INTRODUCTION

The metal phthalocyanines (MPc) are the interesting chemical species that have been considered for numerous applications in the industries.1, 2 The similarity in structure between phthalocyanine (H₂Pc) and other biological molecules viz-chlorophyll and haemoglobin, adds to their interest and a huge number of different MPc have been produced3 over the years.4 As a class of macro cyclic planar aromatic compounds, MPc show special physical and chemical properties and there have been numerous experimental studies of their optical, magnetic and electronic properties. The interpretation of electronic spectra of MPc has been the subject of theoretical investigations.5-10

In continuation of our studies on electronic absorption of H₂Pc and MPc11-14 we have selected a common MPc, Cobalt-phthalocyanine (CoPc) for the study. From the study of literature,15-16 we found that no adequate attention has been given to the electronic absorption studies of CoPc in the solvents of different polarity. Because of this situation we have measured the effects of different solvents of different polarity and sulphuric acid of different concentration on the UV visible spectra of CoPc. Such studies have often been useful in assigning the electronic transitions and degree of solvation and we believe that it must provide good evidence to the nature of the orbitals involved in the transitions.

EXPERIMENTAL

The Electronic absorption spectra of Co-phthalocyanine (CoPc) have been recorded with a view to study the solvent-solute interaction, H-bonding effect and its protonation in the solvents of different polarity especially in sulphuric acid of different strength. The study revealed that the CoPc acts as a weak monoacidic base in aqueous acidic solution. The hypsochromic shift of λmax was observed when concentration of sulphuric acid decreased from 36N to 6N suggesting the formation of H-bonding of H₂S₂O₇ with atom N(2), N(3) and N(4) of CoPc and extra cyclic monoprotonation occurred irrespective to the concentration of H₂SO₄.

Keywords: Phthalocyanines, protonation, solvation, H-bonding and hypsochromic shift.
RESULTS AND DISCUSSION

Raman spectroscopic data\textsuperscript{17} indicate that overall symmetry of CoPc (in solution) is $D_{4h}$. The structure of CoPc is given as Fig. 1.

The conjugated $\delta$-system leads to intense electronic absorption bands in the visible region. The plots of electronic absorption of CoPc in suitable polar solvents are presented in Fig. 2 & 3 respectively and the values of $\lambda_{\text{max}}$ and associated molar absorptivity are given in Table-1.

![Figure 1](image_url)

Table - 1 (At constant temperature 30°C)

| Solvent used                  | $\lambda_{\text{max}}$ (nm) | Absorbance |
|-------------------------------|-----------------------------|------------|
| a. 36N H$_2$SO$_4$            | 660.00                      | 1.90       |
| b. 18N H$_2$SO$_4$            | 650.00                      | 1.86       |
| c. 12N H$_2$SO$_4$            | 640.00                      | 1.70       |
| d. 6N H$_2$SO$_4$             | 600.00                      | 1.25       |
| e. $\alpha$-Chloronaphthalene | 650.00                      | 1.80       |
| f. Gl.Acetic acid             | 640.00                      | 1.75       |
| g. Quinoline                  | 630.00                      | 1.60       |

The spectra of CoPc contain one principal visible band, Q- band that is attributed to the allowed $a_{1u} \rightarrow 2e_g$ transition. The calculated and experimental electronic transition energies are 1.56(1.85) eV for Q band.

The spectral results showed that $\lambda_{\text{max}}$ decreases with decrease in concentration of H$_2$SO$_4$ and band is observed in concentration lower than 6N. Thus, we can say that the hypsochromic shift of about 60 nm seems to be inversely proportional to the concentration of sulphuric acid.
The results also indicate that strong chemical interactions e.g. acid-base interaction may take place as

\[ \text{CoPc}(s) + \text{H}_2\text{SO}_4 \rightarrow \text{CoPcH}^+ + \text{HSO}_4^- \]

The absence of electronic donor center in the CoPc molecule at the intracyclic N-atoms and the strong hypsochromic shift due to decrease in acid concentration of leaves no doubt that H+ is attached to the external, so called extra cyclic N-atom of CoPc. The dependence of \( \lambda_{\text{max}} \) of CoPc in variable concentration of \( \text{H}_2\text{SO}_4 \) suggests that it is somewhat weak monoacidic base in an aqueous acidic solution. The observations further indicate that the proton in CoPcH+ complex responds to change in the solvating capacity of the medium with special reference to \( \text{H}_2\text{S}_2\text{O}_7 \) where hypsochromic shift observed. Obviously, we can say that hypsochromic shift may be attributed as a result of H-bonding of \( \text{H}_2\text{S}_2\text{O}_7 \) with atom N(2), N(3) and N(4) of the CoPcH+. The spectra of CoPc in sulphuric acid on long storage suggest that no slow reactions e.g. sulphonation, oxidation ...etc. take place in the solution.

The electronic absorption spectra of CoPc in selected organic solvents show the bath chromic shift of \( \lambda_{\text{max}} \) as the dielectric constant of solvents decreases. These electronic transitions seem to
be $\pi \rightarrow \pi^*$ transitions. The red shift observed is assumed to be due to solvent stabilization through H-bonding that decreases the energy difference between HOMO and LUMO. The excited state due to H-bonding interactions in polar organic solvents stabilizes more strongly than ground state which shifted the $\pi \rightarrow \pi^*$ to lower energy i.e. red shift.

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