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Thermal diffusivity of some polymer supported halogeno benzimidazole complexes of cobalt(II) and copper(II)—a photoacoustic study

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The thermal diffusivities of some polystyrene supported Schiff base complexes of cobalt(II), copper(II) with complexes of the type, $[ML_2X_2]$, (where M = Co(II) or Cu(II); L = NBPBI, 1-nitrobenzyl-2-nitrophenyl benzimidazole and X = Cl^-, Br^- or I^-) have been determined by the laser induced photoacoustic effect. The effect of the metal as well as the halogen part on the thermal diffusivities of these complexes has been studied.

The photoacoustic (PA) effect has now emerged as an elegant, sensitive and non-destructive method to obtain information on the thermal and optical properties of materials [1–8]. The success of this new spectroscopic technique is mainly due to the fact that only the absorbed light contributes to the signal giving a large signal to noise ratio. According to the Rosencwaig-Gersho theory [1], the primary source of the acoustic signal in the cell arises from the periodic heat flow from the solid to the coupling medium, as the solid is cyclically heated by the absorption of chopped light. The periodic flow of this heat into the coupling medium produces pressure fluctuations which are detected as an acoustic signal by a microphone at the modulation frequency, f. The thermal properties of the sample play a significant role in this energy conversion (optical to acoustical). This suggests the possibility of using the PA effect for the study of thermal properties of solids such as the thermal diffusivity and specific heat capacity. A search through the literature reveals that very few PA studies have been carried out on metal complexes and that no work has been reported on polymer supported benzimidazole complexes.

Complexes of benzimidazole have attracted a great deal of attention in recent years due to its potential applications in various fields like bio-medical, biochemistry etc. because of its antibacterial, antifungal, antiviral, anticancer, anti-inflammatory, analgesic, antipyretic, antihelmentic, germicidal and immunochemical agent activities. Complex compounds of transition metal ions with imidazole, benzimidazole and their substituted ligands have been studied extensively [9–13]. Some of the Co(II) and Cu(II) complexes reported have shown better catalytic activity, particularly towards synthetically important reactions of oxidation of substituted phenols, in which Co(II) and Cu(II) play a major role in catalyzing these types of reactions. Polymer-bound complexes also gained considerable attention recently due to their pronounced catalytic efficiency [14, 15] particularly in the oxidation reactions. Studies on magnetic and optical properties reveal that the polymer support brings about modifications in the structure of the complex. Other physical parameters like melting point and molar conductance are also found to change on a polymer support [16].

A single beam PA spectrometer is assembled for the present investigation [17]. The 488 nm line of an Argon ion laser (LiCONiX 5300) has been used as the pump source. The acoustic signal generated in the PA cell is detected by a sensitive microphone (sensitivity ∼100 mV/Pa) kept close to the sample compartment in a separate port. The microphone output is processed by means of a lock-in amplifier (EG & G, 5208).

Charpentier *et al.* [7] have presented a frequency analysis of the PA signal for the determination of thermal diffusivity. Determining the characteristic frequency (f_c) from the log(amplitude) vs. log(frequency) plot where there is a change of slope and knowing the actual thickness of the sample (l_s), the thermal diffusivity (α) can be calculated using the relation, $\alpha = l_s^2 f_c$.

The ligand, NBPBI, was prepared by changing only the reaction time from 12 to 24 h as described by Subba Rao and Ratnam [18]. The samples $[Co(NBPBI)_2Cl_2]$ and $[Co(NBPBI)_2Br_2]$ were prepared by adding solutions of cobalt(II) chloride hexahydrate and cobalt(II) bromide solutions respectively to the ligand solution. The resulting greenish solution on refluxing for about two hours, produced crystals which were filtered, washed with chloroform and dried under vacuum over anhydrous $CaCl_2$ [19].

The polymer-bound Schiff base ligand was prepared by condensing aminomethylated polystyrene with quinoxaline-2-carboxaldehyde. A solution of quinoxaline-2-carboxaldehyde (0.5 g in minimum amount of DMF) was added to aminomethylated polystyrene (5.0 g) and the reaction mixture was refluxed for about 5 h. The brown colored product thus formed was filtered, washed several times with DMF and acetone and dried in air and also under vacuum over anhydrous

$CaCl_2$. [Yield = 70–80%]. This was reacted with the halogeno complexes of Co(II) and Cu(II) with NBPBI as parent compound to yield the polymer supported Schiff base complexes of Co(II) and Cu(II). The same synthetic procedure was followed in all the cases. The following is the synthetic route for the polymer-bound Schiff base complex of Co(II).

