. The hydrogen bonded excited state can be produced via two routes as shown by the following scheme in which "S" represents a solvent molecule and "A" represents 1-naphthoic acid fluorophore [15].

$$A+S \rightarrow AS \rightarrow (AS)^*$$
$$A^*+S \rightarrow (AS)^*$$

The sufficiently large values of log ε are assigned to the $\pi - \pi^*$ transitions and also confirms the increasing trend of Stokes' shift values. The red shift in the emission wave length of the 1-naphthoic acidin miceller media is attributed to the hydrogen bonding capacity of the molecule.

CONCLUSION

The present analysis indicates that during solubilization of solubilizate1-naphthoic acid into the surfactant system, the incorporation of the solubilizate influence the balance of favourable and unfavourable forces guiding micellization and structural changes occurring due to aggregation, dissociation and hydrogen bonding. Hence the process of micellization followed by solubilization of 1-naphthoic acid would catalyse its pharmaceutical activities which may serve better results in medicinal and analytical fields. Thus one can generalize the physical understanding to study the phenomenon of micelllar solubilization and 1-naphthoic acid may be used as a micro-environment probe.

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REFERENCES

[1] JR Lakowicz, Principles of Fluorescence Spectroscopy, Plenum Press: New York, **1999**.
[2] B Valeur, Molecular Fluorescence : Principles and Applications, Wiley Interscience: New York, **2002.**
[3] M Andreeff and D Pinkel, Introduction to Fluorescence In Situ Hybridization : Principles and Clinical Applications, Wiley Intersciences: New York, **1999.**

[4] EB Shera, NK Seitzinger. LM Davis, RA Keller and SA Soper , *Chem PhysLett.*,**1990,**74(6),553-557
[5] KL Mittal, Solution Chemistry of surfactants, Vol. 1 and 2, Plenum Press, New York,**1979.**
[6] KL Mittal,Micellization Solubilization and Micromulsion Vols 1 and 2, Plenum Press, New York **1977.**
[7] J H Fendler , Membrane Mimetic Chemistry, Wiley Interscience:New York, **1982.**
[8] C Tanford ,The Hydrophobic effect : Formation of Micelles and Biological Membrane. Wiley: New York**, 1973.**
[9] H Shizuka, M Ekushima, K Fuzu, T Kobayashi, H Ohtani M Hohino, Bull. Chem. Soc. Japan, **1985**, 58,2107.
[10] PH Elworthy, AT Florene, CB Macfarlane , Solubilization by surface active agents, Chapman and Hall , London, **1968.**
[11] Y Moroi, Micelles Theoretical and Applied Aspects, Plenum Press: New York, **1992.**
[12] K Kano, H Goto T Ogawa, *Chem Lett.*,**1981**, 653-656.
[13] A Maciejewski, J Kubicki KJ Dobek, *Phys. Chem. B.*, **2003**, 107, 13986-13999.
[14] D Banerjee, AK Laha, S Bagchi, *Ind. J. Chem sec A***.,1995,** 34 ,94-101.
[15] CA Parker, Photoluminescence of solutions**,** Elsevier Publishing Company,England **1968.**