RJC

RASĀYAN *J. Chem.*
Vol. 7 | No.1 | 28-32 | January - March| 2014
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

STUDY ON SOLUBILIZATION OF 1-NITROSO-2-NAPHTHOL IN SURFACTANT SOLUTION BY SPECTROFUOREMETRY

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ABSTRACT

1-Nitroso-2-naphthol (1-N-2-N) is an excellent color forming chelating agent. The fluorescence and absorption spectra of 1-nitroso-2-naphthol have been studied in presence of different surfactant solutions at room temperature with special reference to solubilization and
micellization.. The explanation for the result could be that nonionic surfactants form micelles in aqueous solution above the critical micellar concentration (CMC) which increase the solubility of species with hydrophobic nature. Solubilization phenomenon is one of the important properties of micelles industrially as well as biologically. The dual nature of surfactant micelle is responsible for the occurrence of surface activity, solubilization and micellization. The maximum solubilization is attributed with the high absorbance as well as fluorescence intensity and it has also been confirmed by theoretically calculated spectral parameters, like empirical fluorescence coefficient (K_f), quantum yield (Φ_f), molal extinction coefficient (log ε) and Stokes'shift

Keywords: Surfactants, 1-Nitroso-2-naphthol , Fluorescence, Solubilization.

INTRODUCTION

Micelles are dynamic microheterogeneous structure containing surfactant molecules and constitute an important research subject[1-3]. 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[4-8] . 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[9]. 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[10-12].

1-Nitroso-2-naphthol (1-N-2-N) is known as an excellent color forming chelating agents[13]. In solution 1-nitroso-2-naphthol exist in tautomeric equilibrium with the corresponding quinine monoxide form[14]. The forms of nitroso and quinine monoxide have been investigated by x-ray and FTIR in solid phase spectrum and the nitroso form is preferential[15, 16].

In this paper we report here the investigation carried out on solubilization of 1-nitroso-2-naphthol (1-N-2-N) occurring in the presence of surfactant micelles employing fluorescence and absorption measurements. The result have been interpreted from the determination of quantum yield of 1-nitroso-2-naphthol (1-N-2-N) fluorescence in micellar medium.

EXPERIMENTAL

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-nitroso-2-naphthol (1-N-2-N) (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-nitroso-2-naphthol (1-N-2-N) at 1 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 Maximum excitation and emission wavelength of 1-nitroso-2-naphthol (1-N-2-N) was observed at 385 nm and 430 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 the emission intensity, initially decreased and a further increase in surfactant concentration in the solution caused a substantial enhancement in the emission peak height. On addition of cationic surfactant for the solution of 1-nitroso-2-naphthol (1-N-2-N) the emission intensity first increase than decreased. 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-nitroso-2-naphthol (1-N-2-N) was found to be maximum at 370 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), λabs, λem, Φ_f, for1-nitroso-2-naphthol (1-N-2-N) on addition of TX -100 are as given in table 2. Stokes' shift for 1-nitroso-2-naphthol (1-N-2-N) 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-nitroso-2-naphthol (1-N-2-N) 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-nitroso-2-naphthol (1-N-2-N) in solution. The result show that TX-100 micelles have solubilized 1-nitroso-2-naphthol (1-N-2-N) 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-nitroso-2-naphthol (1-N-2-N) 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-nitroso-2-naphthol (1-N-2-N) 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-nitroso-2-naphthol (1-N-2-N) 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.

Table-1: Fluorescence intensity (FI) of the 1-nitroso-2-naphthol (1-N-2-N) ($1X10^{-5}$M) in the absence and presence of surfactants.
λex= 385nm, λem= 430nm P.M. Gain = 2, Sensitivity Range = 0.1

Name of Surfactant	Fluorescence Intensity in the absence of surfactant	Concentration of surfactant used (%)	Maximum fluorescence Intensity (nm)
TX-100	33	0.7	54
Tween -80	33	0.7	47
Tween – 40	33	0.7	43
DBSS	33	0.7	43
SLS	33	0.7	45
DSSS	33	0.7	43
CTAB	33	0.03	38
CPB	33	0.03	42
CPC	33	0.01	38

Table-2: Absorption maxima (λabs), fluorescence maxima (λem), Molar extinction coefficient (log ε) and quantum yield (Φ_f) of 1-nitroso-2-naphthol (1-N-2-N) on addition of TX-100.

S.No.	TX-100 used (%)	λabs (nm)	λem (nm)	log ε	Φ_f (dm^{-3} $Mol^{-1}cm^{-1}$)
1.	0.000	370	430	3.884	0.4660
2.	0.01	370	440	3.896	0.4851
3.	0.07	370	440	3.918	0.4945
4.	0.7	370	440	3.957	0.5049

Absorption spectra of 1-nitroso-2-naphthol (1-N-2-N) 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-nitroso-2-naphthol (1-N-2-N) 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-nitroso-2-naphthol (1-N-2-N) 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].

