ESR AND ELECTROCHEMICAL STUDIES ON THE OXIDATION PRODUCTS OF SOME METALLOPORPHYRINS

AKA. LEMTUR

DEPARTMENT OF CHEMISTRY
SCHOOL OF PHYSICAL SCIENCES

A THESIS
SUBMITTED
IN
FULFILMENT OF THE DEGREE OF
DOCTOR OF PHILOSOPHY
TO

NORTH—EASTERN HILL UNIVERSITY
SHILLONG
INDIA

FEBRUARY, 1987

TO

MY PARENTS

and

Brother **TALI** and **IMNA**

Phone:
Grams : NEHU

North-Eastern Hill University

Bijni Complex
Bhagyakul, Shillong-793003 (Meghalaya)

Head,
Department of...Chemistry.......

This is to certify that MR.AKA LEMTUR has completed the following Pre-Ph.D.Courses as prescribed by this University satisfactorily :-

Sl.No.	Course No.	Title of the Course
1	Chem 545	Advanced Concept in Physical Chemistry
2	Chem 650	Molecular orbital and Valence bond theory
3	Chem 505	Advanced Inorganic Chemistry
4	Chem 525	Higlights in Organic Chemistry

H. Junjappa
Professor.

Phone:
Grams : NEHU

North - Eastern Hill University

Bijni Complex
Bhagyakul, Shillong-793003 (Meghalaya)

Dr J.Subramanian
Professor
Department of Chemistry...

I certify that the thesis entitled "ESR AND ELECTROCHEMICAL STUDIES ON THE OXIDATION PRODUCTS OF SOME METALLOPORPHYRINS" submitted by MR.AKA LEMTUR for the degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by him under my supervision. He has been duly registered and the thesis presented is worthy of being considered for the award of the Ph.D.degree. This work has not been submitted for any degree of any other University.

Date :

Place: Shillong

Signature of the Supervisor.

-o0o-

ACKNOWLEDGEMENT

It is my sincere wish to mention here my heartfelt thanks to Prof. ***J. Subramanian*** *for introducing me to the research problem in porphyrin Chemistry, the results of which are embodied in this thesis and also for his constant guidance. His valuable guidance and good wishes will remain a cherished blessing to me. I am grateful to Prof.* ***H. Junjappa*** *for his help and inspiration. My sincere thanks to Dr.* ***D.T. Khating*** *for his encouragement and help.*

I am very grateful to Prof. P.T. Narasimhan, IIT, Kanpur and Prof. A. Chakravorty, IAC Sc., Calcutta for allowing me to use the facilities available in their laboratories.

I am very thankful to Prof. J.-H. Fuhrhop for generously providing samples of octaethyl porphyrin and Mesoporphyrin.

I extend my thanks to the staff of RSIC, Madras and to Dr. Vikram Dhar, II Sc. Bangalore for their help in carrying out ESR measurements.

I am happy to mention my thanks to Dr. B. Myrboh and Dr. Vinay Shedbalkar for their help in every possible way throughout the course of investigation. I am grateful to Miss Mamata Sarkar for her kind help in drawing figures. Thanks are also to Mr. R. Sadhu for typing this thesis. It is worth mentioning here that this research work has been successful due to research fellowships from UGC and CSIR.

Thanks to all faculty members and friends in the Department of Chemistry, North-Eastern Hill University for their encouragement and help.

My gratitude and thanks to my parents, brothers and sisters and my wife for their sincere support and encouragement without which I could not have accomplished this work.

AKA LEMTUR

PREFACE

This thesis deals with the electron spin resonance studies on the oxidation products of some vanadyl porphyrins and supporting cyclic voltammetric studies on these systems. It consists of six chapters.

Chapter I consists of a review on the esr and other structural studies on the oxidation products of TiO, VO, Cr, Mn, Fe, Cu and Ni porphyrins. The material presented in this chapter gives an overall picture about the structural aspects of the oxidation products of transition metal porphyrins. Oxidation products of Mn and Fe porphyrins are considered to be active intermediates in the biological reactions catalysed by enzymes like catalase, peroxidase etc. This review also provides a backdrop for the esr studies on the oxidation products of vanadyl porphyrins presented in the later chapters of this thesis.

The details of the experimental procedures adopted in the present work are described in Chapter II.

