



CHAPTER - 4
CONCLUSION

4 CONCLUSION:

Fluorescence properties exhibited by anthranilic acid and salicylic acid in solvents of different polarity are seen to be different due to amino group ($-\text{NH}_2$) and phenolic ($-\text{OH}$) group respectively. The $-\text{OH}$ group is more basic than amino and hence in the excited state $-\text{OH}$ becomes more acidic than amino group and hence release of proton in S_1 state of salicylic acid is faster than in anthranilic acid. The probability of ESIPT in salicylic acid in polar solvent is more than in non-polar solvent. Since ESIPT in anthranilic acid is slower, this molecule prefers intermolecular hydrogen bonding with hydrogen donor solvent and more solvation in the excited polar solvent. The emission observed in salicylic acid solution in polar solvent is due to intramolecular hydrogen bonding through ESIPT, while in nonpolar solvents the intramolecular hydrogen bonding is inhibited as hydrophilic $-\text{COOH}$ group prefer to undergo intermolecular hydrogen bonding with neighboring molecule and dimers are resulted. The long wavelength emission of SA in nonpolar solvent is attributed to intermolecular hydrogen bonded dimer formed in excited state at higher concentration of salicylic acid. The aqueous solution fluorescence spectrum of SA show single sharp band and attributed to as arising from excited salicylic acid anion.

The combined information provided by absorption, excitation and fluorescence spectroscopy indicate that anthranilic acid undergoes a geometry change between its ground state and first excited electronic state due to $\text{NH}\cdots\text{O}=\text{C}$ intramolecular hydrogen bond present in this molecule. In many solvents fluorescence spectra of anthranilic acid are different than those of salicylic acid may be because of different strength of intramolecular hydrogen bond in the ground state. The hydrogen bond in the ground state in salicylic acid is more strong than that of anthranilic acid. The electronic excited state of salicylic acid involves faster hydrogen atom transfer because of ESIPT while in anthranilic acid it is weaker. The dual emission of salicylic acid is due to ESIPT involving hydrogen atom transfer from $-\text{OH}$. However, in anthranilic acid weaker $-\text{NH}_2$ group does not undergo hydrogen atom transfer in excited state to near by oxygen of carbonyl group. Hence dual emission is not exhibited by anthranilic acid, rather it prefers to undergo intermolecular hydrogen bonding with hydrogen donor solvents.

The aqueous solution of salicylic acid emits at 410 nm while that of anthranilic acid has emission at 420 nm. Salicylic acid emission is from salicylic acid monoanion while that from anthranilic acid should be from water bridge structure of AA through intermolecular hydrogen bonding. The excitation and absorption spectroscopy results indicated that AA exists in intramolecular hydrogen bonded enol tautomer in polar ethanol and acetonitrile in ground state while in excited state the geometry changes yield keto tautomer and emission is observed at 410 nm. The addition of water to the ethanol solution of AA shifts emission from 410 nm to 420 nm because of more stable water bridge structure of AA formed through hydrogen bonding. The addition of base (NaOH) change the emission to 400 nm by opening the intramolecular hydrogen bonded enol structure and emission corresponds to neutral AA molecule. Salicylic acid in these solvents exhibit emission at 430 nm due to dipolar phototautomer formed by ESIPT from -OH to -COOH group. The dilution of salicylic acid by the solvent has quenched the phototautomeric emission and emission at 410 nm become prominent. The different nature of excitation spectra of SA monitored at emission wavelength of concentrated solution and dilute solution indicated existence of two different emitting species.

The behavior of anthranilic acid and salicylic acid in non-polar solvent is also different. In nonpolar solvent SA forms dimer in the excited state through intermolecular hydrogen bonding while anthranilic acid neither undergo intermolecular hydrogen bonding nor intermolecular hydrogen bonding. It behaved as neutral molecule. The observed emission is at 394 nm. The increase in concentration has shifted the emission is to 400 nm may be due to increase in intermolecular force between neighboring molecules. The AA in carbon tetrachloride exhibited red shifted dimeric emission at 450 nm due to intermolecular hydrogen bonding between excited AA and ground state AA molecule.

The polymer films doped by SA and AA have exhibited the most of emission properties as per the expectation. It was expected that locking of molecular species from solution into rigid polymer exhibit similar fluorescence properties. The polymer films doped by AA and SA molecule were prepared from the solution of same concentration used in solution fluorescence studies. The preparation of films involves dissolving the suitable polymer corresponding to 2 wt. % in the solution and evaporation of solvent in

keeping solution in incubator maintained at 45⁰C. The acid doped films of polystyrene, polypyrrolidone, polyvinyl alcohol and polyvinyl acetate were prepared and subjected to fluorescence studies. The film containing larger wt. % of solute are more intense. The emission behavior found same as in solution spectroscopy. The examination revealed emitting species such as photo anion, intramolecular hydrogen bonded molecule by ESIPT and intermolecular hydrogen bonded dimer. The water bridge structure with AA doped in PVA is not evidenced in the fluorescence spectrum because of evaporation of water during films preparation. In film PVA abstract hydrogen in the excited state and hence emission corresponding to that of monoanion is observed.

The goal of present studies to lock the molecules from solution on condensed state by doping in polymer film is achieved. Most of the doped films prepared from solution contained fluorescent solute exhibited emission similar to that seen from solution. The fluorescence from doped film is observed in different region of visible spectrum and can be tuned both by varying amount of solute and also by changing solvent during preparation of solution. The polymer films are suitable for application in polymer light emitting devices. The change in intensity of films observed from films prepared from polymer solution containing varying amounts of solute can also be used to measure the water content. The variation of water content seen to change the intensity of wavelength of maximum emission. Thus the studies presented in the dissertation are of scientific as well as of technological significance.