Fluorescence Studies of Salicylic Acid Doped Poly(vinyl alcohol) Film as a Water/Humidity Sensor

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Received: July 30, 2003; In Final Form: January 9, 2004

Photoluminescence of salicylic acid (SA) and its sodium salt in poly(vinyl alcohol) (PVA) film and its quenching by water/moisture has been studied by steady-state and time domain fluorescence measurements. The results suggest that salicylic acid is completely ionized and present as a monoanion in PVA film, having a molar extinction coefficient (ϵ_{max}) of 3545 M^{-1} cm^{-1}, and its emission shows a large Stokes shifted (~8300 cm^{-1}) fluorescence band with a quantum yield (ϕ_f) of 0.34 and a decay time (τ_f) of 6.7 ns. This emission band is due to excited-state intramolecular proton transfer (ESIPT) and is found to be sensitive to moisture and water contents in organic solvents. The films dipped in organic solvents, viz. dioxane, ethanol, and acetonitrile, containing water shows Stern−Volmer type fluorescence quenching. It is shown that a linear quenching of fluorescence intensity and decay time of SA doped PVA film in the presence of moisture or water in the organic solvents can be useful as an optical sensor for determination of humidity in the range 5%−85% and water contents in these solvents in the range 1%−60% with an accuracy of ±0.2%. The response time of the sensor film is about 2 min, and recovery time is less than 1 min.

1. Introduction

Determination of humidity/water content is an important task in industries producing food, textiles, electronic components, fine chemicals, biomedical monitoring instruments, and environmental monitoring instruments in nuclear reactors. Many types of material such as electrolytes,[1] ceramics,[2] and polymers[3−5] have been proposed for monitoring humidity or water content based on variation of their optical and electrical parameters.[10−20] Humidity-dependent photoluminescence of various dye molecules doped in polymer or sol−gel have been reported in the literature.[6,7] Usually the relative change in emission intensity on variation of humidity has been considered for these sensors. Intensity based sensors suffer from the problems of scattering and contributions from unreacted fluorophores, background, etc. Time-resolved measurements, however, are free from these artifacts and hence are more reliable.[9] A few reports regarding the use of the decay time based sensors for humidity exist in the literature.[5−8] Humidity-dependent fluorescence of coumarin-4 doped in sol−gel coated film for the relative humidity (RH) range 3%−90% has been reported by Takahasi et al.[10] A pyrene doped sol−gel thin film humidity sensor has been reported by Wolfbeis et al.[5,7] in 0−100% RH change with response time 5−10 min. Yang et al.[1] reported a resistive type humidity sensor in poly(vinyl alcohol) (PVA) matrix for the relative humidity range 15%−96%, in which plasma treatment increases the stability of these films. Recently some more humidity sensors based on variation of impedance or proton conduction or capacitance have been reported in the literature.[1−15]

Design of an optical sensor for water content in organic solvents or in micelles is of considerable interest. Recently decay time based sensing of water content has been reported by Chang et al.[16] Different dye doped Nafion film based hydrophilic sensors have also been reported in the literature.[3,17] However, a nonlinear dependence of fluorescence intensity with water content has been reported. A fiber optic sensor for water assay in organic solvents based on polymer swelling was reported by Bai et al.[18] They used a bead of anion exchange resin on porous cross-linked polystyrene with ammonium salt as a sensing element. Blyth et al.[19] proposed a gelatin holographic diffraction grating sensor. The diffraction color of the grating changed with fraction of water content. Yang et al.[20] used a fluorescent dye, 10-allylacridine orange, which was covalently bounded to the support matrix at the end of the optical fiber for measuring water content in the organic solvents. It can sense 0−20% water contents in the organic solvents, but its recovery time is long. Upadhyay et al.[21] have also reported a fluorescence based water sensor of 8-1-anilinonaphthalenesulfonate doped PVA film; however, the decay kinetics is complex and does not obey the Stern−Volmer relationship.

Poly(vinyl alcohol) (PVA), a polar and hydrogen bonding polymer in nature, is a humidity-sensing material which has high affinity for water owing to its hydrophilic functional group.[22] It absorbs and deabsorbs water from atmospheric air, changing the water contents in the film.[23] The polymeric network of PVA is similar to microporous metal oxide. It is soluble in water, due to which its durability is poor. However, on adding electrolyte at the time of film preparation or exposing the film to UV radiation, it becomes insoluble in water, with no change in its humidity-sensing characteristics.[14]

In our recent work we have reported the photophysics and photochemistry of salicylic acid (SA).[24,25] Various ionic species are observed in solution as well as in polymeric media.[26] Hydrogen bonding as well as the viscosity/rigidity of the matrix has been found to decrease the deactivation process in these ionic species. SA monomer and monoanion show a double potential well both in the ground state and in the excited state, which resembles the recent experimental finding of ground-state keto−enol tautomerization of monoanion in a nonprotic: water solvent mixture.[27] Recently fluorescence quenching of SA monoanion by water has been reported by Joshi et al.[28] in a

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10.1021/jp0309365 CCC: $27.50

binary solvent mixture. It has been reported[29] from infrared studies that the cis form of the monoanion of SA is more favorable than the trans form. Denisov et al.[30] also reported that, on deprotonation of SA, the strength of intramolecular hydrogen bonding increases.

