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INFLUENCE OF DIELECTRIC CONSTANT ON SPECTRAL BEHAVIOUR OF COBALT - PHTHALOCYANINE

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ABSTRACT

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 λ_{max} was observed when concentration of sulphuric acid decreased from 36N to 6N suggesting the formation of H-bonding of $H_2S_2O_7$ with atom N(2), N(3) and N(4) of CoPc and extra cyclic monoprotonation occurred irrespective to the concentration of H_2SO_4.

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

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 (H_2Pc) and other biological molecules viz-chlorophyll and haemoglobin, adds to their interest and a huge number of different MPc have been produced[3] 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 H_2Pc and MPc[11-14] 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 required chemicals e.g. CoPc (Aldrich) and solvents H_2SO_4 (BDH),Glacial acetic acid (BDH), Quinoline (E.Merck) and á-Chloronaphthalene (Loba) were supposed to be extra pure for spectroscopic studies. The solutions of known concentrations were prepared by weighing appropriate amount of sample on a chemical balance and dissolving in the appropriate amount of solvents. The 18N, 12N and 6N sulphuric acid were prepared with double distilled CO_2 free water.

A Shimadzu UV-VIS (Model-160A JAPAN) double beam spectrophotometer was used and the spectra scanned through 200-1100 nm using silica cells at 303K temperature. The spectra were obtained in the shape of broad bands as plots of transmittance against wavelength from which the position of maximum absorption were estimated.

With a view to study the effect of solvents on the electronic transitions in CoPc, concentrated sulphuric acid and some organic solvents were tried.

RESULTS AND DISCUSSION

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

The conjugated ð-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 λ_{max} and associated molar absorptivity are given in Table-1.

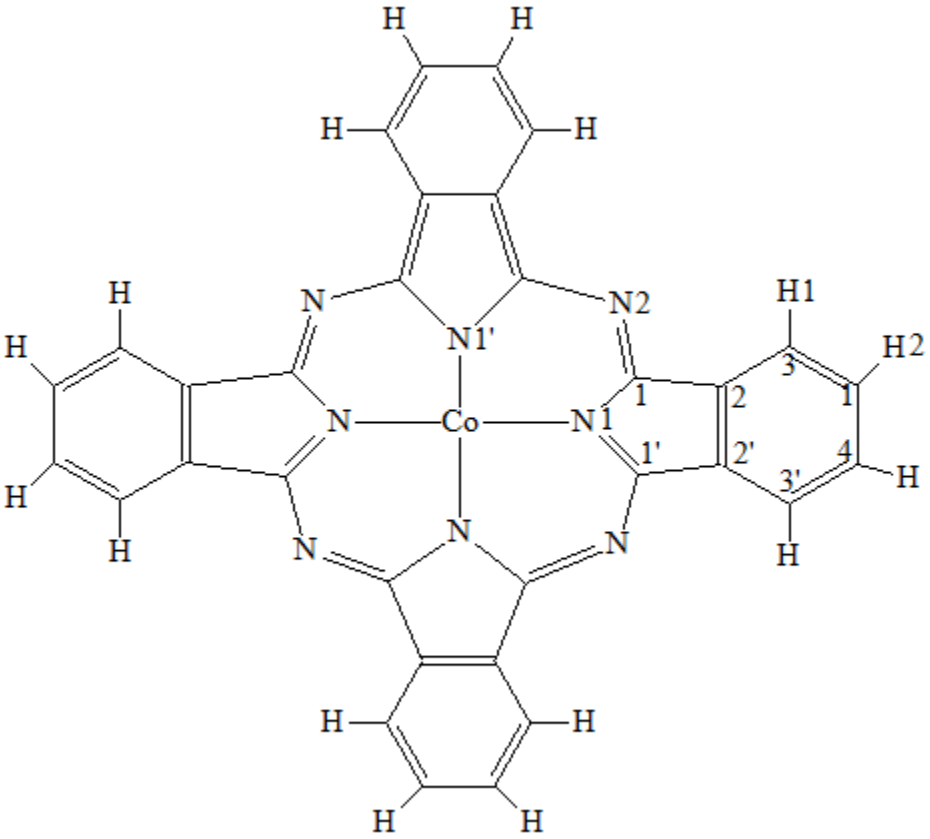

Figure - 1

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 λ_{max} decreases with decrease in concentration of H_2SO_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.

