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Photophysics and photochemistry of salicylic acid revisited

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Abstract

The spectral and photophysical properties of salicylic acid in various solvents have been studied by steady state and time resolved experiments. Various emitting species have been identified. In alcohols, e.g. methanol, both the zwitterion and monoanion show emission. The addition of a small amount of acid results only in zwitterionic emission, whereas in the presence of a small amount of alkali, the monoanion is produced. Only the monoanion shows emission in water. In concentrated sulfuric acid, emission from the cation is observed, whereas in concentrated KOH solution, the dianion is the emitting species. In hydrogen bonding solvents, e.g. diethyl ether, hydrogen bonded monomers are present. In polymer matrix poly(methyl methacrylate) only monomeric emission is observed. The deactivation of the cation is similar to that of the zwitterion, indicating that the presence of an extra proton in the carboxylic group increases the nonradiative process. Hydrogen bonding as well as viscosity/rigidity of the matrix have also been found to decrease the deactivation rate in the zwitterion. © Elsevier Science S.A.

Keywords: Dual emission; ESIPT; Poly(methyl methacrylate); Salicylic acid; Zwitterion

1. Introduction

Some complexities in the photophysics of salicyl derivatives have been noticed from the early days of luminescence research [1,2]. However, it was much later that Weller [3,4] interpreted the dual emission in salicylic acid due to an excited state intramolecular proton transfer (ESIPT) reaction. On excitation, the carboxylic group becomes more electronegative, whereas the phenolic group gains more positive character. Because of this pK gradient, the phenolic hydrogen is transferred to the carboxylic group resulting in a zwitterion. Weller proposed an excited state equilibrium for the ESIPT reaction. His interpretation of the dual emission was later found to be untenable, as the excited state reaction is very fast (in the order of picoseconds). A ground state rather than the excited equilibrium was found to be responsible for the dual emission [5].

Salicylic acid (SA) has been found to form ionic species in polar solvents [6–8], and dimers in the solid state, in nonpolar solvents, and in the gas phase for moderate and high concentrations [9–12]. Kovi et al. [6] have studied the photoautomerisation reaction in its uncharged as well as singly anionic charged forms. The photophysics of SA in the solid state regarding the dependence of its dual emission with temperature and excitation wavelength has been reported by us in recent articles [9,11]. In hydrogen bonding solvents, the dimers are broken and SA exists in the hydrogen bonded form [11].

SA, being a complex molecule because of dimerisation in nonpolar solvents and ionisation in polar solvents, has not been studied, although its derivative MS has been the subject of extensive studies in the past [5,7,13–18]. In nonpolar solvents, it exhibits two fluorescence bands—a U band ≈350 nm (the mirror image of the absorption) and a Stokes shifted B band ≈450 nm—which have been attributed to two conformers.

The kinetic study of B emission in MS has been performed extensively with respect to temperature, viscosity and solvent polarity [13,14]. Smith and Kaufmann [13] found that the dielectric constant of the solvent plays a major role in the deactivation process. Further, no significant change in the deactivation rate is observed when the solvent viscosity is increased, although a shortening in the decay time is observed in hydrogen bonding solvents. Torobio et al. [14] found that solvent viscosity is not responsible for the nonradiative decay.

SA and similar ESIPT exhibiting compounds show potential in the development of proton transfer lasers [18,19], photostabilisers [20] and information storage devices at the molecular level [21,22]. Moreover, derivatives of SA such as 3,5-di-*tert*-butyl salicylic acid have been found to have

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technological importance in the development of charge control additives in dry xerographic toner [23]. Therefore, the study of the photophysics of SA in different media is, naturally, an important aspect for future developments. In our earlier works, we have reported the behavior of SA in the hydrogen bonding solvent Et_2O and in the solid state in detail. The present report is devoted to its study in various media and under different conditions in order to provide a better understanding of its photophysics.

2. Experimental

SA (Aldrich) was recrystallised from ethanol. All the solvents used in the study were of spectroscopic grade. Polymethyl methacrylate (PMMA) doped SA films were cast from the solution. PMMA grains were dissolved in dichloromethane (DCM). The desired amount of SA from its solution in DCM was then mixed with the PMMA solution. The viscous mass was cast in the shape of the film.