It is found that SA is completely ionized in poly(vinyl alcohol) (PVA) polymer film and is present as monoanions at lower concentration (0.05 wt %).[26] The fluorescence characteristics of SA doped PVA are found to be highly sensitive to humidity. In dry atmosphere (summer season) its fluorescence intensity is maximum, while in wet atmosphere (rainy season) its intensity decreases drastically. This prompted us to study the fluorescence characteristics of SA monoanion doped PVA film under varying percentage of water content in the vapor phase (moisture in atmosphere) and in organic solvents.

Basically, an optical sensor (optrode) consists of a fluorescent molecule embedded in a support matrix (polymer, porous glass, etc.). The support matrix is held at the end of a bifurcated optical fiber to carry the excitation and emitted radiation. In the presence of the analyte, the fluorescence properties of the sensor are affected and hence determination of the analyte can be done. To get a good response, the support matrix should be of such a nature that the fluorophore comes into contact with the analyte in a short time and does not leach out. The optical sensors have an advantage over conventional devices/sensors because of their utility for working in adverse conditions as well as narrow spaces (micron size), freedom from electrical interference, remote sensing, and no requirement of a reference cell, etc. With the development of less expensive diode lasers and miniaturization in electronics, these may be cost-effective also.

In the present work, we have investigated SA doped in PVA matrix exposed to moisture or varying percentage of water content with a view to understanding the quenching by H_2O molecules in the matrix and finding out the applicability of such a system as a humidity/water sensor. Salicylate anion is used as a scintillator and is well-known for its photostability. Due to the presence of SA monoanion in groundwater,[29] it can also be used as a model molecule for studying environmental conditions.

2. Experimental Section

(a) Materials. All the solvents used in the study were of spectroscopic grade and used without further purification. SA and PVA (molecular weight 23 000) were obtained from Aldrich Chemicals; sodium salt of SA from Sigma and sodium chloride from BDH chemicals were used. SA was recrystallized from ethanol (Aldrich). HPLC-grade water was used for film preparation.

(b) Preparation of the Sample Films. SA and sodium salicylate doped PVA films were prepared by mixing the desired weight of solute with PVA grains in water. The mixture was kept in an incubator at ~50 °C in a polypropylene dish. Films having thickness ~0.1 mm were prepared. The concentration of SA is ~0.05 wt % in these films. Electrolyte film was prepared by adding sodium chloride in the mixture of PVA and SA in water and spread over a polypropylene dish for polymerization and exposed by UV radiation.

(c) Instrumentation. Absorption spectra were taken with the help of a JASCO V-550 spectrophotometer; corrected fluorescence and excitation spectra were recorded with the help of a JASCO FP-777 spectrofluorometer and analyzed by related software. Decay curves were recorded with the help of an Edinburgh 199 spectrometer. The excitation source was a nanosecond flash lamp with hydrogen as a filler gas or a Nd:YAG mode locked, synchronously pumped and cavity dumped dye laser. The cavity dumped output was again redoubled using an angle tuned frequency converter to generate picosecond (ps) pulses in the UV region (310−340 nm). The duration of picosecond pulses was monitored using an autocorrelator trace in the oscilloscope. The pulse width monitored was ~10 ps. Using the time-correlated single photon counting (TCSPC) technique and a laser as an excitation source, the instrumental profile has a full width at half-maximum (fwhm) of about 600 ps with an XP2020Q PMT as detector. Data were stored at 800 kHz pulse rate. The goodness of fit was judged by the residuals and χ^2 values. The measurement error in decay time was of the order of 0.01 ns. The sample was placed in the sample compartment, and the humidity of the sample compartment was varied by flushing dry air. Humidity was measured by a thermohygrometer (J412-CTH) in the temperature range 10−50 °C with 0.1% precision in measurement and humidity measuring range 2%−99% with a precision of 1%. During the humidity measurements the temperature of the sample compartment was maintained constant to ensure that the particular humidity level was not changed. The relative quantum yield of fluorescence was calculated by the relation[37] $\phi_s = \phi_r A_r F_s n^2_s / A_s F_r\ n^2_r$, where indices "s" and "r" represent sample (SA monoanion) and reference (quinine sulfate dication $\phi_r = 0.54$ (at concentration 10^{-5} M in 1 N H_2SO_4)), A is the absorbance at 300 nm, F is the fluorescence area, and $n = 1.45$ is the refractive index of the PVA film.