Table - 1 (At constant temperature 30 °C)

Solvent used	λ_{max} (nm)	Absorbance
a. 36N H_2SO_4	660.00	1.90
b. 18N H_2SO_4	650.00	1.86
c. 12N H_2SO_4	640.00	1.70
d. 6N H_2SO_4	600.00	1.25
e. α-Chloronaphthalene	650.00	1.80
f. Gl.Acetic acid	640.00	1.75
g. Quinoline	630.00	1.60

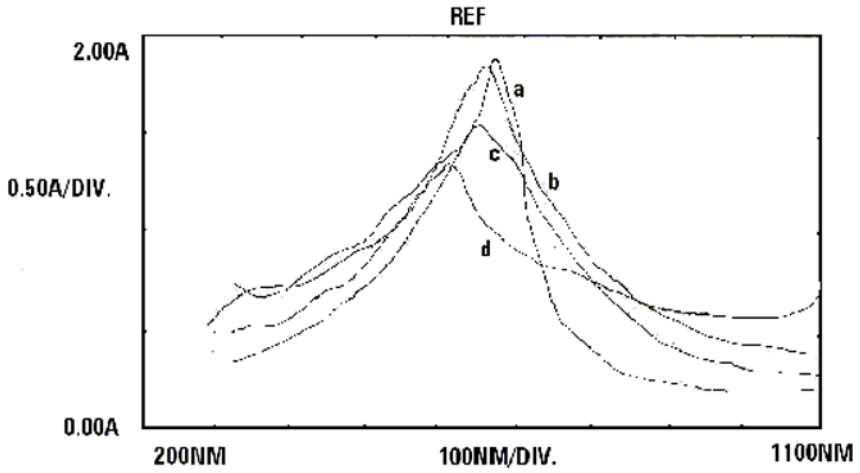

Fig. - 2: Spectra of CoPc in Sulphuric acid solvent

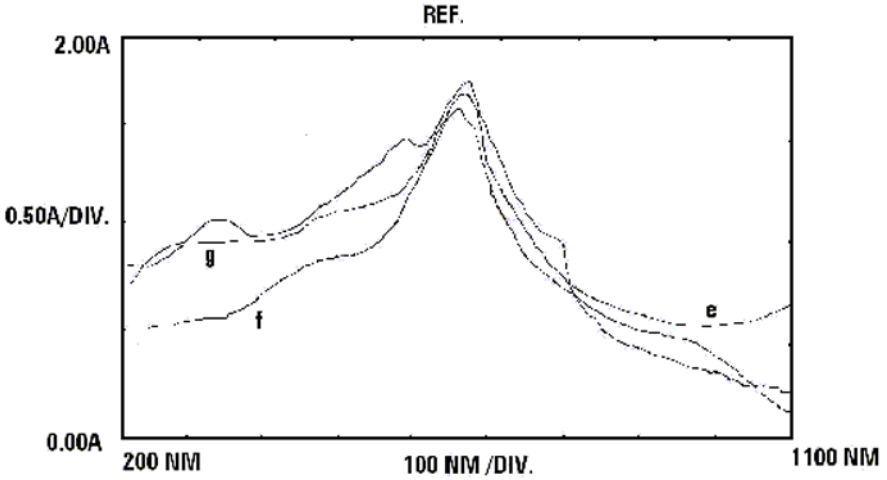

Fig. - 3: Spectra of CoPc in organic solvents

The results also indicate that strong chemical interactions e.g. acid-base interaction may take place as

$$CoPc(s) + H_2SO_4 \rightarrow CoPcH^+ + HSO_4^-$$

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 λ_{max} of CoPc in variable concentration of H_2SO_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 $H_2S_2O_7$ where hypsochromic shift observed. Obviously, we can say that hypsochromic shift may be attributed as a result of H-bonding of $H_2S_2O_7$ 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 λ_{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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