

Solvent Dependence of the Electronic Absorption Spectra of Mercury-Phthalocyanine

K.P. SRIVASTAVA* and A. KUMAR

Department of Chemistry, J.P. University, Chapra-841 301, India
E-mail: kpsri@sify.com

The electronic absorption spectra of Hg-phthalocyanine have been recorded with a view to study the solvent-solute interaction, H-bonding effect and protonation of Hg-phthalocyanine in sulphuric acid of different strengths and other polar solvents. The study revealed that Hg-phthalocyanine acts as a monoacidic base in aqueous acidic medium. The spectra contained two electronic bands, which are assigned as Q-band and Soret band, which are attributed to the allowed $a_{1u} \rightarrow 2_{eg}$ and $a_{2u} \rightarrow 2_{eg}$ transitions respectively. The bathochromic shift of λ_{max} was observed which is due to the H-bonding effect of the polar solvents.

Key Words: Phthalocyanines, Hydrogen bonding, Hypsochromic shift, Bathochromic shift, Protonation.

INTRODUCTION

The metal phthalocyanines (MPc) are the interesting chemical species that have been considered for numerous applications in industry^{1, 2}. These constitute one of the earliest classes of synthetic N₄ microcycles to be obtained³. The similarity in structure between phthalocyanine (H₂Pc) and other biological molecules, *e.g.*, chlorophyll, porphyrins, hemoglobin, etc. adds to their interest and a huge number of different MPc's have been produced over the years^{4, 5}.

As a class of microcyclic planar aromatic compounds, MPc's show specific 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 and experimental investigation⁶⁻⁸.

In continuation of our studies on electronic absorption spectra of H₂Pc and MPc^{9, 10}, we have selected a common but unique Hg-phthalocyanine (HgPc) for study. From literature^{11, 12}, it is clear that no adequate attention has been paid to the electronic absorption studies of HgPc in the solvents of different polarity.

The electronic absorption spectra of HgPc in organic and inorganic solvents differ to a great extent, which indicates the occurrence of strong chemical interactions. We have studied the effects of solvents on the UV-Vis spectra of HgPc. This study may often be useful in assigning the electronic transitions and

the degree of solvation and we believe that it must provide a good evidence of the nature of orbitals involved in electronic transitions.

EXPERIMENTAL

Hg-phthalocyanine (Aldrich), α -chloronaphthalene (Loba), quinoline (E. Merck), sulphuric acid, phosphoric acid, glacial acetic acid, ethyl alcohol, pyridine and xylene were obtained from BDH AR.

Experimental Procedure: The required chemicals were supposed to be extra pure for spectroscopic studies. The solutions of known concentration were prepared by dissolving appropriate amount of sample in the appropriate amount of solvents.

A Shimadzu UV-Vis (Model-160A) double beam spectrophotometer with automatic recording device was used and the spectra were scanned through 200–1100 nm using silica cells at 300 K.

RESULTS AND DISCUSSION

The conjugated π -system of HgPc leads to intense electronic absorption bands in the visible region. The plots of electronic absorption spectra of HgPc in suitable polar solvents are presented in Figs. 1 and 2 and the value of λ_{\max} and associated molar absorptivity are presented in Table-1.

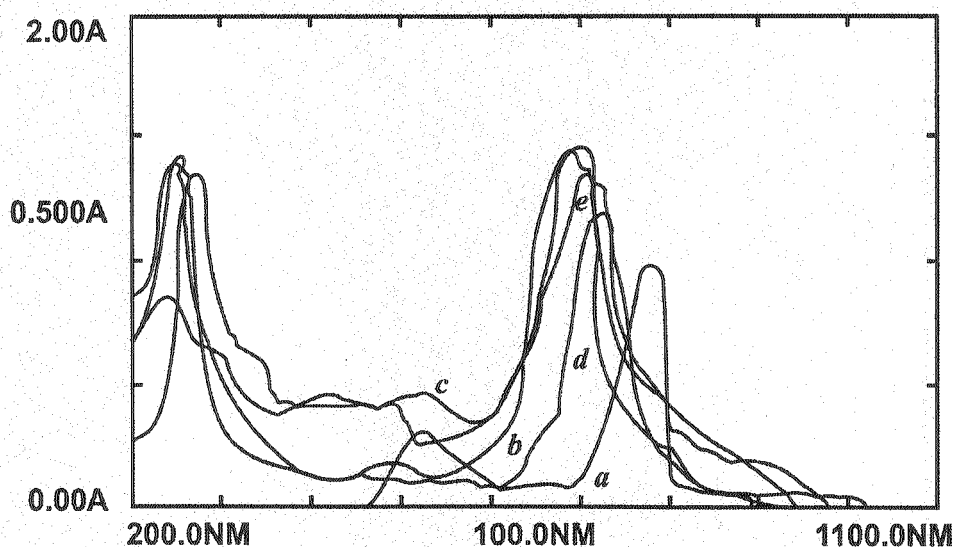


Fig. 1. Electronic absorption spectra of HgPc in sulphuric acid solvent

The spectra of HgPc contain two principal bands: Q-band and Soret band in certain solvents and one band in other solvents. Q-band is attributed to the allowed $a_{1u} \rightarrow 2_{eg}$ transition and Soret band is due to $a_{2u} \rightarrow 2_{eg}$ transition.

