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Fluorescence behavior of intramolecular charge transfer probe in anionic, cationic, and nonionic micelles

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Abstract

The intramolecular charge transfer (ICT) property of *trans*-ethyl *p*-(dimethylamino) cinnamate is used to probe the anionic, cationic, and nonionic micelles by steady-state and picosecond time-resolved fluorescence spectroscopy. The ICT fluorescence band intensity was found to increase with concomitant blue shift with addition of surfactants. All the experimental results suggest that the probe molecule resides in the micelle–water interface rather than going into the core. However, the penetration is more toward the micellar core in nonionic surfactants when compared with ionic micelles. The decrease in nonradiative decay constants in micellar environments indicate restricted motion of the probe toward the formation of ICT state. Critical micelle concentrations were determined from the sharp change in fluorescence intensity and effective dielectric constants of the micelle–water interface were calculated from the correlation diagram of 0, 0 transition energy with polarity of the medium.

Keywords: Intramolecular charge transfer; Micropolarity; Critical micelle concentration; Fluorescence decay; Micelle–water interface

1. Introduction

Over the past few decades, there has been widespread interest in elucidating the micellar characteristics primarily due to the fact that they are one of the simpler membrane mimetic systems [1–5]. Among the various methods employed, fluorescence has turned out to be one of the most powerful techniques due to its excellent sensitivity [6–8]. By comparing fluorescence spectral data obtained in the micellar medium with the calibration curve constructed using various homogeneous systems, mean micellar properties like effective polarity, apparent micellar viscosity, aggregation numbers, and electrostatic mean field potentials at interfaces have been successfully determined [9–12]. However, the large variation in the values of the mean micellar properties was criticized by several authors [13]. Despite these criticisms, measuring the microscopic parameters is still very useful to gain a better understanding of different chemical processes in biologically mimicking complex "microreactors" such as micelles, liposomes, and reverse micelles, formed by self-assembly of amphiphilic subunits. The present investigation is an endeavor in that direction by using the novel intramolecular charge transfer (ICT) fluorescent probe *trans*-ethyl *p*-(dimethylamino) cinnamate (EDAC, Scheme 1 for structure).

The ICT process in electron donor–acceptor systems seems to be an extremely important phenomenon in chemistry and biology. In the most widely studied ICT probe dimethylaminobenzonitrile (DMABN) and its derivatives, twisting of the donor dimethyl amino group with respect to the molecular plane in the excited state is thought to be associated with a large charge transfer from donor to acceptor causing an extra twisted intramolecular charge transfer (TICT) emission band in more polar environment [14,15]. The extreme sensitivity of these TICT probes to polarity prompted a large number of studies in a variety of microheterogeneous media like micelles [16–18] where the polarity decreases gradually from the boundary to the core. The ionic micelles have a charged micelle–water interface and the interface electric field may be

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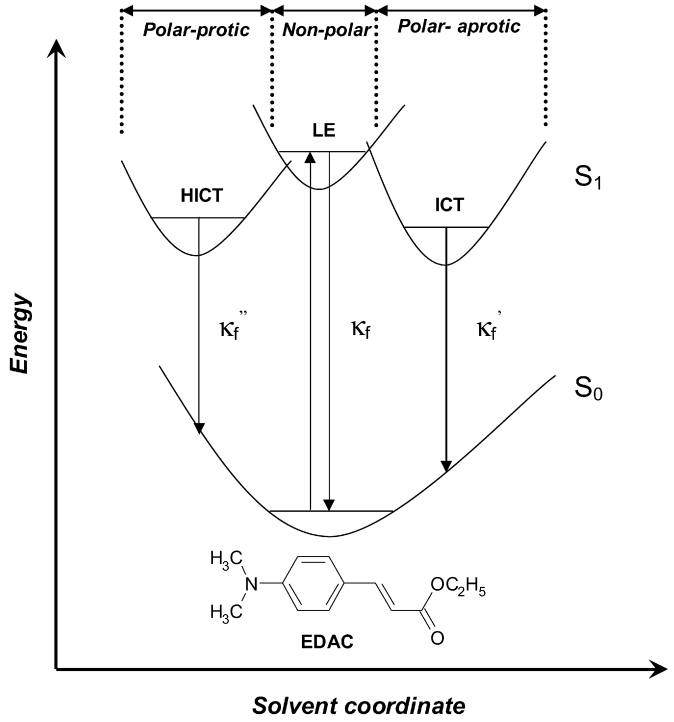

