ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Fluorescence Spectral Study of the Solubilization of 1, 10-Phenanthroline In Micellar Surfactant Solution.

Sunil Kumar Jangir* and Seema Acharya.

Department of Chemistry, Jai Narain Vyas University, Jodhpur (Raj.) India

ABSTRACT

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 1,10-phenanthroline. 1,10-Phenanthroline is a heterocyclic organic compounds. It is a bidantate ligand and is commonly used as a chelating agent for metal ions. It's complexes with Co, Cu, Fe and Zn are widely used for antifungal and antimicrobial activity. The emission intensity of 1,10-phenanthroline is significantly enhanced in nonionic and anionic micellar media. The solubilizing action of the surfactant has also been determined by theoretical calculated spectral parameters like empirical fluorescence coefficient, quantum yield, molar absorption coefficient and stokes' shift value. The fluorescence as well as the theoretically calculated spectral data has been used to characterize the heteroenvironment of the micelles in terms of their polarity, probe solubilization site and critical micellar concentration (CMC). This article briefly discusses the importance of surfactants in biological system model as well as the use of micelles in pharmacy as an important tool that finds numerous applications.

Keywords: Micellization, 1,10-phenanthroline, fluorescence, solubilization.

Corresponding author
Email: sjinorganic@gmail.com

ISSN: 0975-8585

INTRODUCTION

1,10-Phenanthroline is a heterocyclic organic compounds. It is a bidantate ligand and is commonly used as a chelating agent for metal ions. The ligands, 1,10-phenanthroline (o-phen) and 2,2'-bipyridine (bpy) are strong field bidentate ligands that form very stable chelates with many first row transition metals. These ligands, as well as some of their derived complexes, do exhibit antimicrobial properties and antifungal activity. Antimicrobial activities of cobalt(ii), copper(ii) and zinc(ii) mixed-ligand complexes containing 1,10-phenanthroline and 2,2'-bipyridine were carried out by Agwara et al. [1]. Tris(1,10-phenanthroline) iron(II) was studied for antifungal activity by Fernanda et al. [2].

Chen and Sigman [3]. have done the chemical conversion of tryptophan gene (trp) repressor of E.coli into a site- specific nuclease by covalently attaching it to the 1,10-phenanthroline copper complex. Brand et al. [4]. have found that the per oxovanidium compound $VO(O_2)$ 1,10-phenanthroline (bpV(phen) is capable of lowering blood glucose levels and suggest that chelating agent specially 1,10-phenanthroline may be used as penetration enhancers for the delivery of certain compound.

Micelles are dynamic microheterogeneous structure containing surfactant molecules and constitute an important research subject [5-7]. 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 membrane [8-12]. 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 [13]. 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[14-16].

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. Thus, increasing their bioavailability, stay in the blood long enough to provide a gradual accumulation in the required area. Moreover, specific legands can be attached to optimize the controlled release and specificity of pharamacological effect.

METERIAL 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 1,10-phenanthroline (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 1,10-phenanthroline at 1×10^{-5} M. All

the surfactants used were either of sigma (USA) or BDH product. The following surfactants were employed.

- Nonionic: Polyoxyethylene tertoctyl phenol (TX-100) , Polyoxyethylene sorbitan monolauriate (Tween-80) and Polyoxyethylene sorbitan monopalmitate (Tween-40)
- Cationic: Cetyltrimethyl ammonium Bromide (CTAB) , Cetylpyridinium chloride (CPC) and Cetylpyridinium bromide (CPB)
- 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 Maximum excitation and emission wavelength of 1,10-phenanthroline was observed at 315 nm and 365 nm respectively fig 1. Fluorescence intensity increased monotonically with increasing concentration of the nonionic surfactants with 5-10 nm red shift. Among nonionic surfactants TX-100 showed maximum effect. On addition of anionic surfactant to the 1,10 phenanthroline solution an increase in fluorescence intensity with all these three surfactants was observed with 5-10 nm red shift. On addition of cationic surfactant for the solution of 1,10-phenanthroline the emission decreased with 5-10 nm blue shift .

The minimum and maximum fluorescence intensity in absence and presence of nonionic, anionic and cationic surfactants are given in table 1. The fluorescence spectral changes on addition of TX-100 are as given in fig. 2. The absorbance of 1,10-phenanthroline was found to be maximum at 300 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), λ_{abs}, λ_{em}, and quantum yield (Φ_f) for 1,10–phenanthroline on addition of TX -100 are as given in table 2.

ISSN: 0975-8585

Table 1: Fluorescence intensity (FI) of the 1,10-phenanthroline ($1X10^{-5}M$) in the absence and presence of surfactants. λ_{ex}= 315 nm, λ_{em}= 365 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	21	0.7	31
2	Tween -80	21	0.7	37
3	Tween – 40	21	0.7	38
4	DBSS	21	0.7	33
5	SLS	21	0.7	33
6	DSSS	21	0.7	30
7	CTAB	21	0.7	14
8	CPB	21	0.7	18
9	CPC	21	0.7	15

Table 2: Absorption maxima (λ_{abs}), fluorescence maxima (λ_{em}), Molar extinction coefficient(logε) , quantum yield (Φ_f) and empirical fluorescence coefficient ( ) of 1,10–phenanthroline on addition of TX-100.