The spectra results show that long wavelength absorption with lower intensity appears at $\lambda_{\max} = 780$ nm in 36 N H_2SO_4 and 700 nm in 6 N H_2SO_4 and no band is observed in lower concentration than 6N H_2SO_4 . The λ_{\max} remains unaffected by the concentration of H_2SO_4 .

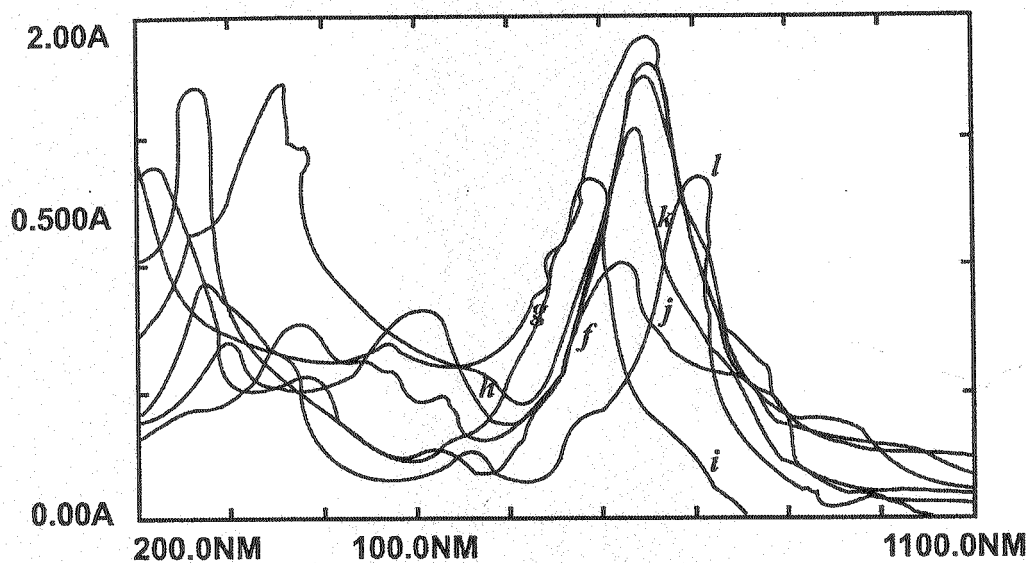


Fig. 2. Electronic absorption spectra of HgPc in organic solvents and water

TABLE-1

Solvent used	λ_{\max} (nm)	Absorbance
(a) 36 N H ₂ SO ₄	780.00	1.25
(b) 18 N H ₂ SO ₄	700.00	1.50
	240.00	1.40
(c) 12 N H ₂ SO ₄	700.00	1.50
(d) 8 N H ₂ SO ₄	740.00	1.25
	230.00	1.40
(e) 6 N H ₂ SO ₄	700.00	1.35
	280.00	1.30
(f) Water	765.00	1.85
	240.00	1.75
(g) Ethyl alcohol	740.00	1.95
	310.00	1.75
(h) Glacial acetic acid	735.00	1.80
(i) α -Chloronaphthalene	700.00	1.50
	240.00	0.90
(j) Quinoline	705.00	1.15
(k) Pyridine	730.00	1.60
(l) Xylene	805.00	1.45

HgPc is found to be readily soluble in water as if it is an ionic compound and it absorbs at 780 nm in long wavelength range. HgPc is readily more protonated than any other MPc in H₂SO₄. The long wavelength absorption peak at 780 nm

shifts to 700 nm when concentration changes from 18 N to 6 N and at 36 N it shows bathochromic shift of about 80 nm. At low acid concentration monomeric unprotonated HgPc particle features a peak at a wavelength of 700 nm in the visible region. Consequently in the range of concentration from 6 N to 18 N H₂SO₄, the shift ($\Delta\lambda$) of the λ_{\max} band of the first protonated spectrally active HgPc is as small as 20–60 nm rather than 100–200 nm in case of other metal phthalocyanines^{13,14}. Hence the spectral features at 700 nm do not fully correspond to an unprotonated to protonated particle, because the atoms N₁, N₂, N₃ and N₄ are not bound by the protons and macro ring is not deactivated within the above H₂SO₄ concentration range perhaps with a strong H-bond.