3. Results and Discussion

The spectral and kinetic results on SA doped PVA in dry state and at different humidity conditions and with varying ratios of water:solvent mixtures have been discussed in the following sections.

(a) Dry Sensor Film. Salicylic acid in PVA (a polar polymer and strongly hydrogen bonding in nature) film (with or without electrolyte) and sodium salicylate in PVA film of concentration 0.05 wt % show an absorption maximum at 298 nm ($\epsilon_{max} = 3545$ mol^{-1} cm^{-1}) and a corresponding Stokes shifted (≈8300 cm^{-1}) emission with a peak at 408 nm. This sample film shows monoexponential decay with a decay time of 6.7 ns. The absorption, excitation, and emission spectra and decay curve of a dry film of SA doped PVA are shown in Figure 1 (parts i, ii, iii, and iv respectively). The full width at half-maximum (fwhm) and the peak position of emission band and decay time are independent of wavelength of excitation. Further, no change in excitation spectra was observed on monitoring the emission spectra at different wavelengths. The calculated fluorescence yield (ϕ_s) is about 0.34 for dry sample. The experimental data reveal that SA is present as monoanion in PVA matrix. On lowering the temperature, the intensity of fluorescence increases with a slight red shift (120 cm^{-1}) accompanied by the lowering of fwhm. The scheme of excited-state intramolecular proton transfer in SA monoanion and the schematic potential energy (PE) diagrams are shown in Scheme 1.

According to Scheme 1 the excited molecule N* undergoes a very rapid intramolecular proton transfer (ESIPT) to form the excited keto tautomer K*, which emits a large Stokes shifted emission. These results correspond to earlier observations that PVA abstracts a proton from the COOH group of SA and forms monoanionic species of SA, in which excited-state intramolecular proton transfer takes place. The large dissociation constant of SA (pK 2.8)[29] stabilizes the monoanion, resulting in an increased quantum yield and longer decay time of the ion. The strength of intramolecular hydrogen bond in SA monoanion is 19.6 kcal/mol in the ground state and 25.9 kcal/

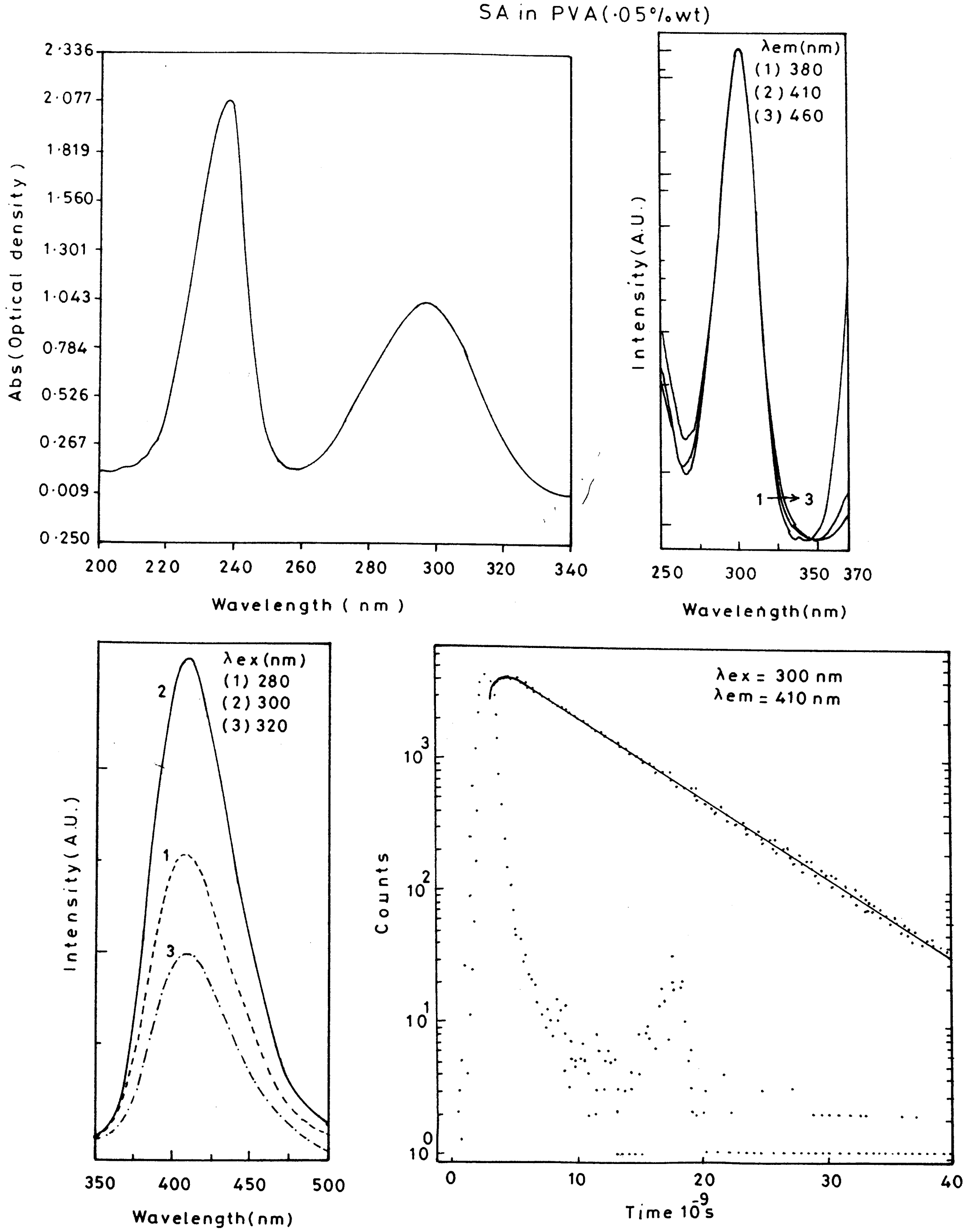
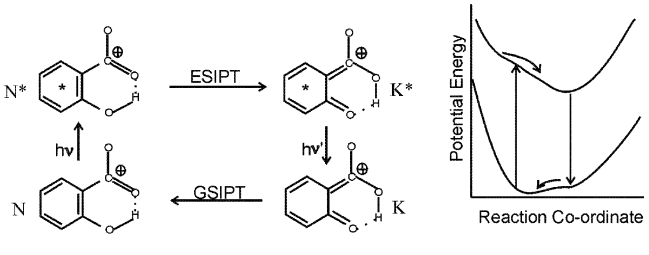


