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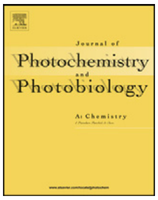

Photophysical properties of 4,4-diaminodiphenyl sulfone in micelles and the role of BF-anion on micellar aggregation

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ABSTRACT

The modulation of already established charge transfer (ICT) emission characteristics of 4,4′-diaminodiphenyl sulfone (Dapsone) in different micelles and also its further alterations due to physicochemical change of micelles in company with added room temperature ionic liquid (IL) have been elucidated in this paper with the help of steady state and time-resolved fluorescence spectroscopy. Dapsone seems to enter inside the cationic micelle beyond interfacial region, as evinced by the emission intensity enhancement and blue shift. In anionic micelle little intensity increase and the blue shift of Dapsone point to the presence of the probe near the interfacial region. From Cu^{2+} quenching study it has been confirmed that among the ionic micelles the probe makes shallow penetration in anionic micelle compared to that in cationic micelle. In non ionic surfactants the accessibility of the probe to the ionic quencher increases with increasing chain length. The probe's emission intensity is highest in non ionic Tween 20, but it starts decreasing with increasing alkyl chain length up to Tween 60 and it drastically reduces in Tween 80 nearly same as that in water. IL seems to affect the micellization of anionic, cationic and nonionic micelles differently resulting in shrinking and inflating the micellar size. The calculated rotational relaxation time of the micelle–probe complex is very slow compared to the probe rotation inside micelle.

1. Introduction

Lots of interests [1] have been engendered in the area of excited state charge transfer (CT) since the observation of dual emission of dimethylaminobenzonitrile (DMABN) in polar solvents. Photoinduced charge transfer in organic molecules play important role in many biological processes [2,3] and in other applications [4,5]. The dual fluorescence of charge transfer compounds in polar solvents [6] comprises of a locally excited (LE) state and the other due to intramolecular charge transfer (ICT) state [7]. Charge transfer process is strongly affected by the local polarity and viscosity [8] of surrounding solvent molecules. The X-ray analysis of 4,4-diaminodiphenyl sulfone (Dapsone) shows that both the phenyl rings are approximately perpendicular to the N–S–N plane [9], could serve perpendicular π-system. Some work on the characteristics of this molecule as charge transfer system and its change in constrained environments [10–12] could be found in the literature. In a recent paper we have exhaustively elucidated the photophysics of Dapsone and characterized the low energy emission band as ICT [13]. Due to incorporation of local anesthetic fluorophore in restricted hydrophobic microenvironments an enhancement in the fluorescence could be observed [14], but surprisingly no work of Dapsone in microheterogeneous system could be found, despite its peculiar structure, and more so when such environments are known to affect enormously the photophysics of the excited state charge transfer process significantly.

Micelles are microheterogeneous organized molecular assemblies formed by the hydrophobic effect and they have recently drawn huge attention of the scientific community [15–17]. At high concentration the amphiphilic molecules self-assemble into aggregates or microstructures known as micelles, with their hydrophilic groups exposed to solvent and their hydrophobic groups shielded in the micellar interior. The micellization process is governed by the balance of interactions of hydrophobic and hydrophilic groups with the solvent and the entropic effects due to association. The onset of the aggregation of free surfactants into micelles in the spontaneous process over a narrow range of surfactant concentration can be quantified by a single concentration value, the critical micellar concentration (CMC). They offer well defined shape, size, critical micellar concentration, and efficient solubilization of many hydrophobic compounds, which leads to significant effect on the photophysical process [18]. Micellization also plays a crucial role in human digestive system to solubilize the fat [19]. Micelles [20–23]

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have a "dry" hydrophobic core (~10–20 Å) consisting of hydrophobic tail groups surrounded by a "wet" spherical shell of hydrophilic head groups called Stern layer. The thickness of Stern layer for sodium dodecyl sulfate (SDS), cetyltrimethyl ammonium bromide (CTAB) is 6–9 Å, whereas for nonionic micelles it is much thicker [24]. A much diffused layer called Gouy–Chapman (G–C) layer lies between the Stern layer and the bulk water [8–11]. Depending on the chemical structure of the constituent monomers and the ionic strength of the medium micelles can be of any desired charge type and can adopt different shapes and internal packing [25,26]. Micelles arouse special interest as complex systems [27] along with reverse micelles [28], cyclodextrins [29–31], or gels [32], in which water molecules probably behave as those in biological membranes. Apart from the properties of bulk aqueous phase microviscosity (expressed by rotational or translational diffusion coefficients of molecules) and micropolarity inside the micellar environments modify a number of photophysical and photochemical processes [24], especially where there is a charge separation after photoexcitation [33–35]. It is observed that different probe molecules are located mainly in the head group region [36] of the micelle. However, as has been recently established, the probe molecules can be placed in the head group and core regions depending on their properties and size [8,36].