Scheme 1. Structure of the polarity probe *trans*-ethyl *p*-(dimethylamino) cinnamate (EDAC) and schematics of the solvent-dependent singlet-state deactivation mechanism. LE, ICT, and HICT indicate the relaxation from locally excited, intramolecular charge transfer and hydrogen-bonded intramolecular charge transfer states, respectively.

modified through counterion binding or incorporation of a neutral species. With the introduction of a proper charge transfer fluorescent probe, one can follow the micellization and also the effect of the micelle–water interface electric field on the charge transfer process of the probe. The nature of the fluorescent probe should be very sensitive to environmental polarity and viscosity to be able to examine the interior of micellar aggregates.

In a recent study it was found that the ICT probe EDAC is extremely sensitive to solvent polarity and that the fluorescence properties show very good correlation with the solvent polarity parameter [19]. The dynamic aspect of ICT phenomena in homogeneous solvent media was probed with picosecond fluorescence decay measurements and femtosecond transient absorption spectroscopy. The characterization of locally excited (LE) and ICT states was done and the changes in dipole moment in the ground and excited states were calculated from steady-state spectral measurements in a series of solvents with varying polarity using the Lippert–Mataga relation [20]. The relaxation of the excited singlet state is strongly dependent on the nature of the surrounding environment (Scheme 1). The large change in fluorescence spectra with solvent polarity prompts us to use EDAC as a probe to study the micellization of nonionic (Triton-X 100, TX-100), anionic (sodium dodecyl sulfate, SDS), and cationic (cetyltrimethylammonium bromide, CTAB) surfactants by steady-state and picosecond time-resolved fluorescence spectroscopy.

2. Experimental

(*trans*)-Ethyl *p*-(dimethylamino) cinnamate (EDAC) was synthesized using a standard procedure based on the Reformatsky reaction [21]. The crude compound was purified by column chromatography and repeated crystallization. Further characterization was done by NMR and infrared spectroscopy. TX-100, SDS, and CTAB were all obtained from Aldrich Chemical Co. and used as received. The water used as solvent in all the measurements was obtained from Elix10 water purification system (Millipore India Pvt. Ltd.).

Steady-state absorption spectra were recorded on a Perkin–Elmer Model Lambda25 absorption spectrophotometer. Fluorescence spectra were taken in a Hitachi Model FL4500 spectrofluorimeter and all the spectra were corrected for the instrument response function. Fluorescence quantum yields (ϕ) were calculated by comparing the total fluorescence intensity under the whole fluorescence spectral range with that of a standard as described before [19].

The fluorescence decay curves in different micelle media were obtained using the time-correlated single photo counting (TCSPC) technique. The excitation was done at 400 nm obtained by focusing the output (800 nm, 2 MHz repetition rate) of a cavity dumped Ti:Sa laser (Cascade, KMLabs Inc., USA) on 1-mm BBO crystal. The detection system for TCSPC measurements was composed of a monochromator (Japan Spectroscopic, CT-10), a microchannel-plate photomultiplier (Hamamatsu, MCP 2809U), a constant fraction discriminator (Tennelec TC454), and time-to-amplitude converter (Tennelec TC864).

3. Results and discussion

3.1. Steady-state spectral properties

The absorption spectrum of an aqueous solution of both EDAC shows a broad and unstructured low-energy band with the maximum centered at around 373 nm. The room temperature fluorescence emission spectra originated from the charge transfer state appear at 485 nm. Before going into the details of the fluorescence properties in a micellar environment, it is worth discussing the behavior of the probe in a homogeneous mixture of water and 1,4-dioxane, as these mixtures are known to mimic the micellar environment very closely [21]. With increasing the volume fraction of 1,4-dioxane, the fluorescence spectra show an hypsochromic shift along with about 4–6 times increase in fluorescence quantum yield (ϕ). Representative spectra in EDAC are shown in Fig. 1 and corresponding data in pure water and 1,4-dioxane are collected in Table 1.

The absorption maximum for the aqueous solutions of EDAC was practically unaffected by the presence of added surfactant; however, the fluorescence spectrum was strongly dependent on the amount of surfactant in solution. The gradual addition of surfactants (SDS, CTAB, and TX-100) is associated with a blue shift in the emission maximum along with an increase in fluorescence quantum yield (Fig. 2), suggesting that the environment around the probe gets perturbed as we