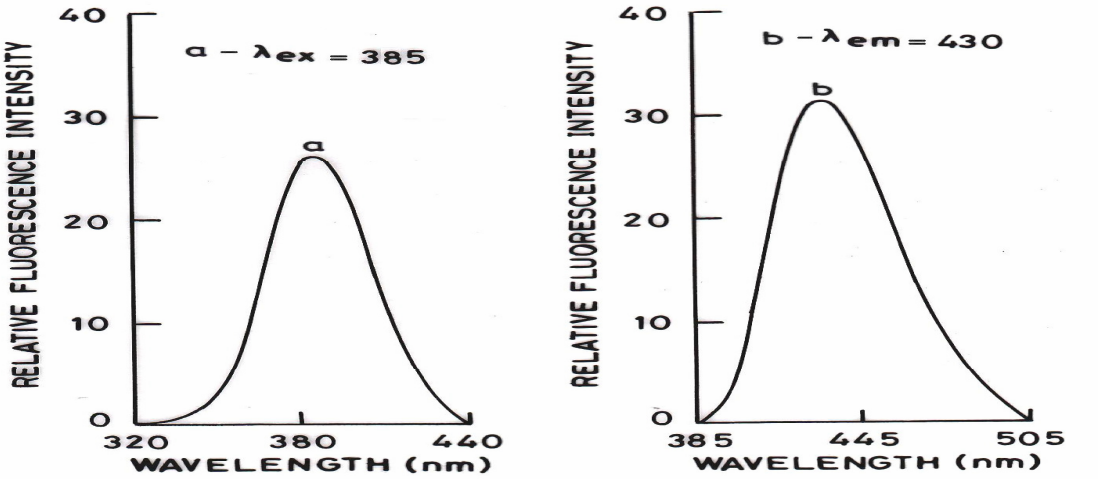

Fig. 1 Excitation and emission spectra of 1-nitroso-2-naphthol

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-nitroso-2-naphthol (1-N-2-N) 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-nitroso-2-naphthol (1-N-2-N) in miceller media is attributed to the hydrogen bonding capacity of the molecule.

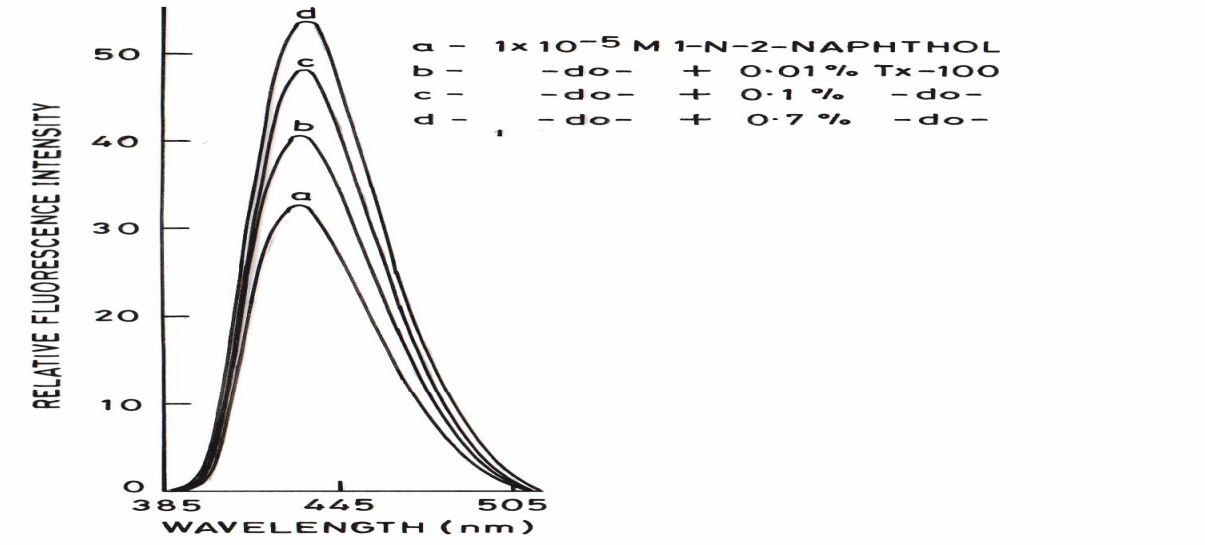

Fig.2. Influence of addition of TX-100 on fluorescence intensity of 1-N-2-N

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-nitroso-2-naphthol (1-N-2-N) is toxic in nature and is an environment pollutant, but, it has some great uses. 1-Nitroso-2-naphthol (1-N-2-N) is used as chealating agent in pharmaceuticals. Hence the process of micellization followed by solubilization of 1-nitroso-2-naphthol (1-N-2-N) 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-nitroso-2-naphthol (1-N-2-N) may be used as a micro-environment probe.

ACKNOWLEDGEMENTS

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

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[RJC-1112/2014]