Asian Journal of Chemistry Vol. 20, No. 5 (2008), 3961-3966

Fluorescence Studies of Salicylic Acid in Solution and Polymer Film

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Fluorescence of salicylic acid in solution of solvents of different polarity and in polymer matrix is studied to investigate its existence in various geometrical and aggregated forms. The different spectral regions observed in the fluorescence spectra of salicylic acid solutions are explained by the mechanism of formation of salicylic acid anion, zwitter ion and intermolecular hydrogen bonded dimer in the excited state. The transparent salicylic acid doped polymer films prepared from these solutions exhibited nearly identical emission regions in the fluorescence spectra due to formation of similar species in the excited state. The formation of salicylic acid species is further confirmed by lifetimes measured at their respective emission wavelengths. The different values of lifetimes indicate the existence of salicylic acid as different species. The blue emitting salicylic acid doped polymer films are suitable for use in fabrication of organic light emitting devices and also for sunscreen protector films.

Key Words: Fluorescence of salicylic acid, Excited state Intramolecular proton transfer, Zwitter ion, Doped polymer films.

INTRODUCTION

Molecules undergoing excited state intramolecular proton transfer (ESIPT) reaction, are important in connection with promotion of laser action[1], conversion of solar energy into electrical[2], the processes related to the absorption of ultra-violet light by chemical or biological systems[3,4], solvation dynamics[5] and in controlling excited state dynamics[6]. Due to its wide spread applications in science and technology, ESIPT reaction has attracted a number of experimental and theoretical scientists[7,8]. The photo physics of intramolecular hydrogen bonds in aromatic systems is of particular interest, since it appears to play an essential role for the functionality of photostabilizers[8], which are in wide use for the protection of organic polymers against degradation by the components[9,10]. Salicylic acids, methyl salicylate

are amongst the simplest systems for which detailed reaction mechanism related to photo stability need to be explored by spectroscopy and computation. The technological relevance of ESIPT necessitates further systematic studies on the mechanism of processes occurring in this bifunctional aromatic acid in solutions of different solvents and in polymer matrix. Present work reports the fluorescence studies of salicylic acid in different polar and non-polar solvents and also in suitable matrix and to examine the existence of emitting species of salicylic acid. These studies have given salicylic acid doped polymer films emitting at different wavelengths and are suitable for use in organic light emitting devices.

EXPERIMENTAL

Salicylic acid obtained from Merck is used after purity testing. All solvents were of spectrograde quality and used after further purification. The 0.001 wt. % solutions were prepared in solvents such as water, ethanol, acetonitrile, toluene and benzene. The polymers polyvinyl alcohol (PVA) water soluble, polyvinyl pyrrolidone (PVP) alcohol soluble, polyvinyl acetate (PVAC) acetonitrile soluble and polystyrene (PS) benzene and toluene soluble were obtained from acros organics and used as received. The polymers corresponding to 2 wt. % are dissolved in salicylic acid solution. The solution is poured into polypropylene dish kept in incubator maintained at 40 ºC. The solvent evaporates and films of thickness (*ca.* 0.1 mm) are pealed out from dish[11]. The absorption spectra of the solutions were measured on UV-Visible spectrophotometer (Sistronics, India) and wavelength of maximum absorption (λ_{ab}) are obtained. The excitation and fluorescence spectra were recorded on the spectroflurimeter (Jasco, Japan FP-750 PC). The values of λ_{ex} are obtained from the excitation spectra of the solution and fluorescence spectra were monitored at these excitation wavelengths. Similarly fluorescence spectra of films were also recorded by using special front surface attachment provided with the instrument. Lifetimes of excited species in solutions were measured using time correlated single photon counting technique (IBH Datastaition Hub, Horiba).

