



## Spectral features of 4,4-diaminodiphenyl sulfone in anionic and cationic inverted micelles

Prosenjit Bhattacharya<sup>1</sup>, Sankar Chakravorti\*

Department of Spectroscopy, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

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### ABSTRACT

This Letter reports the photophysics of 4,4-diaminodiphenyl sulfone in anionic and cationic reverse micelles (RM). Decreased fluorescence intensity with significant blue shift of intramolecular charge transfer (ICT) fluorescence maximum and longer emission lifetime of the entrapped probe in motionally restricted water nano-pool of anionic RM could be observed. Bi-exponential decay in anionic RM appears due to polarity heterogeneity in the pool. In a nut shell, experiments establish that the probe is anchored in the micellar head group region of anionic RM vis-à-vis far away from the core in cationic RM. Increasing pool size show the opposite effect to the probe.

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### 1. Introduction

Certain amphiphilic molecules have the ability to assemble in non aqueous media to form reverse micelles (RM) with polar heads of the amphiphiles to form a micellar core and the hydrocarbon tails extended into the bulk organic solution. The solute particles may be located in three different parts of RM: (a) the external organic solvent, (b) the micellar interface and (c) the internal polar core [1–3]. Among the anionic surfactants Aerosol OT (AOT) (sodium 1,4-bis-2-ethylhexylsulfosuccinate) is the extensively studied surfactant for its ability to form reverse micellar aggregates in nonpolar solvents and the addition of water solubilizes surfactant AOT by creating a water pool surrounded by the surfactant [4]. The shape of the aggregates formed in the AOT reverse micellar system is a sphere with 15 Å radius in the absence of water [5,6]. The cationic surfactant, benzyl-*n*-hexadecyl dimethylammonium chloride (BHDC), also forms reverse micelles in benzene without addition of a co-surfactant and water can be solubilized up to  $W \sim 25$  depending on the surrounding non polar medium, the solute and the temperature [7,8]. The hydrodynamic radius of the spherical aqueous micellar core increases monotonically with the increment of molar water to surfactant ratio  $W = [\text{water}]/[\text{surfactant}]$  [9]. At lower value of  $W$  only bound water exists and for the higher value of  $W$  a dynamic equilibrium exists between the bound and bulk water molecules [10,11]. The size, as well as the microviscosity and micropolarity, of the bulk water pool vary with the pool size [11–16]. Parameters such as solvent polarity, hydrophobicity and the overall charge influence the average location of the fluorophore in the reverse micellar system. Many

steady state and transient infrared studies supported the 'core-shell' model of confined water [17–19].

The photoinduced intramolecular charge transfer (ICT) of organic molecules containing electron donor and acceptor groups has always engendered research interest in the scientific community because of its similarity with the biological and chemical energy conversion [20–22]. The formation of the ICT state could give dual fluorescence in polar solvent attributed to locally excited (LE) state and a low energy intramolecular charge transfer (ICT) state [23,24]. The charge transfer state sometimes may involve geometry change in the excited state by twisting its initial planar structure (Twisted intramolecular Charge Transfer State, TICT) and this process is strongly affected by the local polarity and viscosity surrounding the fluorophore [25].

The photophysical characteristics of a potential probe 4,4-diaminodiphenyl sulfone (Dapsone, [chart 1](#)), has been described in different solvents from experimental observations and theoretical calculations [26]. The inclusion complex of Dapsone inside cyclodextrin cavity increases both the ICT fluorescence intensity and lifetime due to the loss of rotational freedom in the confined form [27]. In ionic liquid-micelles system photophysics of Dapsone unveils the shrinking and inflating micellar size in anionic and cationic micelles, respectively [28]. From the <sup>1</sup>H NMR study [29] of DiPalmitoyl Phosphatidyl Choline (DPPC) in CdCl<sub>3</sub> at various concentrations it was shown that the amino group of Dapsone interacts with the head group of reverse micelle DPPC.

