CHAPTER 5

PHOTOACOUSTIC MEASUREMENT OF THERMAL DIFFUSIVITY IN METAL PHTHALOCYANINES

5.1. ABSTRACT.

Thermal diffusivity values in iron, nickel, manganese, zinc phthalocyanines and in a metal free phthalocyanine as well as in their iodine doped samples have been determined using photoacoustic (PA) technique. Samples in the form of a pressed pellet have been used along with an Ar + laser for exciting the PA effect in a suitable photoacoustic cell and the amplitude of the PA signal was measured with a lock-in amplifier. The method involves the determination of the characteristic frequency $f_c$ obtained by measuring the variation of the amplitude of the photoacoustic signal as a function of the chopping frequency of the laser beam. The results indicate that doping with iodine enhances the thermal diffusivity in a substantial manner in Metal Phthalocyanines (MPcs). It is also found that the thermal diffusivity values obtained for metal phthalocyanines are comparable with that of zinc naphthalocyanines which are also organic semiconductors like phthalocyanines.
5.2. INTRODUCTION.

Phthalocyanines have received more attention recently because of their chemical flexibility, charge transport properties and technological applications. Most of this work has been carried out on polycrystalline samples, owing to the difficulties encountered in obtaining single crystals of sufficient size. Porphyrin like structure with high chemical and thermal stability makes phthalocyanine compounds a very attractive class of materials in the field of organic semiconductors. Metal phthalocyanines have found wide use as paint pigments and dyes. Because of their extremely good stability to acids, alkalis and solvents phthalocyanines are particularly useful in spin dyeing. Phthalocyanine pigments in the form of aqueous dispersions are used in pad dyeing with resin emulsions. Many of these metal phthalocyanines can be used as catalysts. Cobalt, Nickel and Iron phthalocyanines catalyse the oxidation of many organic compounds. Similarly, the photoconducting property of MPcs has been extensively studied for use in electrophotographic systems, diodes, laser printers, photovoltaic cells and photoelectrochemical devices [1-5].

However, metal phthalocyanines such as FePc, NiPc, MnPc and ZnPc are of considerable interest as new candidates for optical, electronic, photoelectric, electrochemical and photovoltaic applications. Recent reports show that organic dyes such as phthalocyanines are very good material for optical data storage (ODR) applications in place of metallic substances because of their chemical stability and feasibility for synthetic engineering [6,7]. It has also been reported that phthalocyanines possess non-linear optical properties and many of these exhibit large $\chi^3$. 
values [8]. Highly conjugated π - electron system has been considered as the most suitable organic materials for third- order non-linear optics. As a result measurement of their thermal, chemical and optical properties has acquired great significance.

Photoacoustic technique (PA) is a versatile method for the measurement of thermal and optical properties of materials of various kinds. It is also a very reliable technique which yields fairly accurate values for the above parameters when only small sample volumes are available. In PA method the energy of intermittent optical radiation incident on a sample surface generates periodic heating which is finally converted into a sound signal. The composite nature of the acoustic signal generation with definite amplitude as well as phase constitutes the main feature of the PA effect in comparison with other measurement methods. The signal produced is sensitive only to the absorbed radiation which is converted to PA signal by nonradiative processes. This chapter describes the photoacoustic measurements of thermal diffusivity in metal free phthalocyanines (H₂Pc), metal phthalocyanines and their iodine doped forms using front surface excitation technique. A knowledge of the thermal diffusivity of these molecular electronic materials will be very useful in situations involving heat flow problems encountered in device fabrication and application.
5.3. THEORY.

As seen in chapter 4, following the one dimensional model of Rosencwaig and Gersho [9], the pressure variation \( \delta P \) at the front surface of an optically thick sample irradiated with a chopped beam of monochromatic radiation depends on the thermal diffusivity \( \alpha_s \) of the sample. The theoretical expression of \( \delta P \) may be written as

\[
P = X \cdot Y
\]

In the above relation,

\[
X = \left[ 1 + g \frac{h^+ + h^-}{h^+ - h^-} \right] \left[ g + \frac{h^+ + h^-}{h^+ - h^-} \right] \frac{1}{\alpha_s^2 l_s^2}
\]

where,

\[
h^+ = \exp(\sigma_s l_s)
\]

\[
h^- = \exp(-\alpha_s l_s)
\]

\[
\sigma_s = (1 + j) \left[ \frac{\pi f}{\alpha_s} \right]^{1/2}
\]

\[
g = \frac{e_b}{e_s} = \left[ \frac{K_b}{K_s} \right] \left[ \frac{\alpha_s}{\alpha_b} \right]^{1/2},
\]

the ratio between the effusivities of the backing material \( e_b \) and the sample \( e_s \).