In Chapter III, the esr studies of the one-electron oxidation products of vanadyl octaethylporphyrin at liquid nitrogen temperature are presented. The radical cation has been found to exist~~s~~ as a dimeric species in triplet state. From the triplet state -esr spectrum the distance between the two vanadium atoms in the dimer has been obtained.

Cyclic voltammetric studies on zinc, Cu and vanadyl complexes of proto- and mesoporphyrins are presented in Chapter IV. Evidence for the existence of dimers in solution has been obtained in the case of Zn, and VO protoporphyrins. The oxidation potentials for the monomeric and dimeric forms of VO mesoporphyrin have been obtained.

In Chapter V detailed esr studies on the oxidation products of vanadyl protoporphyrin-IX dimethylester and mesoporphyrin IX dimethylester are presented. ESR spectra of the samples at room temperature and liquid nitrogen temperature and at about 10K are presented. Wherever possible, computer simulations of the esr spectra have been included. Monomeric radical cations ($S = 1$) and dimeric radical cations ($S = \frac{3}{2}$) have been identified in solution at room temperature. Different types of dimeric species have been shown to exist at low temperatures. A monomeric radical cation has also been identified at 10K. The results presented in this chapter are amply supported by the cyclic voltammetric studies discussed in Chapter III.

The results of cyclic voltammetric studies on some metal complexes of tetrabromo tetraphenyl porphyrin (Cu, Ni, VO and Zn) are discussed in Chapter VI. Wherever possible, the oxidation products were characterised by esr and optical spectroscopy.

The oxidation products of transition metal porphyrins offer challenging structural problems to the chemist and a study of these systems is important to understand the redox reactions occuring in biological system. In this thesis an attempt has been made to identify the products obtained on oxidation of vanadyl porphyrins which are the simplest systems among the transition metal porphyrins.

CONTENTS

Page No

CHAPTER I A BRIEF REVIEW ON THE ESR STUDIES ON THE OXIDATION PRODUCTS OF TRANSITION METAL PORPHYRINS 1 - 34

I.1 Introduction 1

I.2 Titanium and Vanadium Porphyrins 2

I.3 Chromium Porphyrins 5

I.4 Manganese Porphyrins 7

- I.4.1 Mn(III) Porphyrin Radical Cations 7
- I.4.2 Higher Valent Mn Porphyrin 8
- I.4.3 Monomeric Mn(IV) Porphyrin 9
- I.4.4 μ-oxo Mn(IV) Porphyrins 10
- I.4.5 Mn(V) Porphyrins 12
- I.4.6 MnP-O_2 Complexes 13

I.5 Iron Porphyrins 13

- I.5.1 Electrochemical Oxidation of Fe(III) Porphyrins 14
- I.5.2 Fe(III)P Radical Cation 15
- I.5.3 μ-oxo Iron Porphyrins 18
- I.5.4 Fe(IV) Porphyrins 19
- I.5.5 Fe(IV) Radical Cation 21

I.6 Nickel Porphyrins 22

I.7 Cu Porphyrins 23

I.8 Ag Porphyrins 24

References 26

CHAPTER II DETAILS OF EXPERIMENTAL TECHNIQUES 35-49

II.1 Introduction 36

II.2 Solvents 36

II.3 Oxidising Agents 37

II.4 Reagents and Supporting Electrolytes 38

II.5 Metalloporphyrins 40

II.6 Instrumentation 46

II.6.1 Cyclic Voltammetry 46

II.6.2 EPR 47

References 49

CHAPTER III ESR SPECTRA OF DIMERIC SPECIES OBTAINED FROM THE OXIDATION PRODUCT OF VANADYL OCTAETHYLPORPHYRIN 50-59

III.1 Introduction 50

III.2 Experimental Details 52

III.3 Results and Discussion 54

III.3.1 Theoretical Background 54

III.3.2 Discussion 56

III.4 Conclusion 56

References 58

CHAPTER IV CYCLIC VOLTAMMETRIC STUDIES ON SOME METAL COMPLEXES OF PROTO- AND MESO PORPHYRINS 60-72

IV.1 Introduction 60

IV.2 Basic Principle of Cyclic Voltammetry 64

IV.3 Experimental 66
IV.4 Results and Discussion 67
  IV.4.1 Cyclic Voltammetry of Zinc Protoporphyrin 67
  IV.4.2 Cyclic Voltammetry of Copper and Vanadyl Protoporphyrins 69
  IV.4.3 Voltammetry of Vanadyl Meso Porphyrins 70
  IV.4.4 Cyclic Voltammetry of Iron Hemato-Porphyrin 71
IV.5 Conclusion 71
References 72