Emission and excitation spectra were recorded by a Spex Fluorolog 1902 and a JASCO FP-777 spectrofluorimeter, and absorption by a V-550 spectrophotometer. Decay data and time resolved spectra were recorded with the help of an Edinburgh 199 time domain spectrometer using the single photon counting method. The excitation source was a thyratron gated lamp with hydrogen as the filler gas. Details of the setup are described elsewhere [24]. The goodness-of-fit for the decay curves was assessed by inspection of the χ^2 distribution of residuals and autocorrelation [25]. Measurements at various temperature were carried out using either a Eurotherm temperature controller (available with the 199 spectrometer) or liquid nitrogen in a quartz jacket.

3. Results and discussion

The various photophysical parameters of SA in different media are given in Table 1.

3.1. Polar media

3.1.1. Steady state data

In methanol (MeOH) the fluorescence spectra of SA show a red shift on increase in concentration and the spectrum broadens (Fig. 1). At a concentration of 10^{-2} M two overlapped bands are evident. However, the absorption spectra show a blue shift with concentration. The emission spectra are dependent on excitation wavelength, particularly for higher concentrations. The addition of a small amount of acid results in emission with a maximum at ~450 nm, whereas the addition of a small amount of KOH shows a maximum at ~405 nm (Fig. 2). The absorption maximum is observed at 305 nm in the former case, whereas it shifts to 297 nm in the latter one.

In water, the emission maximum is observed at 405 nm, whereas the absorption maximum is at 297 nm. In 6 N KOH, the emission is blue shifted (λ_{max} ~ 395 nm) and the absorption maximum is observed at ~302 nm. In conc. H_2SO_4, the emission maximum is at ~407 nm and the absorption is shifted to 328 nm.

3.1.2. Decay data

The decay data of SA in MeOH for different concentrations at three emission wavelengths are shown in Table 2. The decay is biexponential, but the relative amplitudes of these components are dependent on the concentration as well as the emission wavelength. A typical fitted decay curve is shown in Fig. 3. The amplitude corresponding to the shorter component increases on increasing the concentration and also at longer emission wavelengths. As both the components have positive amplitudes, this indicates the presence of two emitting species.

When a small amount of acid is added, the decay becomes exponential and the observed decay time is ~550 ps (Fig. 3(b)). This value compares well with the value of the shorter component of the decay time in MeOH. In methanol:ethanol (MeOH:EtOH = 1:1) glass forming solvent, the decay is again exponential, and a decay time of ~0.7 ns is observed which increases to 9.78 ns at 80 K (Table 3). The addition of a small amount of KOH again results in exponen-

Table 1
Photophysical parameters of SA in various media

Solvent	Conc. (M)	λ_{max}(abs.) (nm)	λ_{max}(em) (nm)	Decay time(s) (ns)	Emitting species
MeOH	10^{-4}	303	420	0.56, 5.71	Monoanion and zwitterion
MeOH + H^+	10^{-4}	305	450	0.55	Zwitterion
MeOH + OH^-	10^{-4}	297	405	6.01	Monoanion
H_2O	10^{-4}	297	405	4.2	Monoanion
6 N KOH	10^{-4}	302	397	4.5	Dianion
Concentrated H_2SO_4	10^{-4}	328	407	0.3 [a]	Monocation
$CHCl_3$	10^{-3}	308	450	1.3	H-bonded zwitterion
Et_2O	10^{-3}	308	450	1.9	H-bonded zwitterion
PMMA	10^{-3}	308	450	1.77, 5.94	Zwitterion

[a] From Ref. [13].