\[
Y = \frac{P_0 \gamma W_a l_s^2}{2 l_g T_0 K_s} \left[ \frac{\alpha_g}{\alpha_s} \right]^{1/2}
\]

-------------------(5.2)
Here \( l, K, \rho \) and \( C \) are length, thermal conductivity, mass density, and specific heat, and subscripts \( g, s, \) and \( b \) refer to the gas (air), sample and backing material respectively. \( P(T_0) \) is the ambient pressure (temperature), \( \gamma \) is the specific heat ratio for air, \( W_a \) is the absorbed power of light. The effusivity of the gas in the cell has been neglected compared to the effusivity of the sample, since their ratio is always less than 1%. The term \( X \) depends on the modulation frequency \( f_c \) through the product \( \sigma_s l_s \), which can be written as

\[
\sigma_s l_s = (1 + j) \left( \frac{\pi f}{f_c} \right)^{\frac{1}{2}} \tag{5.3}
\]

where the characteristic frequency \( f_c \) is given by

\[
f_c = \frac{\alpha_s}{l_s^2} \tag{5.4}
\]

It can be found out by plotting \( \log A \) against \( \log f \) where \( A \) is the amplitude of the PA signal (which is directly proportional to \( \delta P \)). When chopping frequency \( f \) becomes equal to \( f_c \), a change in slope occurs in the above plot.

5.4. EXPERIMENTAL.

5.4.1. Synthesis, Purification and Characterisation of Phthalocyanines.

Phthalocyanine metal complexes may be prepared by various methods. The technological importance of the phthalocyanine pigments has generated renewed interest in their synthesis, purification and characterisation. One
of the important methods available for the synthesis of metal phthalocyanines is the reaction of phthalonitrile with a metal or metal salt in a high boiling liquid like nitrobenzene or quinoline. In this method phthalonitrile and metal chloride with mole ratio 4:1 is heated to 180°-190° C for two hours in quinoline or in a mixture of quinoline and trichlorobenzene. Iron, Nickel, Manganese and Zinc phthalocyanines have been synthesised by this method [10,11]. The reaction may be written as,

$$MeCl_2 + 4 \text{[phthalonitrile]} \rightarrow MPc Cl + Cl^-$$

This reaction takes place in the presence of urea, or quinoline act as accepters for the halogen atoms which enter the phthalocyanine molecule to an appreciable extent when the accepters are not present.

A formidable hurdle in phthalocyanine chemistry is the isolation of phthalocyanine in its purest form. Every method of synthesis of phthalocyanines results in the contamination of the product with unreacted materials such as phthalic anhydride, urea, phthalimide or phthalonitrile. The phthalocyanine formed itself is a mixture of oligomers. Classical purification techniques such as acid and alkali washing, solvent washing, solvent extraction, regeneration by concentrated H_2SO_4, vacuum sublimation and chromatography are used to purify the crude phthalocyanines.

The first step in the purification of phthalocyanine involves washing with 10% caustic soda, 2M HCl, methanol and benzene successively. The solid mass so obtained is slurried in concentrated sulphuric acid and dropped on ice. The precipitate which is essentially a mixture of various polymorphs of metal phthalocyanines is washed with water and dried. Though this method is sufficient for the removal of
unreacted materials, the different polymorphs and oligomers cannot be separated. The unreacted phthalonitrile was removed by soxhlet extraction with benzene. It is again purified by vacuum sublimation.

The method of preparation of metal free phthalocyanines is quite different. Magnesium phthalocyanine that is already prepared is dissolved in concentrated sulphuric acid and the solution thus obtained is poured over ice. Metal free phthalocyanines precipitate and which can be purified by the procedure described above.

The whole samples prepared were characterised by elemental analysis; UV-Vis and IR Spectroscopy.

5.4.2. Structure of Phthalocyanines.

Phthalocyanines are macrocyclic compounds containing four pyrrole units and structurally similar to porphyrins and tetraazaporphins. More generally, they include tetraazaporphins in which the four pyrrole units are fused to an aromatic structure. In addition to the structural similarity of phthalocyanines to porphyrin, they are closely related in many other respects. Both are stable to alkalis, less so to acids, both are highly coloured, and form complex metallic compounds, both are degraded by oxidation to the imides of dibasic acids. The order of stability of the metallic derivatives of the two classes are also similar.