Figure 1. (i, top left) Absorption spectrum, (ii, top right) excitation spectrum, (iii, bottom left) emission spectrum, and (iv, bottom right) decay curves of SA in dry PVA film.

SCHEME 1



(a) ESPT in SA-Mono-anion (b) PE diagram

mol in the excited state, estimated by HF-6-31G** calculations.[25] The strength of intramolecular hydrogen bonding is very strong in the monoanion,[25−30] due to which both emission and absorption spectra are blue shifted in comparison to those for neutral salicylic acid molecule. The activation energy of the monoanion is estimated to be 1.8 kcal/mol.[28] Recently Friedrich et al.[27] have reported the stabilization of the ground-state keto form of SA monoanion in acetonitrile (aprotic) solvent, which results from ground-state intramolecular proton transfer (GSIPT) and is solvent dependent. However, this is not found in the present system. It may be due to the protic nature of the PVA. At 80 K, the red shift of the emission spectrum indicates that the monoanion gets more stabilized and the increase in intensity is due to contraction of the film resulting in increase in concentration.

(b) Film Exposed to Moisture. When the SA doped PVA film is exposed to moisture, no change in absorption and emission is observed. However, the intensity of the fluorescence

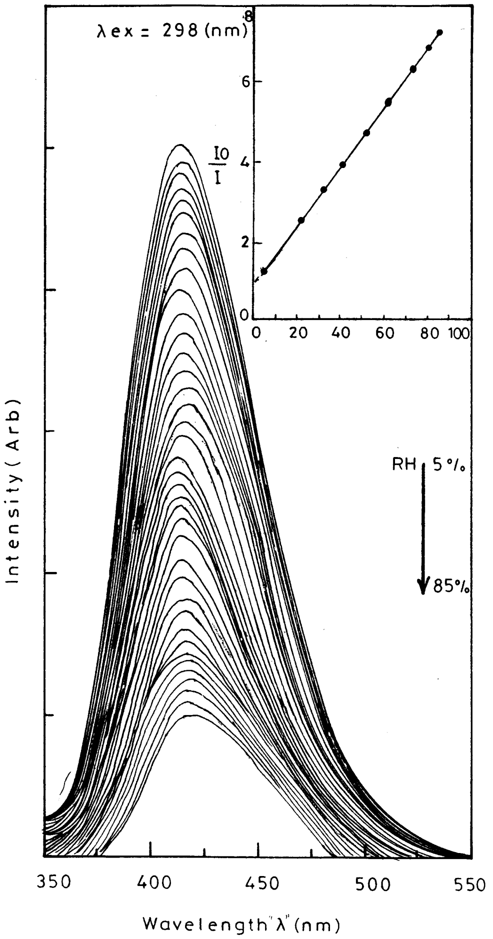


Figure 2. Fluorescence quenching curve of SA doped PVA film for various amounts of relative moisture. Inset shows Stern−Volmer plot for relative fluorescence intensity for SA in PVA with relative percentage of humidity.