CHAPTER V ESR STUDIES ON THE OXIDATION PRODUCTS OF VANADYL PROTO- AND MESO PORPHYRINS 73-88

V.1 Introduction 73
V.2 Experimental Details 73
V.3 Results and Discussion 76
  V.3.1 ESR Spectrum of the Radical Cation of Vanadyl Protoporphyrin at Room Temperature 76
  V.3.2 ESR Spectra of Vanadyl Meso Porphyrin at Room and Low Temperatures 80
V.4 Conclusion 87
References 88

CHAPTER VI CYCLIC VOLTAMMETRIC STUDIES ON SOME METAL COMPLEXES OF TETRABROMO MESO TETRAPHENYL PORPHYRIN 89-94

VI.1 Introduction 89

VI.2 Experimental Details 90

VI.3 Results and Discussion 91

VI.4 Conclusion 93

References 94

Summary 95-98

Appendix 99

CHAPTER I

A BRIEF REVIEW ON THE ESR STUDIES ON THE OXIDATION PRODUCTS OF TRANSITION METAL PORPHYRINS

CHAPTER I

A BRIEF REVIEW ON THE ESR STUDIES ON THE OXIDATION PRODUCTS OF TRANSITION METAL PORPHYRINS

I.1 INTRODUCTION

The aim of this review is to provide the background material which has motivated us to undertake the esr and electrochemical studies of the oxidation products of some transition metal porphyrins, especially vanadyl porphyrins. The oxidation products of transition metal porphyrins are being investigated currently by many groups using magnetic resonance techniques (NMR, ESR and Mössbauer) and magnetic susceptibility measurements.[1] The interest in these system is two-fold. The magnetic resonance data, especially the esr spectra require the development of new theoretical approaches for their interpretation. Apart from this challenging aspect, these systems play important roles as intermediates in heme enzyme - catalyzed reactions.[2] A Fe(IV) porphyrin is postulated as an intermediate in the reaction involving catalase and peroxidase. In the present review we shall restrict ourselves mainly to the magnetic resonance studies on the oxidation products of transition metal porphyrins. A systematic review is not available in the literature, though the esr of oxidation products of iron porphyrins have been discussed in detail.[3,4] Since a large number of reviews[5,6,7] have appeared on dioxygen adducts of metalloporphyrins this aspect is not included in this review.

I.2 Titanium and Vanadium porphyrins

Till now there has been no report in the literature on the oxidation products of titanium porphyrins. In the course of our own investigations on vanadyl porphyrins, we had observed that treatment of titanyl octaethylporphyrin with trifluoroacetic acid leads to the appearance of single line esr signal at room temperature (width $\simeq$ 20G) and a radical cation type optical absorption spectrum. No further esr studies have been made on this system.

Vanadyl porphyrins also lead to the formation of radical cation on one-electron oxidation (oxidation potential $\simeq$ 1.0V vs SCE).[8,9] Of the various vanadyl porphyrins that have been studied, namely, vanadyl octaethylporphyrin, vanadyl protoporphyrin, vanadyl mesoporphyrin and vanadyl tetraphenylporphyrin, the esr spectra of the oxidation products of these systems are quite different from each other. The following is a summary of the previous work on esr studies on the oxidation products of vanadyl porphyrins.

Vanadyl octaethylporphyrins on oxidation forms a radical cation.[9] This system is monomeric containing two unpaired electrons per molecule, one on the d-orbital and the other in the porphyrin π orbital. The esr spectrum of this radical cation at room temperature consists of eight lines with the spacing being one-half of the value obtained for the unoxidised product. Unusual linewidth effects have also been observed with this spectrum, the outer lines being narrow and the inner lines very broad. The esr spectrum has been analysed in terms of a spin Hamiltonian

$$H = \frac{(g_1 + g_2)}{2} \beta B_o \quad (S_{z1} + S_{z2}) + a \hat{I}.\hat{S}_1 + J \hat{S}_1.\hat{S}_2 \qquad \ldots \quad (I.1)$$

