Journal of Molecular Liquids 191 (2014) 128–136

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Modulation of the fluorescence properties of 5-amino salicylic acid by triethylamine

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ARTICLE INFO

Article history:
Received 20 March 2013
Received in revised form 2 October 2013
Accepted 19 November 2013
Available online 2 December 2013

Keywords:
5-Aminosalicylic acid
Excited state intramolecular proton transfer
Triethylamine
Enhancement
Hydrogen bonding

ABSTRACT

In this paper we report the effect of triethylamine (TEA) on 5-amino salicylic acid (5-ASA) and subsequent changes in the fluorescence properties. In nonpolar solvents it shows emission maximum at ~420 nm (V) corresponding to neutral species. However, addition of TEA results in a new band at ~480 nm (G) corresponding to anion. In protic polar solvents a large Stokes shifted G emission (~480 nm) is observed with a small hump at 420 nm. The G band is enhanced on the addition of TEA. On the other hand, in aprotic polar solvents the emission shows red shifted BG band (463 nm) and V band is not observed. With addition of TEA, the emission is further red shifted with enhanced intensity. Modulations in the ground state and thus change in the excited state properties of 5-ASA upon addition of TEA have been explained on the basis of perturbation in the solvent cage, hydrogen bonding interaction and anion formation.

1. Introduction

Salicylic acid (SA) and its derivatives (SAD) have attracted considerable interest in recent years due to their potential applications in field like conditions [1–11]. SA and SAD are considered as representatives of the complexing functional groups in humic substances and can serve as model compounds for investigating the photochemical and photophysical properties of natural acids [12]. In particular SADs have been studied extensively [13–40] for their possible use as probes for solvent properties, such as polarity and hydrogen bonding capacity, and as probe for microenvironments in proteins and membranes [41]. In addition these reactions are also challenging from the theoretical point of view [41–52].

Weller's [53–55] seminal work on SA and SAD suggested that the photo-induced excited state intramolecular proton (hydrogen) transfer (ESIPT/ESIHT) reaction takes place between the phenol group (–OH) and the adjacent carboxylic group (–COOH). Further, in earlier studies it was shown that 5-amino salicylic acid (5-ASA) exhibits proton transfer reaction in excited state in aqueous medium [56]. In a recent report we found that the presence of iodide results in enhancement in the intensity of fluorescence in aprotic media which we have attributed to the hydrogen bonding interaction.

To further elucidate the effect of hydrogen bonding, in the present work, we have systematically investigated the interaction of 5-ASA with triethylamine (a strong hydrogen bonding agent/strong proton acceptor) in non-polar and polar protic/aprotic media. The spectral changes of the 5-ASA–TEA system have been studied, and the effects of the hydrogen-bonding interaction and the change of solvent polarity on the intermolecular photo-induced processes of the 5-ASA–TEA system are discussed.

2. Experimental section

2.1. Materials

5-ASA (obtained from Aldrich) of 98% purity was tested for its fluorescence purity and used as such. The purity of the compound has been checked by fluorescence run test. We checked the fluorescence spectra in acetonitrile and DMF by exciting with different wavelengths but did not find any change in spectrum or development of any new band. TEA was 99% pure (Sigma Aldrich). The stock solution of TEA (0.1 M) was prepared from the stock solution of 5-aminosalicylic acid. From this solution diluted solutions of TEA were prepared. This ensured that the probe concentration did not change on the addition of TEA. All the solvents used either were of spectroscopic grades or were checked for their fluorescence purity. Dehydrated solvents were used for all measurements.

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http://dx.doi.org/10.1016/j.molliq.2013.11.019

2.2. Instrumentation

Steady state absorption spectra, at room temperature, were recorded by dual beam JASCO V-550 spectrophotometer. The excitation and emission spectra were recorded by using JASCO FP-777 spectrofluorimeter and data were analyzed by related software. Transparent quartz cuvette was used for the absorption and emission measurements and frontal geometry was used in recording emission to avoid inner filter effect. Fluorescence decay times were recorded with the help of Edinburgh-199 time domain spectrometer and analyzed by TCC-900 software. The excitation source was a thyratron-gated (hydrogen filled) nanosecond flash lamp. Lamp profile was measured at the excitation wavelength using Ludox scatterer. The pulse width was ~1.5 ns with a repetition rate of 30 kHz. Time correlated single photon counting (TCSPC) technique was used to collect the decay curves and the resolution of the system was about 200 ps. The number of counts in the peak channel was at least 10,000. Time-resolved fluorescence decay curves were analyzed by deconvoluting the observed decay with the instrument response function (IRF) to obtain the intensity decay function represented as a sum of discrete exponentials; $I(\alpha, t) = \Sigma_i \alpha_i \exp(-t/\tau_i)$, where, I(t) is the fluorescence intensity at time t and α_i is the amplitude of the ith life time such that $\sum_i \alpha_i = 1$. The average lifetime, $<\tau>$ was calculated as follows