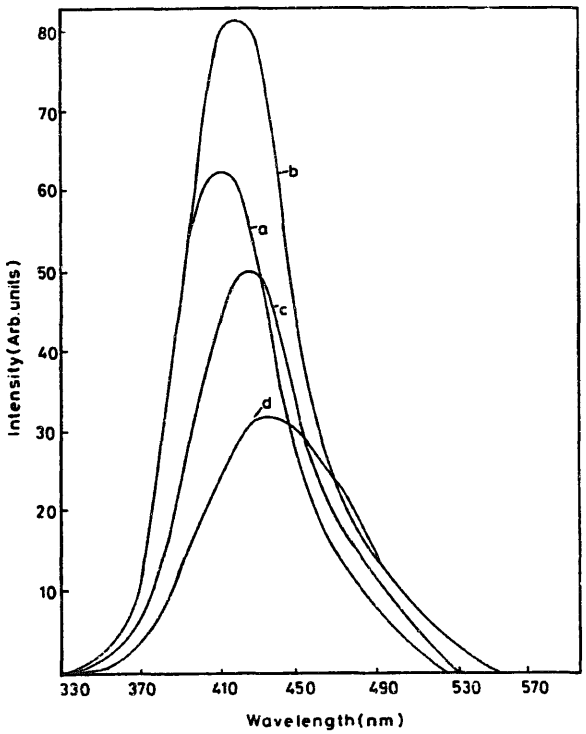

Fig. 1. Emission spectra of SA in MeOH at 290 K (λ_{exc} = 300 nm); (A) 10^{-5} M, (B) 10^{-4} M, (C) 10^{-3} M and (D) 10^{-2} M.

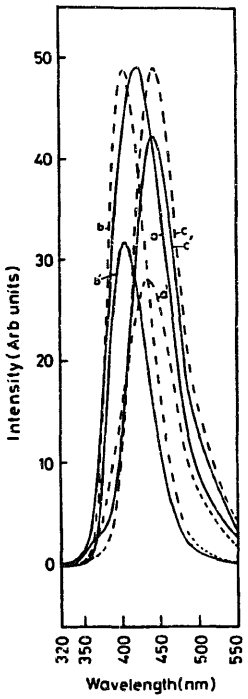

Fig. 2. Emission spectra of SA (conc. 10^{-3} M) in MeOH (a) λ_{exc} = 300 nm and (a') λ_{exc} = 260 nm; in the presence of OH^- ions (b) λ_{exc} = 300 nm and (b') λ_{exc} = 260 nm; in the presence of H^+ ions (c) λ_{exc} = 300 nm and (c') λ_{exc} = 260 nm.

tial decay (Fig. 3(c)), but the decay time is 6.01 ns (corresponding to the longer component). At 80 K, the decay is again exponential with a decay time of 8.01 ns (Table 3).

In water, however, the decay is exponential with a decay time of 4.2 ns. In 6 N KOH, the decay is again exponential with a decay time of 4.5 ns. We did not record the decay times in aqueous solutions at 80 K as a glass is not formed.

In conc. H_2SO_4, the decay time is 300 ps [13] which increases to 12.18 ns at 80 K (Table 3).

To see the effect of viscosity on the nonradiative deactivation in SA, we studied the behavior of SA in other alcohols, e.g. EtOH, *n*-butanol and *n*-octanol in the presence of H^+. It is interesting to note that the decay time increases when higher alcohols are used (Table 4).

We have also studied the temperature behavior of SA in EtOH from 20 to 60°C (Table 5). It is evident that with an increase in temperature, τ_1 decreases while τ_2 remains constant.

The spectral and decay data of SA in these media can be understood by considering various species according to the scheme suggested by Kovi et al. (Fig. 4). In concentrated acid, it is present as the monocation (I). The very short decay time of SA [13] accompanied by a decrease in fluorescence intensity in conc. H_2SO_4 indicates increased nonradiative deactivation in the cationic form. In MeOH, the dependence of the emission on the excitation wavelength and concentration, the double exponential decay and the change in the

Table 2
Decay parameters of SA in MeOH at 290 K (λ_{exc} = 300 nm)