The polymer-bound Schiff base ligand (2 g) was swollen in acetone for 1 h and the solvent was decanted off. Fresh acetone (4 ml) was again added along with the chloro complex of Co(II) derived from 1-nitrobenzyl-2-nitrophenyl benzimidazole, $[Co(NBPBI)_2X_2]$ (100–200 mg). The reaction mixture was shaken well for up to 1 h and was warmed over a water bath during shaking. The product formed was then filtered and washed several times with acetone and dried in air and also under vacuum over anhydrous $CaCl_2$. Yield = 70%.

Thermogravimetric analysis shows that the sample does not decompose at temperatures lower than 280 °C. Hence, exposure to the intensity modulated (chopped) laser beam of the power level used in the present experiment (∼100 mW) does not decompose the samples.

The experimental set-up is standardized by determining the thermal diffusivities of copper and aluminum. The values obtained in the case of copper (1.18×10^{-4} m^2/s) and aluminum (0.979×10^{-4} m^2/s) agree well with the reported values viz. 1.16×10^{-4} m^2/s and 0.98×10^{-4} m^2/s respectively. The values are correct up to the third digit.

To determine the thermal diffusivity, the sample was pelletized under high pressure. Keeping the sample in the PA cell, the frequency dependence of the acoustic signal was studied. The log-log plot of the variation of signal amplitude with frequency for polymer supported $[Co(NBPBI)_2Br_2]$ is shown in Fig. 1.

The thermal diffusivity values of the polymer supported complexes obtained from the present study are given in Table I. In the case of polymer supported $[Co(NBPBI)_2X_2]$, thermal diffusivity (α) increases whereas the thermal diffusivity of polymer supported $[Cu(NBPBI)_2X_2]$ decreases in the order of X = Cl, Br and I. The metal as well as the halogen part

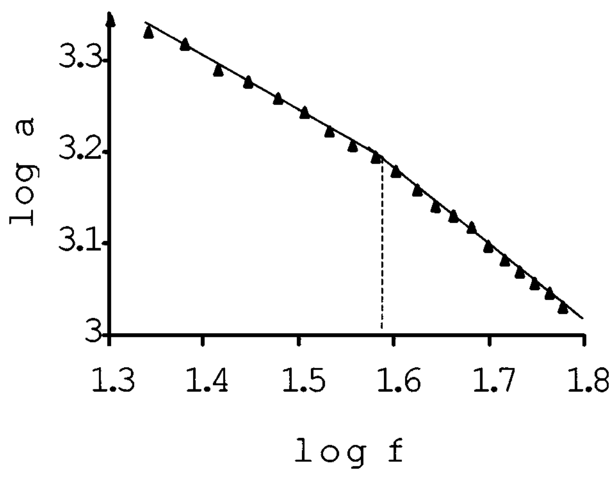

Figure 1 The log-log plot of the variation of signal amplitude with frequency for $[PCo(NBPBI)_2Br_2]$ ($l_s = 1.18$ mm; $f_c = 39.1$ Hz).

TABLE I Thermal diffusivities of polymer supported halogeno benzimidazole complexes of cobalt(II)

Sample	$10^4 \times$ thermal diffusivity (m^2/s)
$[P\text{-}Cu(NBPBI)_2Cl_2]$	0.305 ± 0.001
$[P\text{-}Cu(NBPBI)_2Br_2]$	0.242 ± 0.001
$[P\text{-}Cu(NBPBI)_2I_2]$	0.195 ± 0.001
$[P\text{-}Co(NBPBI)_2Cl_2]$	0.454 ± 0.001
$[P\text{-}Co(NBPBI)_2Br_2]$	0.544 ± 0.001
$[P\text{-}Co(NBPBI)_2I_2]$	0.640 ± 0.001

P—polymer

of the complex is found to have a profound effect on the thermal diffusivity values.

From the studies of magnetic and optical properties of the Co(II) complexes, similar to the present complexes, it has been found that the anchoring of the complexes to the polymer support brings about modifications in the structure of the complexes [16]. The physical parameters like melting point and molar conductance are also found to change when the complex is supported on the polymer [19]. Our studies show that thermal diffusivity is another parameter which seems to change on the polymer support.

The thermal diffusivities of the newly synthesized polymer supported complexes of Co(II) and Cu(II) have been determined by the laser induced photoacoustic technique. The effect of metal as well as the halogen part on thermal diffusivity of polymer supported complexes has been studied. The thermal diffusivity of Co complexes is found to increase while it decreases in Cu complexes with Cl, Br and I substitutions respectively. The compounds being new, the physical parameters essential for the analysis is not available. Only through a single crystal study on structural and physical properties of the sample can a conclusive result be obtained. Detailed work in this direction is in progress.

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