$$<\tau> = \Sigma \alpha_i \tau_i / \Sigma \alpha_i.$$

3. Results and discussion

Steady state and time resolved spectroscopic experiments in solvents of different polarities were carried out at 290 K. Steady state parameters of 5-ASA in different solvents are summarized in Table 1. The excitation/emission spectra of 5-ASA (10^{-5} M) in non-polar solvents viz Benzene (BENZ) and Toluene (TOL) show maximum at ~320 nm while in the emission spectrum, maximum is observed at ~420 nm (V) at $\lambda_{ex} = 320$ nm (Fig. 1). The corresponding Stokes shift is ~7750 cm^{-1}. Studies at higher concentrations of the probe were not possible as it is marginally soluble in nonpolar solvents. The excitation spectrum of 5-ASA in these nonpolar solvents was found to be independent of monitored emission wavelengths (Fig. 2) indicating absence of aggregates at this concentration. It is likely that these are present as neutrals (N) only in the ground state (Scheme 1) and these excited neutral species (N*) undergo an extreme fast ESIPT reaction to form tautomers (T*) in the excited state which result in large Stokes shifted emission [57] and hence no emission from neutral species (N*).

In aprotic polar solvents viz; dimethylformamide (DMF) and acetonitrile (ACN), 5-ASA exhibit absorption maximum at ~360 nm and the corresponding emission ($\lambda_{ex} = 360$ nm) maximum is observed at ~463 nm (BG). The corresponding Stokes shift is ~6180 cm^{-1}. In aprotic solvents also emission maximum is found to be independent of excitation wavelength. Also, the excitation spectrum was found to be independent of monitored emission wavelength and exhibits a single peak at ~350 nm, which resembles with the absorption spectrum. This also indicates absence of any aggregates or other conformers in the ground state.

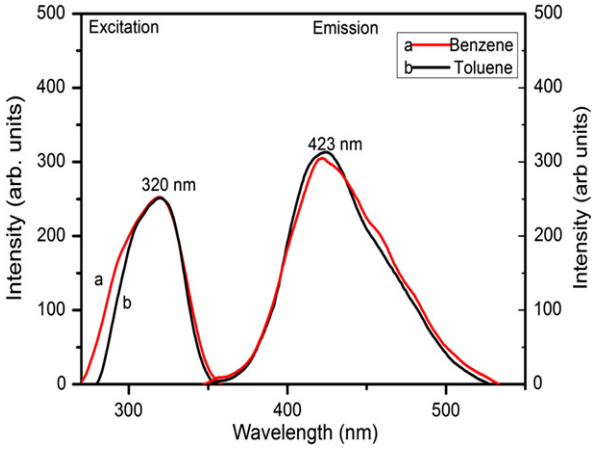

Fig. 1. Excitation spectra (left) and emission spectra of 5-ASA in non-polar solvent (1×10^{-5} M).

In protic polar MeOH, absorption maxima are observed around 300 nm and 340 nm and prominent fluorescence is observed at ~408 nm and ~500 nm, again referred here as V and G bands, respectively (Fig. 3). The excitation spectrum corresponding to V band shows a band with maximum around 300 nm. However, corresponding to G band, the excitation spectrum is red shifted with maximum around 340 nm (Fig. 3, right). The corresponding Stokes shifts for $\lambda_{abs} = 300$ nm are 8823 and 13,333 cm^{-1} for V and G bands, respectively. The excitation spectra clearly reveal that V and G emissions originate from different species viz hydrogen bonded species and anions as discussed in reference [57].

The decay parameters of 5-ASA in different solvents are given in Table 2. For non-polar and polar (aprotic as well as protic) solvents the decay fits with biexponential function. In non-polar solvents the appearance of double exponential decay can be attributed to the emission occurring after ESIPT and probably from an excited state charge transfer state because of the presence of amino group [57].

In case of ACN ($\lambda_{ex} = 360$ nm, $\lambda_{em} = 460$ nm), two decay components of 6.3 ns and 9.5 ns are observed whereas in DMF these two components are 7.7 ns and 12.6 ns. Broad emission coupled with two decay components indicates that there are two emitting species. As mentioned earlier, the emission spectrum is independent of excitation wavelength and hence we rule out the presence of ground state species.

Table 1
Steady state parameters of 5-ASA in various solvent.

Solvent	*ε	*α	*β	λ_{ab}^{max} (nm)	λ_{em}^{max} (nm)			
					$\lambda_{ex} = 300$ nm	$\lambda_{ex} = 320$ nm	$\lambda_{ex} = 340$ nm	$\lambda_{ex} = 360$ nm
MeOH	25.3	0.83	0.77	303, 341	410	410, 470#,490	490	–
EtOH	24.5	0.86	0.75	306, 342	410	410, 470#, 490	490	–
ACN	38.0	0.19	0.40	363	463	463	463	463
DMF	36.7	0.00	0.69	356	470	470	470	470
THF	7.6	0.00	0.55	364	460	460	460	460
Toluene	2.4	0.00	0.11	320	422	422	422	–
Benzene	2.3	0.00	0.1	320	423	424	423	–

*ε, α and β are dielectric constant, hydrogen bond accepting and hydrogen bond donating parameters [58,59].
#Indicates a hump.