S.No.	TX-100 used (%)	λ_{abs} (nm)	λ_{em} (nm)	log ε ($dm^{-3}Mol^{-1}cm^{-1}$)	Quantum yield	$x10^4$ (per mole)
1.	0.000	300	365	3.767	0.6723	210
2.	0.01	300	370	3.787	0.6856	280
3.	0.07	300	375	3.891	0.6920	330
4.	0.7	306	375	3.928	0.7114	380

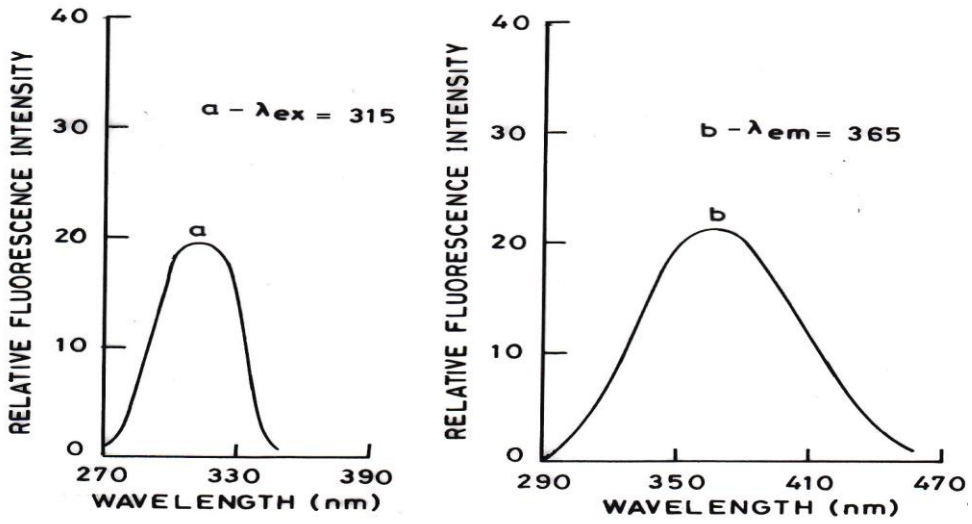

Fig.1 Excitation and emission specta of 1,10 phenanthroline

ISSN: 0975-8585

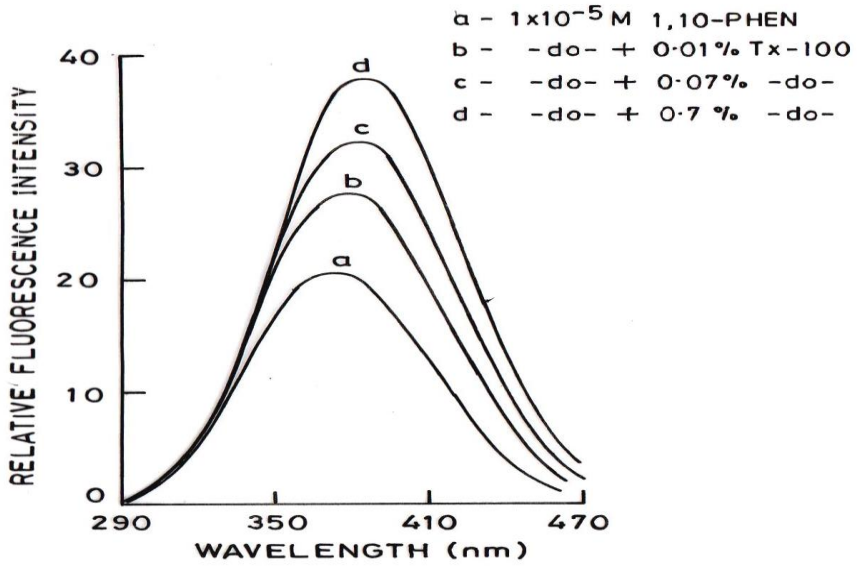

Fig.2 Influence of addition of TX-100 on fluorescence intensity of 1,10-phenanthroline

Stokes' shift for 1,10–phenanthroline 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 1,10-phenanthroline 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 flourescence[17].

Thus, increase in quantum yield suggest that the surfactants have solubilized the suspended molecule of 1,10-phenanthroline in solution. The result show that TX-100 micelles have solubilized 1,10-phenanthroline very efficiently even at its low concentration. To explain its action, an oblate ellipsoid model has been postulated for TX-100 [18]. 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. [19] 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 1,10-phenanthroline 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 [20]. 1,10-phenanthroline 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 1,10-phenanthroline molecule 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 1,10-phenanthroline are 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 1,10-phenanthroline 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 1,10-phenanthroline are 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 [21]. 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 1,10-phenanthroline fluorophore

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

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 1,10–phenanthroline in miceller media is attributed to the hydrogen bonding capacity of the molecule.

CONCLUSION

The present analysis and interpretation suggest that experimental results obtained and the theoretically calculated spectral data are found to be in good agreement. This proves the validity of the investigation made. Although 1,10-phenanthroline is toxic in nature and is an environment pollutant, but, it has some great uses. 1,10-phenanthroline is used as chealating agent in pharmaceuticals. Hence the process of micellization followed by solubilization of 1,10-phenanthroline would catalyse its pharmaceutical activities which may serve better results in medicinal and analytical fields. In the study made, the authors have put an effort to reveal on the most important application of the surfactants as micellar drug solubilization [22]. Thus one can generalize the physical understanding to study the phenomenon of micelllar solubilization and 1,10-phenanthroline may be used as a micro- environment probe.

ACKNOWLEDGEMENT

The authors are thankful to Head, Department of Chemistry, J.N. Vyas University, Jodhpur for providing necessary research facilities.

ISSN: 0975-8585

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