Since RMs play a crucial role in the applications like synthesis of nanoparticles, toward controlling the size and shape of the nanostructures, protein extraction, transport processes in biological systems the knowledge of formation of different RM and its interior seem to be important. In this Letter we intend to study the photophysical changes of Dapsone inside anionic *n*-heptane/AOT/water and cationic benzene/BHDC/water RMs with the help of different

\* Corresponding author. Fax: +91 33 24732805.

E-mail address: [spsc@iacs.res.in](mailto:spsc@iacs.res.in) (S. Chakravorti).

<sup>1</sup> Presently at: Budge Budge Institute of Technology, Budge Budge, Kolkata, India.

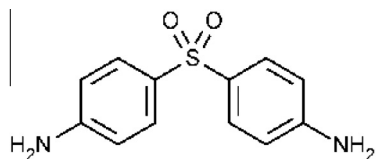


Chart 1. Chemical structure of Dapsone.

spectroscopic techniques. By following the spectral signature we might be able to identify the region of the RM in which the probe is anchored and decipher its characteristics in these micropolar and microviscous region. The effect on the emission characteristics of the probe molecule with varying pool size of the RM would also be aimed at.

## 2. Experimental section

4,4-Diaminodiphenyl sulfone (Dapsone) was received from Aldrich Chemical Company, USA and was recrystallized in ethyl acetate/petroleum ether before use. AOT, BHDC (ultra grade) were purchased from Sigma Chemical Co. and were used for the preparation of reverse micelle after making free from moisture to ensure correct  $W$  values. Millipore Milli-Q Water was used in the preparation of water-in-oil microemulsion. The spectroscopic grade  $n$ -heptane, benzene and acetonitrile are from Aldrich Chemical, USA. Concentration of primary stock solution of Dapsone in ethanol was maintained constant at 5 mM.

Steady state absorption spectra were measured on a UV-2401 PC Shimadzu absorption spectrophotometer. Fluorescence measurements were performed with a Hitachi F-4010 spectrofluorometer. Both of the absorption and fluorescence measurements were performed using 1 cm path length quartz cuvettes. Fluorescence anisotropy or polarization measurements were performed in the usual way [27]. The time resolved emission spectra (with excitation at 295 nm) were recorded using time correlated single photon counting (TCSPC) technique in a Horiba Jobin Yvon instrument [27,30].

## 3. Results and discussions

### 3.1. Absorption and fluorescence spectral features

Figure 1 shows the absorption spectrum of Dapsone in water,  $n$ -heptane, dry AOT (0.1 M) and in reverse micelles of varying size. The 290 nm absorption band of Dapsone in pure water shifts to 281 nm in  $n$ -heptane with very low absorbance and addition of

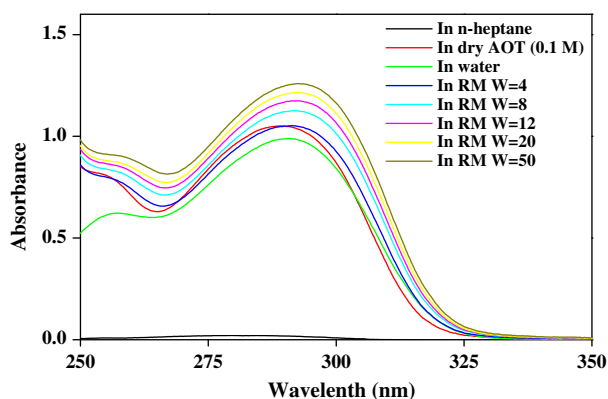


Figure 1. UV-visible absorption spectra of Dapsone (5  $\mu$ M) in  $n$ -heptane, dry AOT (0.1 M), water and in reverse micelle of different  $W$  values.

dry AOT to the  $n$ -heptane solution shifts to 289 nm with sharp increase in absorbance. Upon addition of water to this solution the absorbance increases with peak shifted to 293 nm ( $W = 50$ ). This red shift may indicate the formation inclusion/association complex of the probe with reverse micellar cavity [27,31].

