

CHAPTER 2
EXPERIMENTAL

2.1 Materials-

2.1.1 Fluorophore:

The organic fluorescent materials used in the present studies are substituted aromatic acids. Fluorescent acids such as anthranilic acid (AA) from S.D. fine, salicylic acid, benzoic acid and 4-amino benzoic acid (4-ABA) from Merck were used. The AA, SA, BA, 4-ABA are used after confirming the spectral properties. Details of all organic acids and data of preparation parameter of solutions are given in Table 2.1

2.1.2 Solvents:

Solvents procured from Merck were distilled twice dehydrated by adding anhydrous Na₂SO₄ and ethanol in the present experiment was vacuum distilled Benzene, toluene, carbon tetrachloride, ethanol, ethyl acetate, acetonitrile and water were used as solvents. These solvents found non-fluorescent in the spectral region in which the fluorescence of aromatic acids of the present work are studied.

2.1.3 Polymers:

The polymers such as polystyrene (PS) (Asian Chemicals), Poly-vinyl pyrrolidone (PVP) (Sisco Research lab), Poly vinyl alcohol (PVA) (Rasayan lab) were used as received. These polymers provide a suitable solvent in which it is dissolved.

2.2 Purification and purity testing:

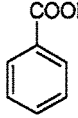
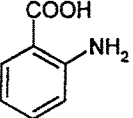
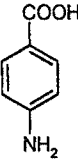
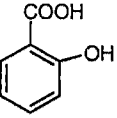
Fluorescence of acids is sensitive for presence of trace of impurity and found to change fluorescence color as well as intensity of the fluorescence. The present work consists of proton transfer in the aromatic acids. The compounds used under such studies

should be of high purity. Benzoic acid, anthranilic acid, 4-aminobenzoic acid and salicylic acid were recrystallised from its saturated solution in ethanol.

2.2.1 Purity testing –

Fluorescent organic acids were tested for their purity by taking melting points and fluorescence spectra. Melting points of all materials were recorded and compared with the literature values⁸⁴ (Tables 2.1).

Table 2.1 Parameters of fluorophore:

| Compound | Structural Formula | Molecular Formula | Melting Point ($^{\circ}\text{C}$) | | Substituent group | Nature of substituent |
|----------------------|---|--|--------------------------------------|------------|---------------------------|---|
| | | | Experimental | Literature | | |
| Benzoic Acid |  | $\text{C}_7\text{H}_6\text{O}_2$ | 121 | 122 | —COOH —NH ₂ | Electron withdrawing |
| Anthranilic acid |  | $\text{C}_7\text{H}_7\text{O}_2\text{N}$ | 147 | 146 | —COOH —NH ₂ | Electron withdrawing Electron donating |
| 4-Amino Benzoic acid |  | $\text{C}_7\text{H}_7\text{O}_2\text{N}$ | 181 | 181 | —COOH —OH | Electron withdrawing Electron donating |
| Salicylic acid |  | $\text{C}_7\text{H}_6\text{O}_3$ | 160 | 159 | -COOH -OH | Electron withdrawing Electron donating |

The fluorescence is characteristic property of the given compound, which is independent of the excitation wavelength used. The presence of impurity in the given compound may produce its own spectrum. Hence the purity of compounds was further confirmed by recording their fluorescence spectra obtained at different excitation wavelengths in the range 250 nm – 450 nm as most of the aromatic acids are UV sensitive. It is seen that the fluorescence spectra excited at different wavelengths were identical for the given compound is an indication of absence of fluorescent impurity. The data given in the table reveal that the melting points match with the literature values within experimental limits. The photo-luminescence spectra of crystalline aromatic acids used in the present studies were also recorded and all of them found weakly fluorescent in the crystalline state. However they have exhibited very interesting photophysical properties when placed in different solvents and doped in polymer films.

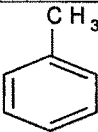
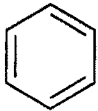
2.3 Setting of the experiments –

2.3.1 Preparation of stock solutions –

Stock solution of fluorescent acids was prepared by dissolving calculated amounts of solutes in to different solvents. The solutes were accurately weighted by using Mettler Toledo make balance, Model – AB204-S, of sensitivity = ± 0.1 mg. These solutions were prepared in different polar and non-polar solvents.