band decreases as the moisture absorbed by the film increases as shown in Figure 2. The data were taken after there was no change in intensity indicating that the film is equilibrated at that moisture level. The water content in the film at a given value of RH was measured as

$$\text{percentage of moisture} = \frac{I_0 - I_q}{I_0} \times 100$$

where I_0 is the fluorescence intensity of the dry PVA film, and I_q is the fluorescence intensity of the moisture-exposed PVA film. The decrease in intensity obeys the Stern−Volmer (SV) relation (Figure 2, inset) with varying percentage of moisture.

$$\frac{I_0}{I} = 1 + K_s[Q]_{H_2O}$$

where K_s is the quenching constant and $[Q]_{H_2O}$ is the water content. Yang and Chen[1] have reported that relative humidity (RH) vs water content has two linear regions (0−80% and 80%−100%) with different slopes in PVA. Therefore, we have assumed a linear behavior for RH and water content in our experiment. The calculated SV quenching constant is found to be $K_s = 9.3$ M^{-1}. This shows the sensitivity of the SA monoanion in the PVA toward moisture. The decay time value shows only a slight change with moisture ($\tau = 6.7$ ns at 5% RH, while $\tau = 6.5$ ns for 85% RH). The observed quenching is thus nearly static in nature. Also, the increase in decay time and intensity with temperature (278−323 K) can be explained due to the decrease of fraction of water molecules because of decreased humidity. The temperature measurement of SA anion shows a very small contribution from other nonradiative deactivation processes to explain why the temperature behavior appears to be very small.[36] The PVA matrix absorbs and desorbs moisture in the atmosphere, and changing the water content in the film is very fast.[1,23] We observed that fluorescence intensity of the sample film shows reversible results on increasing and decreasing the humidity of sample as shown in Figure 3.

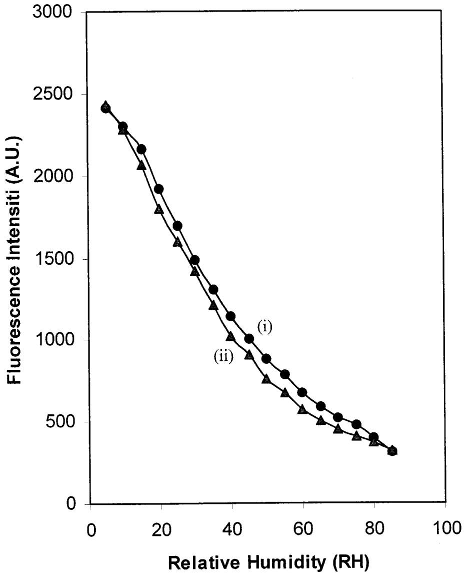


Figure 3. Plots of fluorescence intensity vs humidity, showing the reversibility of the sensor film with (i) increasing humidity and (ii) decreasing humidity.

(c) Film Dipped in Varying Percentages of Solvent:Water Mixture. The SA doped dry PVA film, when immersed for 4 min in neat 2−4 dioxane, shows no change in absorption and emission characteristic with regard to the peak position and intensity. However, for the same film, when immersed in dioxane:water mixture for the same duration of time, a drastic decrease in fluorescence intensity and decay time is observed as shown in Figure 4. The shape and position of the emission maximum remain unchanged; thus the emitter remains a monoanion.

Figure 5 shows the dependence of fluorescence intensity vs the immersion time of the film in dioxane:water mixture for increasing water content. It can be seen that depending on the immersion time the fluorescence intensity initially decreases and becomes constant after 2 min for all the samples containing different water contents; however, no further change in intensity is observed if the film is dipped for more than a period of 2 min. This shows that the response time of the system is about 2 min while the recovery time for the humidity is within a few seconds[1] because PVA absorbs and desorbs water quickly.[23] All the measurements are, therefore, taken by immersing the SA doped PVA film for about 4 min in dioxane:water mixture. When the film is removed from the solution of dioxane:water mixture, the solution does not show any measurable absorption and fluorescence corresponding to salicylic acid anion. This indicates the salicylic anion in PVA film is immobile and cannot leach out. Similar results were observed in ethanol:water and acetonitrile:water mixtures.