The compound usually referred to under the phthalocyanine class consists of metal derivatives of phthalocyanine. The two hydrogen atoms attached to the two isoindole group can be replaced by metal atoms from every group of the periodic table.
to form the metal phthalocyanines (Fig. 5.1). Also, each of the sixteen peripheral hydrogen atoms on the four benzene rings can be substituted by a variety of atoms and groups.

The Phthalocyanine can be considered as a weak dibasic acid and the metal derivatives as its salts. For example, in metal phthalocyanines, the metal atom supplies one electron to the nitrogen atoms of the isoindole groups and these isoindole nitrogen atoms in turn supplies an electron to the metal atom, forming a covalent bond. The unshared pairs of electrons in the remaining two isoindole nitrogen atom presumably form coordinate covalent bonds with the metal atom. The unusual stability of these metal complexes can be explained by the coordination of the central metal atom.

5.4.3. Doping in Metal Phthalocyanines.

The effect of doping on the electrical and photoconductivity of molecular solids is well known. The electrical and photoconductivities of phthalocyanines are also found to be increased by the addition of dopants like iodine. A study of the doping effect on the organic semiconductors give a clue to the electronic processes such as charge carrier generation upon irradiation, the process being essential in photosynthesis and solar energy conversion [12]. However, by doping with iodine, the conductivity of phthalocyanines can be markedly increased [13,14]. Because of the high stability of \( \text{I}_3^- \) polar environments, and its ability to accommodate itself into channels in one dimensional lattices, iodine is an advantageous dopant for
Fig (5.1). Structures of (A) Phthalocyanines and (B) Metal Phthalocyanines.
the oxidation of planar organic molecules. Iodine doping forms stacks of partially oxidized metal phthalocyanine units and parallel chains of $I_3^-$ counter ions [15]. The oxidation of purified metal phthalocyanines and metal free phthalocyanines by iodine vapour or solutions results in dark coloured solids with a range of stoichiometries [16], the exact composition obtained depending on the conditions,

$$M\text{Pc} + \frac{1}{2} I_2 \rightarrow M\text{Pc}(I)_x$$

FePc, NiPc, MnPc, ZnPc and H$_2$Pc samples were doped with iodine in the solution phase as reported in the case of cobalt phthalocyanine earlier [17,18]. 200mg each of the samples was stirred with a saturated solution of iodine in carbon tetrachloride (CCl$_4$) for 48h. The doped materials were filtered, washed with CCl$_4$ till there was no extraction of iodine. These samples were dried at 800°C in vacuum for 2h before pelletising the same. The measurements were made on pressed (2000 kg cm$^{-2}$) pellets of the samples having thickness 0.065 cm. The saturation pressure (2000 kg cm$^{-2}$) was determined by pressing the sample to a level at which the density remains unaltered with further increase in pressure.

5.4.4. Instrumental.

Block diagram of the experimental set up is shown in Fig.(5.2). Fig. (5.3) shows a photograph of the experimental set up. The light source used is the 488 nm radiation from an Ar$^+$ laser (Liconix -5000 series) at a power level of 30 mW. The laser beam is chopped by a mechanical optical chopper (Stanford Research System model SR 540). The non-resonant type PA cell used for the measurement is shown in Fig.(5.4). It has a cylindrical cavity of length 0.5cm and diameter 1cm made in a
solid block of stainless steel. The glass window and the microphone are sealed with O’ rings and air at atmospheric pressure acts as the coupling gas medium. The signal is detected by Knowle’s 1753 electret microphone kept inside the PA cell and the output is analyzed using a digital lock-in amplifier (EG & G model 5208). The response of the PA cell to the incident radiation was evaluated using carbon black as the sample [Fig. (5.5) and Fig. (5.6)].