From the position of the band, it is suggested that the protonation in HgPc-H₂SO₄ is partial and HgPcH⁺ ion is formed. The protonation process is expressed as



In this process the determining role is played by the basic property of the acid anion. Owing to greater tendency of the Hg atom in HgPc to coordinate to the anion in the presence of H₂SO₄, HgPc is more readily protonated than other MPc and even than H₂Pc. Its protonation depth is less because its λ_{\max} is more hypsochromic.

The short wavelength bands (240–310 nm), which appear in concentrated H₂SO₄, water, ethanol and α -chloronaphthalene have been explained in terms of loss of symmetry due to solute-solvent interaction.

The electronic absorption spectra of HgPc in selected organic solvents and water show the bathochromic shift of λ_{\max} as the dielectric constants of solvents decrease. The electronic transitions seem to be $\pi \rightarrow \pi^*$ transitions in the organic part of HgPc. The bands are the result of longer wavelength electronic transitions in the highly conjugated system.

The red shift observed is due to the solvent stabilization owing to H-bonding which decreases the energy difference between HOMO and LUMO. The excited state due to H-bonding interactions in polar solvents stabilizes more strongly than ground state which shifted the $\pi \rightarrow \pi^*$ to lower energy, *i.e.*, red shift.

Conclusions

This systematic study of solvation effects on the electronic absorption spectra of HgPc in solvents of different polarity has led to the following conclusions:

- The protonation of HgPc in H₂SO₄ solvent occurred at the peripheral N atom of phthalocyanine with the loss of non-bonding electrons.
- Only monoprotonation of HgPc occurred which is irrespective of acid concentration and temperature.
- The bathochromic shift is observed in organic solvents which is due to solvent stabilization of excited state by H-bonding.
- The short wavelength bands appeared in some solvents due to loss of symmetry owing to solute-solvent interaction.

ACKNOWLEDGEMENTS

The authors are grateful to Prof. (Dr.) Abhay Kumar, Head, Department of Chemistry, L.S. College, Muzaffarpur for his encouragement and suggestions.

REFERENCES

1. A.B.P. Lever, M.R. Hempstead, C.C. Leznoff, W. Liu, M. Mebrik, W.A. Nevin and P. Seymour, *J. Pure Appl. Chem.*, **58**, 1467 (1986).
2. E. Orti and J.L. Bredas, *J. Am. Chem. Soc.*, **114**, 8669 (1992).
3. N. Kobayashi, H. Lam, W.A. Nevin, P. Janda, C.C. Leznoff, T. Koyama, A. Monden and H. Shirai, *J. Am. Chem. Soc.*, **116**, 879 (1994).
4. H. Ali and J.E. van Lier, *Chem.*, **99**, 2379 (1999).
5. F.H. Moser and A.L. Thomas (Eds.), *The Phthalocyanines*, Vols. 1 and 2, CRC Press, Florida (1983).
6. L.K. Lee, *J. Phys. Chem.*, **86**, 23926 (1982).
7. F.W. Kutzler and D.E. Ellis, *J. Chem. Phys.*, **84**, 1033 (1986).
8. A. Ghosh, P.O. Gassman and J. Almolf, *J. Am. Chem. Soc.*, **116**, 1932 (1994).
9. K.P. Srivastava and A. Kumar, *Asian J. Chem.*, **12**, 723 (2000).
10. K.P. Srivastava and A. Kumar, *Asian J. Chem.*, **13**, 1539 (2001).
11. B.D. Berezin, *Zh. Nkh.*, **7**, 2507 (1962).
12. B.D. Berezin, *Zh. Nkh.*, **18**, 965 (1973).
13. Meng-Sheng and S. Schemer, *J. Chem. Phys.*, **114**, 9780 (2001).
14. R.B. Singh, Ph.D. Thesis, BRA Bihar University, Muzaffarpur (2002).

(Received: 8 October 2005; Accepted: 5 June 2006)

AJC-4947

2006 DISASTER MENTAL HEALTH CONFERENCE

NOVEMBER 8-11, 2006

CASPER, WYOMING

Presenter: Rocky Mountain Region Disaster Mental Health Institute

The general theme of this conference is Taking Charge in Troubled Times: Response, Resilience, Recovery, and Follow-up. Topics will include cultural concerns, ethnicity, political concerns, religious considerations, children, and mitigation, among others.

Presentation abstracts are due July 15, 2006.

To learn more, contact:

Rocky Mountain Region Disaster Mental Health Institute

PO Box 786, Laramie, WY 82073-0786

Tel: (307)399-4818

E-mail: rockymountain@mail2emergency.com

Website: <http://www.rmrinstitute.org/call2006.pdf>