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Optical transition rates of a meso-substituted thiacarbocyanine in methanol-in-oil reverse micelles

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Abstract

We report the photophysical properties of 3,3′-diethyl-5,5′-dichloro-9-phenylthiacarbocyanine (DDPT) in methanol-in-oil (m/o) reverse micellar systems which form methanol droplets stabilized with anionic surfactant aerosol-OT (AOT) in n-heptane. The fluorescence quantum yield of DDPT is enhanced by a factor of 17 in the methanol droplet in comparison with bulk methanol. The fluorescence lifetimes of DDPT in m/o reverse micelles are prolonged up to 2.2 ns with increasing molar ratio of methanol to surfactant ($w_0 = [\mathrm{MeOH}]/[\mathrm{AOT}]$), whereas the fluorescence lifetime of DDPT in bulk methanol is 75 ps. The non-radiative rate constants of DDPT in the droplets are decreased by a factor of 40, resulting in a remarkable enhancement in quantum yields, indicating that internal motions of DDPT in the droplets are significantly reduced due to strong electrostatic interactions between the positively charged DDPT and the negatively charged sulfonate head-groups of AOT and the spatial confinement induced by the reverse micellar structure.

Keywords: Enhanced fluorescence; Cyanine dyes; Reverse micelles; Methanol-in-oil-droplet; Spatial confinement

1. Introduction

Utilization of surfactant aggregation in non-aqueous polar solvents, such as ethylene glycol, glycerol, formamide, acetonitrile and methanol, have been recently of interest [1,2]. Reverse micellar systems consisting of nanometer-sized droplets of non-aqueous polar solvents, dispersed in an oil-continuous phase have potential as novel reaction media. Although, to date, there have been very few reactions studied in these solvent combinations, there are reports on structural studies performed on sodium dodecyl sulphate (SDS)/formamide/hexanol/alkane [3] and pentakis(ethylene glycol)dodecyl ether/glycerol/alkane systems [4,5]. Glycerol and water were shown to

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behave in a very similar manner when dispersed in alkane solvents, when aerosol-OT (AOT, see chemical structure in Fig. 1) or cetyltrimethylammonium bromide (CTAB) is used as surfactants [6,7]. AOT- or CTAB-stabilized glycerol-in-oil microemulsions were reported to exhibit metal ion/ligand complexation reactions [8]. The AOT/formaldehyde (with added NaBr)/styrene system has been used for studies of polymerization processes [9].

Solvation dynamics of water and non-aqueous polar solvents in reverse micelles were demonstrated to depend on the molar ratio of solvent to surfactant [2,10–15]. Shirota and Horie reported that the solvation dynamics were retarded by up to four orders of magnitude because of the presence of hydrogen-bonding network in reverse micelles [10]. It was proposed that the absence of the hydrogen-bonding network for the non-aqueous solvents such as acetonitrile in reverse micelles causes a weaker interaction between the solvent molecules [10].

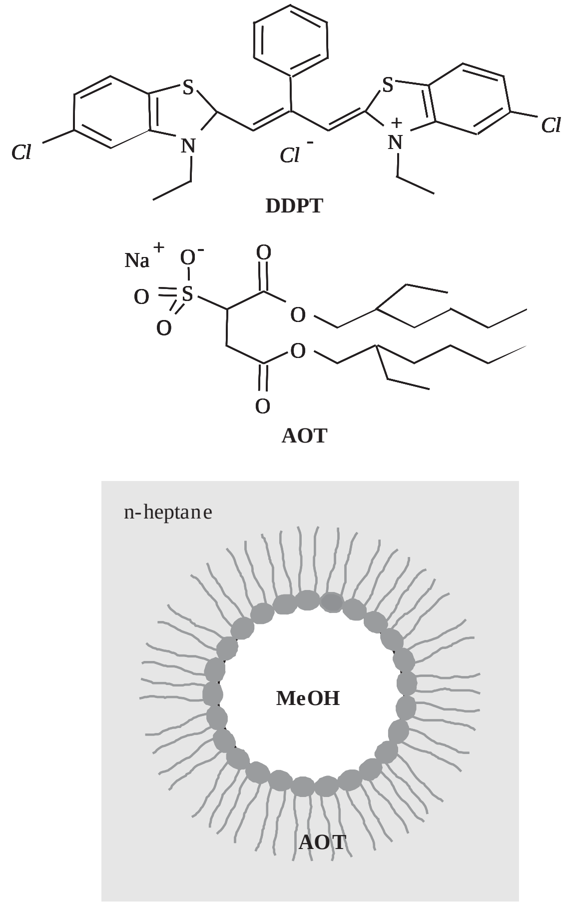

Fig. 1. Chemical structures of DDPT and AOT and a schematic drawing for reverse micelle structure.

Photophysical properties of some cyanine dyes have also been investigated in reverse micelles [16,17]. The slower rate of photoisomerisation of a diethyloxacarbocyanine in reverse micelle was proposed to arise from electrostatic interactions between the dye and head group of the surfactant [16]. The position of the dye was thought to be the interface region of the reverse micelles [16]. A meso-substituted cyanine dye structurally similar to DDPT (Fig. 1 for its chemical structure) was employed for the investigation of the isomerization and aggregation in normal and reverse micellar environment [17]. The incorporation of the dye into the micelles resulted in formation of the *trans*-isomer, whereas the *cis*-isomer predominantly existed in bulk water [17]. In reverse micelles the dye forms J-aggregates when water- to- surfactant molar ratio is bigger than five, and only in the presence of an ionic surfactant such as AOT. On the other hand, the optical rate constants of rhodamine dyes in reverse micelles were proved to depend on the refractive index of the surrounding environment [18,19]. Gacoin et al. proposed that reverse micelles could be an accurate system for measuring quantum efficiencies [18,19].

The methanol-in-oil (m/o) dispersions were prepared using $w_0 = 2$, 4 and 6, where w_0 is the molar ratio of dispersed methanol to surfactant (w_0=[MeOH]/[AOT]) [10,12-13]. In the case of water-in oil microemulsions, w_0 values can be incorporated into an empirical formula to determine the radii of dispersed water droplets in oil [20]. The radius is known to increase with increasing w_0 values. There is, however, no empirical formula to support the systematic increase of droplet sizes in the case of methanol dispersions. The radii of the AOT-stabilized methanol droplets in n-heptane for $w_0 = 2$, 4 and 6 were measured by dynamic light-scattering methods and reported to be 1.3, 1.2, and 1.5 nm,