RESULTS AND DISCUSSION

Fluorescence spectra of 0.001 wt % salicylic acid in different solvents were recorded at excitation wavelengths obtained from excitation spectra of the solutions. Fig. 1 shows fluorescence spectra of salicylic acid solutions in solvents water, ethanol, acetonitrile, toluene and benzene. The figure indicates that the shapes of the spectra are identical but clearly shows the spectral shift towards longer wavelengths with respect to solvent parameter. The excitation and absorption spectra of these salicylic acid solutions were recorded and spectral data collected from these spectra are listed alongwith

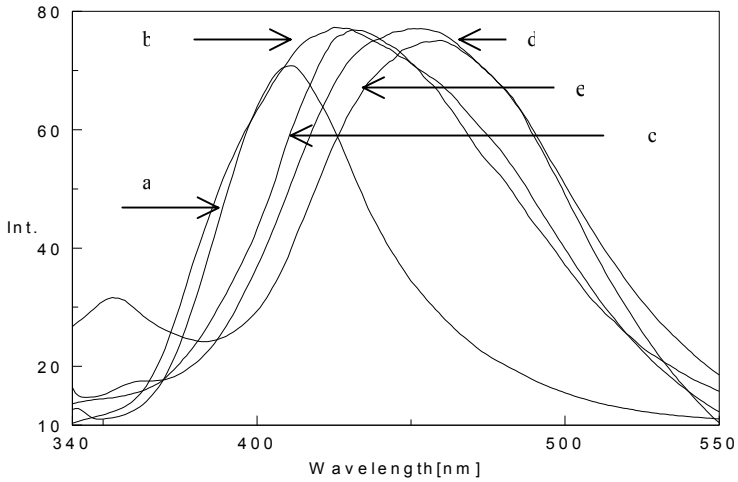


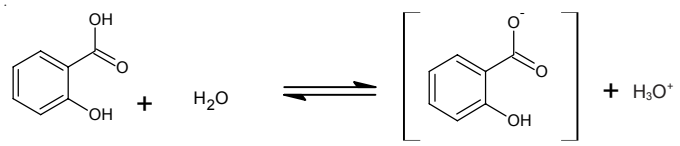
Fig. 1. Normalized fluorescence spectra of 0.001 wt. % salicylic acid in different solvents, (a) water, (b) ethanol, (c) acetonitrile, (d) toluene and (e) benzene

the wavelength of maximum fluorescence in Table-1. The spectral shapes of absorption and excitation spectra were nearly identical. The values of λ_{ex} given in Table-1 are slightly red shifted than the λ_{ab} values of nearly all solutions. The fluorescence spectra of salicylic acid in different solvents are sharp bands and wavelength of maximum emission (λ_{em}) are seen bathochromically shifted. The increase in values of λ_{em} in going from polar to non-polar solvents is because of the existence of salicylic acid in different forms in the solvents of different polarity[12]. In the aqueous solution of salicylic acid, the excitation wavelength is different from absorption maximum. The salicylic acid undergoes deprotonation in the aqueous solution.

TABLE-1
SOLVENT AND SPECTRAL PARAMETERS OF SALICYLIC ACID

Solvents	Δf	λ_{ex} (nm)	λ_{ab} (nm)	λ_{em} (nm)		τ (ns)	Δν (cm^{-1})
				Solution	Film		
Water	0.31930	316	296	411	411	3.24	9389
Ethanol	0.18150	317	304	430	428	4.88	8319
Acetonitrile	0.30540	317	304	425	440	4.87	7660
Toluene	0.02800	319	309	451	424	2.89	10187
Benzene	0.00303	319	309	459	451	2.89	10573

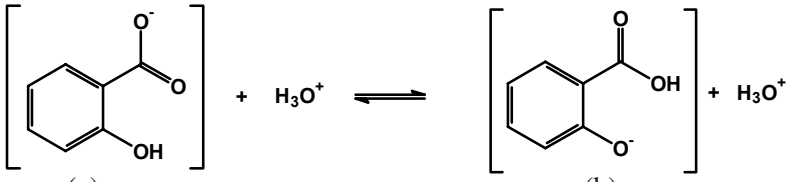
Δf = Solvent polarity parameter, λ_{ex} = Excitation maximum, λ_{ab} = Absorption maximum, λ_{em} = Emission maximum, τ = Lifetime, Δν = Stokes shift.