In transient measurements, SA doped PVA film dipped in neat dioxane shows monoexponential decay with a decay time of 6.7 ns. When the film is treated with dioxane:water mixture,

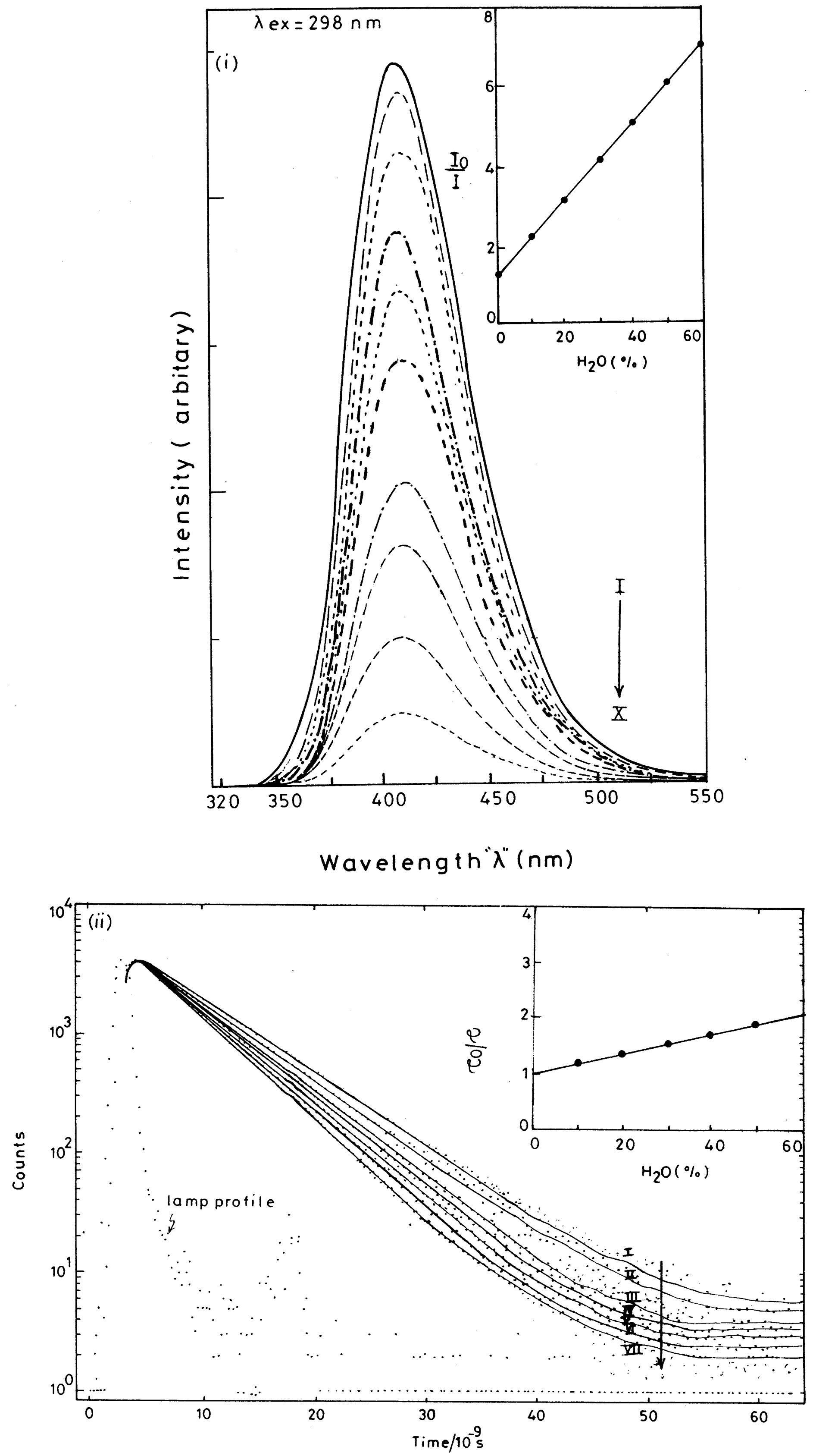


Figure 4. Fluorescence quenching of SA by water in dioxane: (I) 0:100, (II) 10:90, (III) 20:80, (IV) 30:70, (V) 40:60, (VI) 50:50, and (VII) 60:40 mixture. Inset shows Stern–Volmer plot for relative water percentage in dioxane:water mixture. (i) Fluorescence quenching and (ii) decay time quenching.

the decay remains monoexponential even for the highest solvent: water mixture used (60:40). However, the decay time shows successive decreases when the film is immersed in mixtures of dioxane:water with increasing water contents as shown in Figure 4(ii). It can be seen that the decrease in fluorescence intensity is greater than the decrease in decay time. We do not expect