Conc. (M)	λ_{em} (nm)	τ_1 (ns)	τ_2 (ns)	α_1	α_2	%1	%2	χ^2
10^{-5}	370	5.81 ± 0.03	0.54 ± 0.06	0.38	0.01	99.7	0.3	1.04
	410	5.62 ± 0.05	0.55 ± 0.04	0.31	0.03	99.0	1.0	0.99
	470	5.76 ± 0.05	0.57 ± 0.02	0.27	0.04	98.5	1.5	1.09
10^{-4}	370	5.78 ± 0.02	0.54 ± 0.04	0.20	0.16	93.0	7.0	0.90
	410	5.71 ± 0.09	0.56 ± 0.03	0.25	0.42	85.8	14.2	0.93
	470	5.78 ± 0.03	0.55 ± 0.03	0.21	0.52	80.9	19.1	1.09
10^{-3}	370	5.72 ± 0.08	0.56 ± 0.02	0.12	0.26	82.5	17.5	0.96
	410	5.69 ± 0.08	0.55 ± 0.03	0.14	0.46	75.9	24.1	0.99
	470	5.81 ± 0.06	0.58 ± 0.02	0.13	0.56	69.9	30.1	0.96
10^{-2}	370	5.51 ± 0.06	0.53 ± 0.06	0.07	0.31	70.8	29.2	0.93
	410	5.82 ± 0.06	0.57 ± 0.05	0.06	0.35	63.6	35.4	0.90
	470	5.79 ± 0.06	0.56 ± 0.02	0.01	0.19	35.2	64.8	1.02

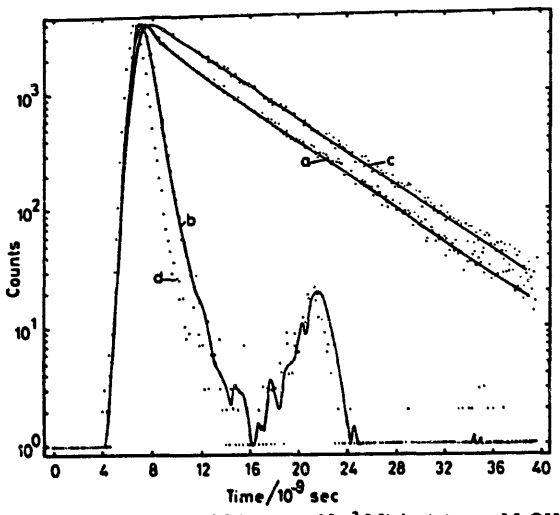

Fig. 3. Fitted decay curves of SA (conc. 10^{-3} M) in (a) neat MeOH, (b) in the presence of H^+ ions and (c) in the presence of OH^- ions. The instrumental profile is shown as a dotted curve (d).

Table 3
Decay times of various species of SA at 80 K

Solvent/glass	Conc. (M)	Emitting species	Decay time (ns)
MeOH:EtOH(1:1)+H^+	10^{-4}	Zwitterion	9.78
MeOH:EtOH(1:1)+OH^-	10^{-4}	Monoanion	8.01
H_2SO_4	10^{-4}	Monocation	12.18

Table 4
Decay data of SA in the presence of H^+ ions in different alcohols at 290 K (λ_{exc} = 300 nm, λ_{em} = 450 nm)

Solvent	Viscosity (η) at 20°C	Decay time τ (ns)	k_{nr} (s^{-1})
MeOH+H^+	0.6	0.55	1.716×10^9
EtOH+H^+	1.2	0.91	0.997×10^9
BuOH+H^+	2.9	1.52	0.555×10^9
Octanol+H^+	8.2	2.21	0.350×10^9

amplitudes of the corresponding decay times with concentration and emission wavelength can be rationalised as attributable to the presence of the neutral monomer (II) and monoanion (IV). When a small amount of acid is added, only neutral molecules will be present, and in the presence of KOH the absorbing species will be the monoanion (IV). As shown in the scheme, the neutral monomer on excitation undergoes ESIPT to form the zwitterion (III) with an emission maximum at ~450 nm and a decay time of 0.55 ns, while the monoanion (IV) on excitation is produced after the ESIPT formation of VI which emits at ~410 nm with a longer decay time.

In MeOH, on decreasing the concentration, both the absorption and emission shift towards shorter wavelengths, and the amplitude corresponding to the longer decay component increases (Table 2). It can be concluded that for low concentrations the number of monoanions increases as compared to neutral molecules, and hence there is less contribution from the zwitterionic species.