The characteristic features of the solvents used in the present studies are given in Table 2.2. All solutions were deaerated by purging nitrogen prior to fluorescence measurements.

Table 2.2 Physical parameters of the solvents:

| solvents | Structural formula | Molecular weight gm/mole | Boiling point °C | Dielectric constant ϵ | Dipole moment μ | Density gm/cm ³ d | Refractive index n | Polarity parameter Δf |
|----------------------|---|--------------------------|------------------|--------------------------------|---------------------|------------------------------|--------------------|-------------------------------|
| Benzene |  | 78.108 | 80.103 | 2.284 | 0 | 0.8736 | 1.4979 | 0.0030 |
| Toluene |  | 92.134 | 110.62 | 2.379 | 0.39 | 0.8623 | 1.4941 | 0.0130 |
| Carbon tetrachloride | CCl ₄ | 153.82 | 77 | 2.17 | 0 | 1.5842 | 1.4601 | 0.028 |
| Ethanol | CH ₃ CH ₂ OH | 46.086 | 78.325 | 24.30 | 1.68 | 0.7850 | 1.3594 | 0.1815 |
| Ethyl acetate | CH ₃ CH ₂ CO OCH ₃ | 88.104 | 77.114 | 6.02 | 1.81 | 0.8945 | 1.3697 | 0.1995 |
| Acetonitrile | CH ₃ CN | 29 | 81 | 36.6 | 3.92 | 0.786 | 1.3441 | 0.3054 |
| Water | H ₂ O | 18 | 100 | 80 | 1.85 | 1 | 1.3333 | 0.3194 |

The stock solution of AA of concentrations 0.1wt % were prepared in different solvents and solutions of different concentrations were prepared from stock solutions. The solutions were deaerated by purging nitrogen gas and then used for fluorescence and absorption measurements.

2.3.2 Preparation of thin films –

Fluorescent acids doped in polymer films were prepared by mixing the desired weight of solute with polymer in different solvents. The mixture was kept in an incubator at 40C in

a polypropylene dish. Films having thickness ~ 0.1 mm were prepared. The solute was doped in different polymers such as PS, PVA, PVAc and PVP from its solutions in the solvents carbon tetrachloride, toluene, benzene, water, acetonitrile and ethanol respectively.

2.4 Optical measurements / Instruments-

2.4.1 Fluorescence spectrometry –

The fluorescence and fluorescence excitation spectra of the solutions i.e. organic aromatic acids in different solvents were recorded on P.C. based spectrofluorometer specifications procured under DAE project in December 1999. The experimental setup is shown in the photograph i.e. Figure.2.1. It is of following specifications.

Instruments**PC based spectrofluorometer**

| | |
|---------------------------|--|
| Make | : JASCO, Japan. |
| Model | : FP-750. |
| Light Source | : 150 watt xenon lamp with shielded lamphouse. |
| Monochromator | : holographic grating with 1200 line/mm. |
| Wavelength range | : 220 to 730nm. |
| Spectral bandwidth | : 10, 20nm on both excitation and emission Monochromator. |
| Wavelength accuracy | : ± 3 nm. |
| Wavelength throw speed | : 30,000 nm/min. |
| Wavelength scanning speed | : 60, 250, 1000, 4000 nm/min. |
| Response | : Fast, Medium, Slow. |
| Sensitivity | : S/N ratio of Raman band of water higher than 300:1. |
| Photometric display | : -999 to +999. |
| Sample chamber | : Single cell holder. |
| Detector | : Silicon photodiode for excitation and photomultiplier tube for emission monochromator. |

During recording the fluorescence and fluorescence excitation spectra the parameter like spectral bandwidth (10 nm), data (1 nm) and wavelength scanning speed (250 nm/min) were kept constant. The other parameters such as excitation emission wavelengths were varied as per requirement of the experiments.

A special front surface attachment provided with instrument was used to perform the fluorescence measurements of the films

2.4.2 Absorption spectrometry –

Absorption spectra of solution were measured on UV-Visible Spectrophotometer Shimadzu UV-VIS-NIR Spectrophotometer UV-360 (206-23000).