Dapsone in benzene shows an absorption peak at 286 nm (Supplementary Figure 1) and addition of 0.1 M BHDC to benzene solution it shows a red shift (300 nm). The gradual increase in the reverse micellar size ( $W = 0$ –20) shows the gradual blue shift of the absorption peak position (Supplementary Table 1).

The emission of Dapsone in  $n$ -heptane is very weak with emission maximum at 318 nm (excitation  $\sim$ 290 nm) while in aqueous solution the emission maximum was at 459 nm. Addition of 0.1 M AOT to the  $n$ -heptane solution of Dapsone the peak shifts to 381 nm with huge increase in fluorescence intensity (Supplementary, Figure 2a). However, when the probe is excited at wavelengths greater than 290 nm in  $n$ -heptane and in  $n$ -heptane/AOT binary solution less intense emission spectrum was observed. Upon addition of aqueous solution to the  $n$ -heptane/AOT binary solvent the emission peak position gradually shifts towards red (432 nm for  $W = 50$ ) with a decrease in intensity as the water-to-surfactant ratio increases from  $W = 4$ –50 (Figure 2a). The emission maximum seems to be blue-shifted than that of Dapsone in bulk water (459 nm) by about 27 nm. The blue shift indicates the polarity of the reverse micellar environment is less than the polarity of the bulk water. As the emission of Dapsone in dilute hydrochloric acid–water mixture does not indicate any change of position of ICT

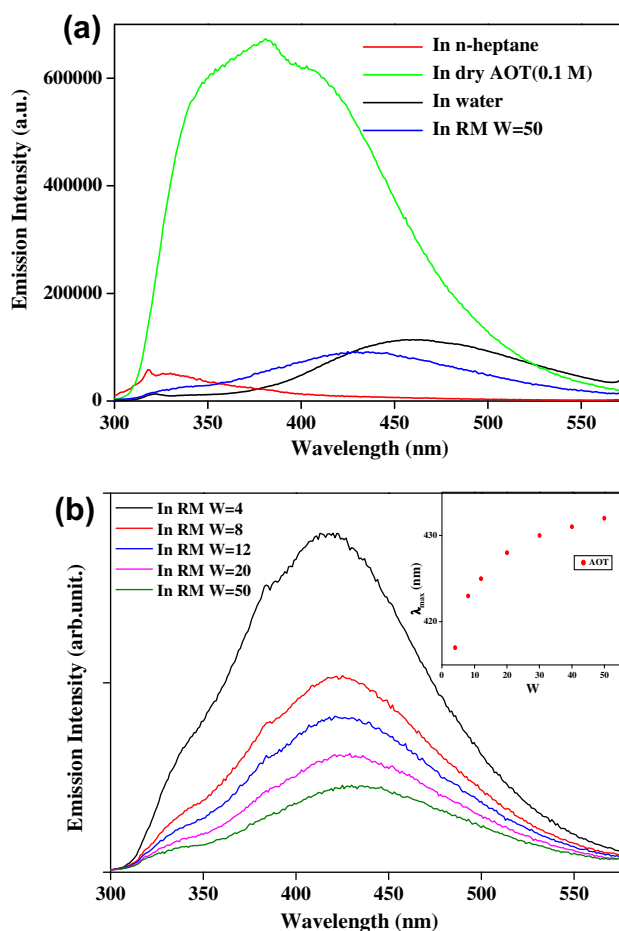


Figure 2. (a) Steady state fluorescence spectra of Dapsone in  $n$ -heptane, dry AOT (0.1 M), water and in reverse micelle at  $W = 50$ . (b) Fluorescence spectra of Dapsone at different values of  $W$  in AOT reverse micelle. Inset: Variation of fluorescence maximum of Dapsone in AOT reverse micelles as a function of  $W$

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