The increase in decay time of the zwitterion in higher alcohols (Table 4) indicates that viscosity is responsible for the decrease in deactivation in the zwitterion for SA, although such a viscosity effect was not found in MS [13,14]. The change in solvent polarity (decreasing from MeOH to octanol) cannot explain this behavior, as the zwitterion has a very short lifetime even in nonpolar solvents, e.g. cyclohexane (CH) which will be discussed later. From the logarithmic plot of the relationship between decay time τ_f and solvent viscosity η [26] given by

$$\tau_f = c\eta^{\alpha} \quad (1)$$

we have found the value of α to be 0.53. The correlation between log τ_f and log η indicates that large amplitude internal motion is responsible for the deactivation of the zwitterion. Assuming that nonradiative losses are negligible at 80 K and a radiative lifetime τ_r of 9.78 ns for the zwitterion (Table 3), we have calculated the nonradiative rate k_{nr} for the zwitterion in different alcohols using Eq. (2) (given in Table 3):

$$k_{nr} = 1/\tau_f - 1/\tau_r \quad (2)$$

which also shows that k_{nr} decreases significantly with increasing viscosity. The decrease in τ_1 with temperature (Table 5) also indicates a similar dependence.

In water, all the molecules are present in monoanionic form and hence the decay is exponential. This can be attributed to a higher pK for the deprotonation of the carboxylic group in water [27]. In 6 N KOH, the absorbing as well as the emitting species are the dianion (VI).

From the temperature variation of the decay behavior of SA in concentrated H_2SO_4 and in the presence of acid/base in alcoholic media (Table 3), it is interesting to note that both the zwitterion and monocation (in conc. H_2SO_4) have a similar type of deactivation. From the scheme given in Fig. 4, it can be inferred that when the carboxylic group has an extra

Table 5
Temperature variation of SA (10^{-3} M) in EtOH (λ_{exc} = 300 nm, λ_{em} = 450 nm)

Temperature (°C)	τ_1	τ_2	%1	%2	χ^2
20	0.99	5.72	89.00	11.00	1.17
35	0.59	5.09	80.76	19.24	1.10
50	0.40	5.37	70.74	29.26	0.99
60	0.34	5.47	63.80	36.20	1.01

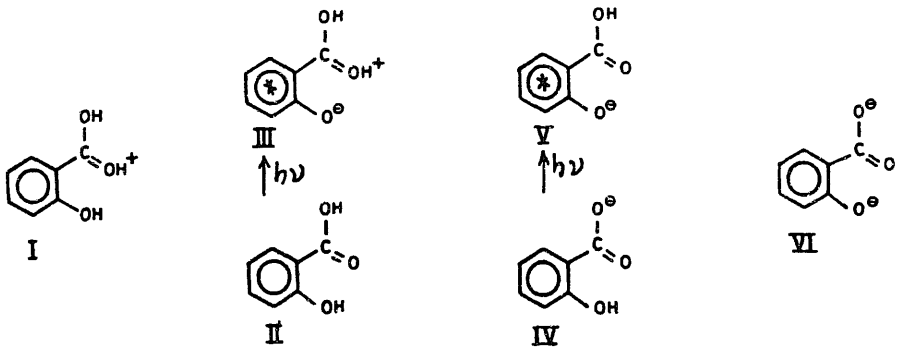

Fig. 4. Various species of SA.

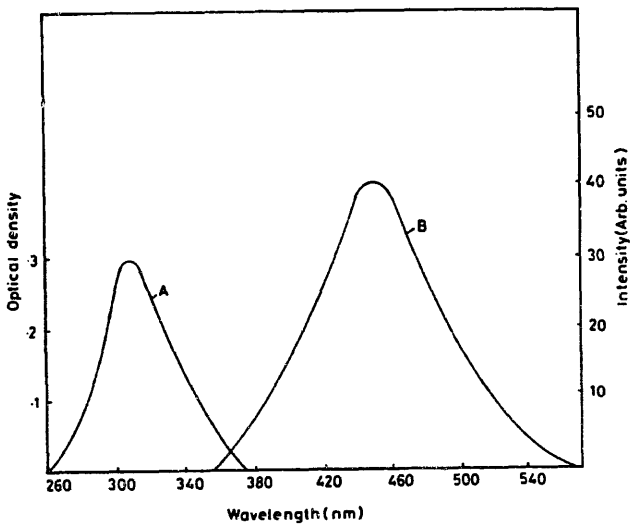

Fig. 5. Absorption (A) and emission spectra (B) of SA (10^{-3} M) in PMMA at 290 K. The excitation wavelength is 310 nm for the emission spectrum.

proton, as in case of the zwitterion and monocation, increased deactivation results.