(a)

Scheme-I

The observed absorption wavelength (296 nm) is because of ground state enol tautomer of salicylic acid anion (a). However, upon proto excitation of aqueous solution of salicylic acid, the phenolic –OH becomes more acidic while –COOH behaves as a basic[13]. Therefore equilibrium dynamics becomes as,

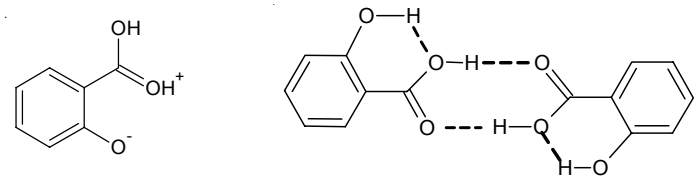


(a) (b)

Scheme-II

The excitation wavelength is because of excited state keto tautomer of salicylic acid anion (b) whose formation involves ESIPT[14]. Thus the different values of λ_{ab} and λ_{ex} are because of the existence of salicylic acid anion in different forms. The λ_{em} of salicylic acid anion is nearly equal to the similar anion formed from aqueous solution of sodium salicylate (λ_{em} = 407 nm)[12]. This fact supports the proposed mechanism of emission arising from salicylic acid anion.

The solvents ethanol and acetonitrile prevents the deprotonation and salicylic acid exists as neutral molecule. The absorption maxima are similar in both the solvents (304 nm). The photo excitation of solution in these solvents generates the dipolar species known as zwitter ion (c) by ESIPT, whose emissions appeared at nearly identical wavelengths in the fluorescence spectra (430 nm) shown in Fig. 1. The spectral results obtained in non-polar solvents benzene and toluene show large spectral shift to red side in fluorescence spectra. The salicylic acid exists as neutral molecule in these solvents and λ_{ab} values are identical (309 nm). The photo excitation of solutions of salicylic acid in non-polar solvents excites neutral molecule and hence λ_{ex} values in both solvents are identical. The fluorescence spectra of salicylic acid in these solvents exhibit large spectral shift (*ca.* 10573 cm^{-1}) and spectra are broad bands. These observations indicate that the salicylic acid molecules are forming dimeric species (d).



(c) (d)

Scheme-III

The existence of different excited state species of salicylic acid in the excited state proposed above are also supported by the lifetime (t) results of excited state species. The value of excited state lifetimes given in Table-1 is different and suggests the existence of salicylic acid in various forms.

The fluorescence spectra of salicylic acid doped polymer films are presented in Fig. 2. The spectra of the films are sharp bands in polar solvents while those prepared from solution from non-polar solvents are broad bands. The wavelengths of maximum emission given in Table-1 are identical with those observed from the respective solution from which films are prepared. This observation indicates that salicylic acid species existing in the solvents get dispersed and deposited in polymer matrix. The color tuning of the films is thus possible by incorporating salicylic acid in different solvents or polymer matrixes. The polymer films are of use as emitting materials for electroluminescent diodes.

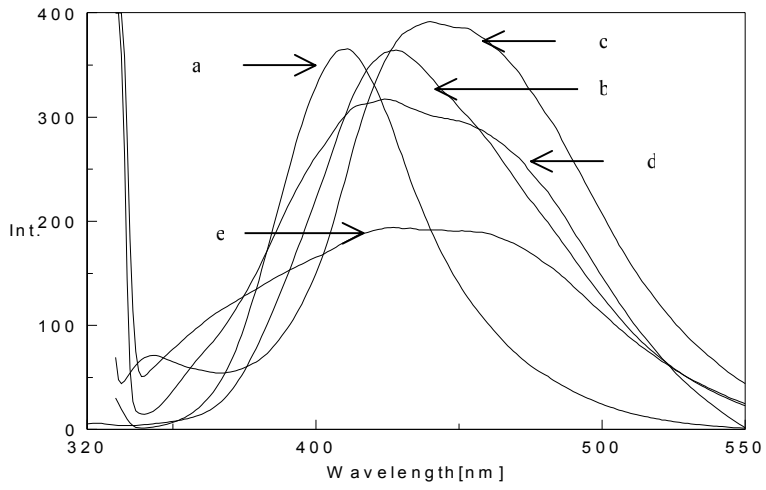


Fig. 2. Normalized fluorescence spectra of 0.001 wt. % salicylic acid doped in polymer films in different solvents, (a) water, (b) ethanol, (c) acetonitrile, (d) toluene and (e) benzene

ACKNOWLEDGEMENTS

The authors gratefully acknowledge Department of Science and Technology and University Grants Commission, New Delhi for providing Grants to the Department of Chemistry, Shivaji University, Kolhapur under FIST and SAP program, respectively.

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(*Received*: 31 October 2007; *Accepted*: 9 February 2008) AJC-6336