5.5. RESULTS.

The amplitude of the PA signal $A$ is measured as a function of the chopping frequency $f$ which ranged from 20 to 200 Hz for all the five samples and for their iodinated forms. The log $A$ vs log $f$ plots obtained for FePc, NiPc, MnPc, ZnPc and H$_2$Pc and their iodine doped forms are shown in Figures (5.7a, 5.7b, 5.7c, 5.7d, 5.7e). The characteristic frequency (frequency at which sudden change in slope occurs) for each of the substance was obtained from these graphs. The calculated values of thermal diffusivity are given in the Table 1. The results can be considered as reliable within 2%.
Fig.(5.2). Block diagram of the experimental set up.
Fig (5.3). Photograph of the experimental set up.
Fig (5.4). Schematic diagram of the PA Cell.
Fig (5.5). log-log plot of the PA signal amplitude versus chopping frequency of carbon black.
Fig (5.6). Variation of the PA phase with chopping frequency for carbon black.
Fig. (5.7a). log-log plot of the PA signal amplitude versus chopping frequency for FePc (a) and FePcI (b)
Fig. (5.7b). Log-log plot of the PA signal amplitude versus chopping frequency for NiPc (c) and NiPcI (d)
Fig. (5.7c). log-log plot of the PA signal amplitude versus chopping frequency for MnPc (e) and MnPcI(f)
Fig (5.7d). log-log plot of the PA signal amplitude versus chopping frequency for Zn Pc (g) and ZnPcI (h)
Fig. (5.7e) log-log plot of the PA signal amplitude versus chopping frequency for H₂ Pc (i) and H₂Pci (j)
<table>
<thead>
<tr>
<th>Samples</th>
<th>Characteristic frequency ($f_c$) Hz</th>
<th>Thermal diffusivity $\alpha$, cm$^2$/sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FePc</td>
<td>36.76</td>
<td>0.17</td>
</tr>
<tr>
<td>FePcI</td>
<td>49.74</td>
<td>0.23</td>
</tr>
<tr>
<td>NiPc</td>
<td>33.14</td>
<td>0.14</td>
</tr>
<tr>
<td>NiPcI</td>
<td>49.70</td>
<td>0.21</td>
</tr>
<tr>
<td>MnPc</td>
<td>32.35</td>
<td>0.14</td>
</tr>
<tr>
<td>MnPcI</td>
<td>39.81</td>
<td>0.17</td>
</tr>
<tr>
<td>ZnPc</td>
<td>31.12</td>
<td>0.13</td>
</tr>
<tr>
<td>ZnPcI</td>
<td>36.48</td>
<td>0.15</td>
</tr>
<tr>
<td>H$_2$Pc</td>
<td>28.18</td>
<td>0.12</td>
</tr>
<tr>
<td>H$_2$PcI</td>
<td>33.81</td>
<td>0.14</td>
</tr>
</tbody>
</table>
5.6. DISCUSSION.

From the result presented here it may be noted that the thermal diffusivity values are substantially higher in the case of iodine doped metal phthalocyanines in comparison with iodine free samples. It may also be noted that the magnitude of thermal diffusivity values obtained here for phthalocyanines are comparable with the values reported for zinc naphthalocyanines which is also an organic semiconductor like phthalocyanines [19].

Since the thermal diffusivity \( \alpha = \frac{K}{\rho C} \) where \( K \), the thermal conductivity, \( \rho \) the density, and \( C \), the specific heat capacity of the sample, the variation in \( \alpha \) may be contributed by any of the above three quantities. Studies have shown increased value of density in iodinated metal phthalocyanines [17]. As the structure of the metal phthalocyanines considerably changes on doping with iodine, the variation in specific heat capacity should also be taken into account [15]. Specific heat capacity of metal phthalocyanines increases on iodination because the thermal activation energy of the iodinated sample is 50 fold greater than the undoped complexes [20]. Nevertheless we see a substantial increase in the thermal diffusivity value on iodination. As a result we can safely conclude that there must be a significant increase in thermal conductivity of MPcs on iodination and the increase in thermal diffusivity in MPcs on doping with iodine arises mainly from a change in thermal conductivity of the materials. It must be added here that a very large increase in electrical conductivity values also has been observed in these materials on doping with iodine [18]. This points to the significant role of electronic carriers in
contributing to the heat conduction mechanism in organic semiconductors like phthalocyanines.

The simplicity and convenience of the experimental set up together with non contact nature of measurement strongly favour the present technique for determining thermal diffusivity of solid samples. The PA method has the added advantage that accurate measurement of thermal diffusivity is possible for sample materials available in small quantities.

5.7. CONCLUSION.

In conclusion the thermal diffusivity values for five MPcs and their iodinated forms have been determined from PA measurements. The iodinated MPcs are found to exhibit higher values for the thermal diffusivity. These results point to a substantial enhancement of thermal conductivity of these materials on iodination.
5.8. REFERENCES.