In a recent study on photoinduced proton transfers in 3,5-di-*tert*-butyl salicylic acid (BSA) [23], it was indicated that the solvent molecules H-bonded with *t*-BSA form cluster complexes with increased quantum yield. However, the temperature variation of SA in EtOH (Table 5) shows that the contribution from the shorter decay component does not increase at higher temperatures. According to our hypothesis, it is expected that with an increase in temperature, more SA molecules will ionise to form monoanions; this is, of course, supported by these data. Therefore, the present study substantiates the presence of different ionic species rather than the presence of clusters (the number of clusters will decrease at higher temperatures).

The very weak emission at 360 nm (Fig. 2(c')) in MeOH in the presence of acid may be due to the presence of such conformers for SA which do not undergo ESIPT similar to MS [6].

3.2. Nonpolar solvents

In nonpolar solvents, e.g. CH and carbon tetrachloride, the emission consists of two bands U (~380 nm) and B (~450 nm) at moderate concentrations. With an increase in concentration, the U band gains in intensity, although the B band is present even at very high concentrations or in the solid state. We have found that even the dimers which have a proper intramolecular hydrogen bond for ESIPT can also give rise to B emission. Thus, the U band can be assigned to those dimers which cannot undergo ESIPT and the B band to ESIPT in monomers as well as dimers.

The decay fits a biexponential function (conc. 10^{-4} M) with decay components 1.41 ns and 360 ps which have been attributed to dimers and monomers respectively. The decay fits this function even at a concentration of 10^{-5} M. However, we could not measure the decaytime at lower concentrations because of weak intensity. At 80 K, the decay of 10^{-4} M SA in a toluene:methyl cyclohexane (1:1) glass forming mixture again fits a biexponential function with decay times of 3.1 ns and 8.97 ns, which can be attributed to the overlap of dimers (U emission) and monomers exhibiting ESIPT (B emission); the shorter decay time 3.1 ns corresponds to dimers and the longer one to monomers. Details of dual emission in SA dimers have been reported by us in our earlier work [8,9].

3.3. Hydrogen bonding solvents

In hydrogen bonding solvents, e.g. diethyl ether (Et_2O) and $CHCl_3$, the dimer emission is not observed and the B emission at 450 nm is present. The decay is exponential, and the decay time is 1.9 ns for Et_2O and 1.3 ns for $CHCl_3$. This can be attributed to a decreased nonradiative process due to hydrogen bonding. More details of hydrogen bonding in SA have been discussed elsewhere [10].

3.4. Polymer matrix (PMMA)

3.4.1. Steady state results

In PMMA, the absorption spectrum of SA (10^{-3} M) shows a maximum at 308 nm. It is interesting to note that only B emission is present (Fig. 5). The U emission is not observed unlike in nonpolar solvents, although PMMA is nonpolar. This indicates that dimers are not present in this matrix, which has also been substantiated by absorption spectra. This absence can be attributed to trapping of the molecules in such an environment (probably hydrogen bonded with the polymer) which inhibits the formation of dimers.

3.4.2. Decay data

SA (10^{-3} M) fits well with a double exponential function in this matrix. The two decay components observed are 1.7 ns and 5.94 ns. Moreover, the decay components vary across the emission profile. The short component τ_1 has a ~20% contribution. The value of the major component τ_2 in this matrix at 80 K approaches the value for the zwitterion in MeOH:EtOH glass at 80 K. However, the double exponential decay may be due to inhomogeneity of the matrix. Similar behavior is observed when MS is incorporated into this matrix. More details will be published elsewhere.

These results indicate that the rigidity of PMMA inhibits the nonradiative process to a considerable extent.

4. Conclusions

In summary, in the present work we report the spectral as well as the decay behavior of SA in various media. Various emitting species have been carried out. In alcohols, the presence of the monoanion as well as the zwitterion as the emitting species is verified. The addition of H^+ ions results in the zwitterion as the emitting species, whereas in the presence of OH^- ions the monoanion is found. Protonation of the carboxylic group has been found to provide a pathway for deactivation. Hydrogen bonding as well as the viscosity/rigidity of the matrix have been found to decrease the deactivation process in the zwitterion.

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