Room temperature ionic liquids (ILs) are considered to be interesting environment which has attracted both academic and industrial research communities [37,38] due to their environment friendliness. Most of the room temperature ionic liquids have low vapor pressure and they can form micelles. Normally ionic liquids (ILs) are composed of cations and anions, the cations are charged head groups with unit charge and the nonpolar tail group with negligible charge [39]. The interactions between the head groups and the anions are dominated by electrostatic interactions, while the nonpolar parts of the side chain interact mainly through the collective short-range interactions. Simulations of multiscale coarse-graining (MS-CG) approach of room temperature ionic liquid [38,40–42] show that with sufficient long side chains the tail groups of the cations aggregate to form spatially heterogeneous tail domains. Modulations of physicochemical properties of aqueous solution of nonionic surfactant by ionic liquid resulting in change of micellar size and aggregation number and increase in critical micellar concentration could be found in literature [43].

Dapsone has got a peculiar V-shaped structure [12] with two loan pair N-sites (Chart 1) so we thought to investigate the modulation of the charge transfer properties of this molecule in different neutral and ionic micelles and also the modification of these properties in probe-micellar systems due to the interaction of ionic liquid [bmim][BF_4]. The help of steady state, time-resolved emission spectroscopy and dynamic light scattering have been taken in this investigation. The effect of varying chain length of micelle on the probe molecule emission characteristics and the role of IL on the micellar aggregation condition would also be aimed at.

2. Experimental

2.1. Materials

The probe 4,4-diaminodiphenyl sulfone (Dapsone) was purchased from Aldrich Chemical Company and was recrystallized before use. Sodium dodecyl sulfate (SDS, purity ≥ 98.5), Cetyltrimethyl Ammonium Bromide (CTAB, purity ≥ 99), Tween 20 (TW-20), Tween 60 (TW-60), Tween 80 (TW-80) and hydrophilic ionic liquid (IL) 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4] (purity ≥ 97.0) are from Aldrich Chemical, U.S.A. All of the chemicals were of the highest available purity and were used as such. Deionized water from Millipore was used in the preparation of the micelle samples. The concentration of the probe was maintained constant at 0.005 mM to avoid aggregation. The concentrations of detergents used were double or more than the CMC of the respective detergent to ensure that they are in the micellar state.

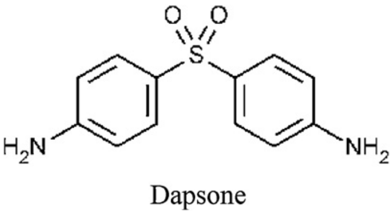

Chart 1. Chemical structure of Dapsone.

2.2. Methods

2.2.1. Absorption and emissions

The absorption spectra at 298 K were measured on a Shimadzu absorption spectrophotometer model UV-2401 PC. Steady state emission measurements were made on a Hitachi F-4500 or Horiba Jobin Yvon Fluromax 4 fluorescence spectrophotometer. Both of the absorption and emission measurements were performed using 1 cm path length quartz cuvette.

2.2.2. Fluorescence decay

Fluorescence lifetimes were determined from time-resolved fluorescence intensity decays using time correlated single photon counting (TCSPC) technique in a Horiba Jobin Yvon instrument. This machine use a picoseconds diode laser (IBN Nanoled-07) as the excitation source and the probe was excited at 295 nm and the signals were collected at a magic angle of 54.7°. The data were collected using a DAQ card as a multichannel analyzer. The obtained spectra were analyzed with the software DAS6 at data station v2.3 through exponential fitting. The quality of the fit was determined in terms of weighted residuals and reduced χ^2 values. The lifetime of Dapsone in neat aqueous solution, in different micellar solutions and also those in presence of ionic liquid were found to fit well with an exponential function as [44].

$$I(t) = \sum D_i \exp \frac{-t}{\tau_i} \tag{1}$$

where τ_i is the fluorescence lifetime associated with the different species and D_i is the pre-exponential factor. An inbuilt motorized polarizer in the emission side was used for the study of anisotropy decays. The emission intensities at parallel (I_{II}) and perpendicular ($I_{\perp}$) polarizations were collected alternatively until a preset (5000 counts) peak difference (to get maximum data) was reached. The time resolved anisotropy [$r(t)$] was calculated using the following relation [44]:

$$r(t) = \frac{I_{II}(t) - GI_{\perp}(t)}{I_{II}(t) + 2GI_{\perp}(t)} \tag{2}$$

where G is the correlation factor for the detector sensitivity to the polarization detection of the emission.

2.3. Dynamic light scattering

Dynamic light scattering (DLS) measurements were performed using a Zetasizer Nano ZS (Malvern) instrument. The light source was He–Ne laser operated at 633 nm with a maximum power output of 5 W. The samples of micellar solutions were filtered through 0.2 μm filters (Acrodisc) to avoid interference from dust particles and the sample was poured into a DTS0112 low volume disposable cuvette of 1.5 mL and path length 1 cm. The operation