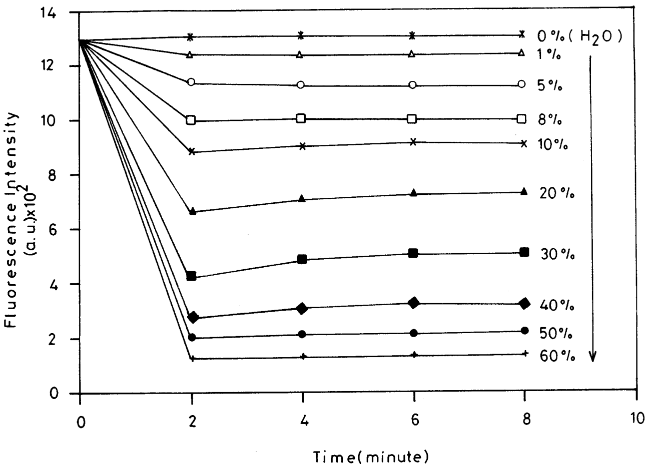


Figure 5. Plots of fluorescence intensity vs immersion time of SA doped PVA film in dioxane:water: (i, *) 100:0, (ii, ×) 90:10, (iii, ▲) 80:20, (iv, ■) 70:30, (v, ◆) 60:40, (vi, ●) 50:50, and (vii, +) 40:60 mixture.

any aggregate formation in PVA, as the shape and fwhm of the absorption and emission bands remain unchanged. It can be seen that the decay time of SA decreases to 4.2 ns for the sample immersed in a mixture of dioxane:water (60:40), which approaches the decay time of SA monoanion in pure water.[24] For higher water percentage the film becomes gel shaped as PVA starts dissolving in water. However, the electrolyte film of SA in PVA does not dissolve up to dioxane:water ratio of 40:60, similar to what is reported by Yang et al.[1] Quenching of fluorescence intensity or decay time vs percentage of water is shown in the insets of Figure 4(i) and 4(ii), respectively. The fluorescence quenching can be described by the well-known Stern−Volmer (SV) relation:

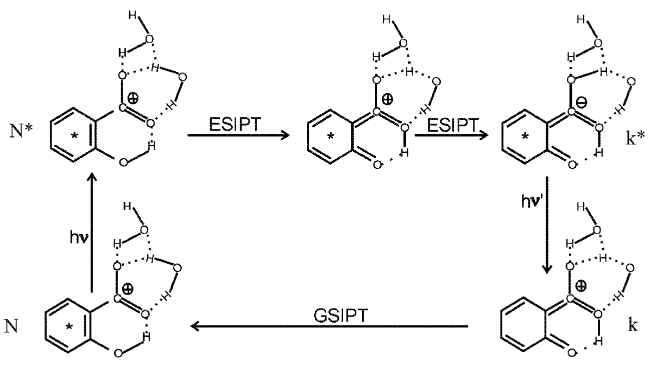
$$I_0/I = \tau_0/\tau = 1 + K_s[\mathrm{Q}]_{\mathrm{H_2O}}$$

where I_0 and τ_0 are fluorescence intensity and decay time in neat dioxane, K_s is the SV quenching constant, and $[\mathrm{Q}]_{\mathrm{H_2O}}$ is the concentration of quencher (water in dioxane).

The quenching constants from steady-state and decay time data are 9.9 M^{-1} and 0.79 M^{-1} per percentage of water, respectively, and the rate of fluorescence quenching is calculated to be $1.4 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. It appears from the SV plot that the quenching is static as well as dynamic because the decay time and intensity SV plots differ and $I_0/I \neq \tau_0/\tau$. We have also measured the water quenching in other solvents, viz. ethanol and acetonitrile and found similar results.

Recently, similar behavior for quenching of fluorescence by water for SA anion in these binary solvents has been reported by Joshi et al.[28] in MeOH/water, acetonitrile/water, and DMSO/water systems. They observed a critical demixing for the formation of water cluster. Furthermore, these authors assume a fast nonradiative process in the protonated molecule. The shift in fluorescence in DMSO/water mixtures can be attributed to the fact that the molecule senses the presence of hydrogen bond donating water molecules in its environment. As DMSO itself cannot donate a hydrogen bond, the increase in lifetime and hence decreased deactivation shows that the molecule is stabilized in these binary solvent mixtures due to increased hydrogen bond donating ability of the mixture. The fluorescence is quenched only when the surrounding water structure is capable of transferring the proton. These observations point to the fact that proton transfer is feasible only when a sufficient number of water molecules are present as hydrated complexes.[38]

SCHEME 2



The presence of organic solvents may break the water structure and hence decrease the protonation. Dielectric measurements also point to this type of behavior in such binary mixtures.[39] Further, in our earlier report[24] we observed that the fluorescence intensity and decay time of SA anion do not change significantly from 80 to 323 K. Similar results are observed in protic polymers.[26] On changing the temperature, therefore, the changes in the intensity and decay time of SA doped PVA film are solely due to evaporation of the water molecule from the sensor film. Thus, the present sensor film can also be used over a wide temperature range.

The observed results can be explained on the basis of the hydrophilic nature and water permeability of PVA film. To explain the quenching behavior in the presence of water, we suggest Scheme 2. Initially hydrogen bond formation between the excited anion and the solvent may stabilize the excited-state ion K*, resulting in an increased quantum yield and longer lifetime of the ion. When this hydrogen bond results in proton transfer to the phenolate oxygen, the fluorescence is quenched.[28] This interpretation is in line with other reports: the importance of the stabilization of the 5-cyano-2-naphthol anion due to hydrogen bond donation by the solvent.[40] In the film containing SA monoanion, when it is dipped in organic solvents containing water, the microenvironmental polarity, viscosity, and free volume may change as water approaches in its vicinity. Consequently, the fluorescence intensity and decay time of SA monoanion decrease by the formation of a water cluster around it. This causes energy deactivation from excited SA anion, and the fluorescence intensity and decay time decrease in the presence of water in solvents or moisture. With regard to the faster decrease of fluorescence intensity compared to a little decrease in decay time, it appears that with increase in water contents the concentration of SA monoanion itself decreases due to increase in the volume of PVA film, whereas the decay time remains constant. (The decay time is independent of concentration in this concentration range.) Further increased water content causes decreased microviscosity of the film, which in effect also causes a reduction in the fluorescence intensity as well as in decay time. However, this effect is observed only when the film is dipped in water containing solvents; the film exposed to differing humidity does not show any significant change in the viscosity. Thus, the decrease in fluorescence decay time as well as intensity can be used as a measure of water concentration in the polymer film.

Although the exact mechanism of quenching of fluorescence of SA with water contents is not clear, it appears to be due to increased nonradiative transitions by protonation of anion in the excited state because of formation of water clusters by anion itself. A similar behavior for quenching in binary solvents has been noted for other systems.[40−42] In the present system the fluorescence emission comes from the anion after undergoing ESIPT and is quenched by excitation energy dissipation into the stretching modes of the hydrogen bonded water clusters or by protonation from water. Moreover, the dependence of the lifetime on the water content is also reflected in the change of the dielectric behavior. In fact, the differences in the quenching behavior in moisture and in organic solvent:water mixtures investigated here point to the fact that different types of organic solvent/water microclusters may be formed. If a sufficient number of surrounding water molecules or another proton source is present, an additional proton-transfer reaction takes place which quenches the fluorescence of the emitting anion.

Interference in these measurements may occur due to fluorescence quenching by dissolved mineral or metal ions, viz. Fe^{3+}, Al^{3+}, etc.,[34−36] present in the groundwater, because the monoanion of SA easily forms complexes with metallic cations or minerals. However, the rate of quenching due to dissolved mineral will be different compared to that for water molecules. SA anion shows quenching by oxygen also,[28] but we did not notice it in PVA probably because of its low permeability to oxygen.

In short, the system presented here can be used as an optical water sensor (range 1%−60% water) in organic solvents and a humidity sensor (range of 5%−85% RH) with an accuracy of ±0.2%. It has good response time (2 min) and reversibility (<1 min) for water molecules compared to other sensors reported in the literature.[20] Thus SA doped PVA film can be used as a sensor head for the humidity or water optrode. With the development of less expensive diode lasers and miniaturization in electronics, these may prove to be cost-effective also. Salicylate ion has good photostability, and it can also provide the advantage of increased life of the sensor.

4. Conclusion

The sensitivity of fluorescence characteristics of salicylic acid in PVA to the moisture content in film has been exploited as a humidity or water sensor. Salicylic acid is completely ionized and present as a monoanion in PVA at lower concentration (0.05 wt %) and is immobilized. The linear dependence of fluorescence parameters of SA doped in PVA film on water content makes the system attractive as an optical sensor for determination of humidity/water contents. The lifespan of the sensor film is very long due to high photostability of the SA monoanion in PVA film. The reversibility and reproducibility of the sensor are adequate for practical applications in a wide temperature range. The sensor is attractive also because of the ease of fabrication and low toxicity of SA and PVA.

Acknowledgment. The authors are thankful to referees of the manuscript and Dr. H. C. Joshi, Scientist, IPR, Ahmadabad, India, for valuable suggestions and critical reading of the manuscript. Prof. S. P. Singh (Botany Department), Kumaun University, is acknowledged for providing the hygrometer. H.M. is thankful to CSIR (India) for a senior research fellowship. V.M. and M.S.M. are thankful to UGC (DSA-COSIST) for financial assistance.

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