Where S_1 and S_2 correspond to the unpaired spin in the vanadium d-orbital and the one in the porphyrin π orbital respectively. The isotropic hyperfine coupling constant of the ^{51}V in the radical cation has been reduced to one-half of its original value in the unoxidised species. This indicates that the exchange interaction J is larger than microwave frequency i.e., $J \gg 0.3$ cm^{-1}. Analysis of the linewidth effects by relaxation matrix theory has yielded the value of zero-field splitting between the two electrons as 2810 Mrad S^{-1}. Assuming that this arises entirely from dipolar interaction, a distance of 4Å was obtained between the two unpaired electrons. In terms of the molecular structure, this information means that the unpaired π electron is confined to the pheripheral positions of the porphyrin framework. The actual estimate~~s~~ of J has not been made so far. Attempts to obtain a correct estimate of zero-field splitting by recording esr spectrum at low temperature have not been successful. In frozen solutions around liquid nitrogen temperature, the radical cation of vanadyl OEP dimerises to yield a new triplet state.[10] This dimer has one unpaired electron each on the V-orbital. The two π electrons seems to have paired up. A distance of 4.2 Å has been obtained between the two vanadium nuclei. A detailed discussion of the esr of this system is presented in Chapter III. Similar work on vanadyl etioporphyrin has been reported by Selyutin <u>et al</u>[11]. No detailed analysis of the spectra has been reported by the authors. In the present thesis detailed studies have been made on the electrochemical and esr behaviour of the oxidation products of the vanadyl complexes of protoporphyrin-dimethylester and mesoporphyrin dimethylester.

A triplet state esr spectrum has been reported for γ-irradiated VO(TPP) in tetrachloro ethane.[12] Only the half-field lines were observed since the $\Delta m_s = \pm 1$ transitions were marked by the strong esr signal of VO(TPP). The half-field signal consists of 8 lines indicating that the irradiated product is monomeric vanadyl porphyrin in a triplet state. This species has been assigned as the one-electron oxidation product of VO(TPP), on the basis of its optical spectrum. An approximate estimate of $D \lll 0.024\ cm^{-1}$ has been made from the H_{min} value in the half field spectrum.

I.3 Chromium porphyrins[13-28]

The most stable oxidation state for Cr in chromium porphyrins is 3. Oxidation of Cr(III) porphyrins leads to Cr(IV) and Cr(V) porphyrins. Reduction leads to Cr(II) porphyrins. Interestingly, the oxidation products of Cr(OH) porphyrins and CrCl (porphyrins) are different.[13,14] Cr(III) porphyrins with hydroxyl group as the axial ligand, on oxidation in alkaline medium with sodiumhypochlorite yield CrO(porphyrin) where Cr is in Cr(IV) state. CrO(TPP) and CrO(OEP) have been isolated in the solid state. The optical spectra of these compounds are very similar to that of vanadyl porphyrins. The magnetic susceptibility as measured by Evans method indicate that these system are diamagnetic. X-ray structure of the oxo chromium(IV) TPP has also been reported.[13,15] CrCl (porphyrins) on oxidation with hypochlorite or iodosylbenzene form Cr(V)O porphyrins.[16-19] A nitrido chromium(V) porphyrin CrN(TPP) has also been reported.[20] Cr(V)O porphyrins exhibit esr spectra typical of

d^1 systems.[23] The following esr parameters have been obtained in solution at room temperature for CrO(TPP)$^{+}$, g_{av} = 1.982, a_N = 0.285mT, a_{cr} (^{53}Cr) = 2.3mT. The esr parameters are very similar to vanadyl porphyrins and hence a similar orbitally non-degenerate ground state has been proposed for Cr(V) porphyrins (d^1_{xy}). A d_{xy} ground state is obtained for the unpaired electron, if we assume a co-ordinate system in which x and y axes are perpendicular to the plane. Treatment of Cr(V)P with t-butylamine leads to axial ligation involving the amine. ESR spectrum also indicates the presence of hyperfine coupling from the axial nitrogen ligand (0.78mT) which is much larger than that of porphyrin nitrogen. Nitride Cr(V) porphyrins also shows hyperfine coupling from the axial nitrogen which is about the same as that from the in-plane nitrogen nuclei. ENDOR measurements that have also been made on these systems, indicate slight differences between the axial and porphyrin nitrogen coupling.[24] The esr data for CrNTPP are as follows.[24] a_N(isotropic) = 0.28mT; a_o (^{53}Cr) = 2.83mT; $a_{\parallel}$ (Cr) = 4.01mT; $g_{\parallel}$ = 1.9583; $g_{\perp}$ = 1.9945. The closeness of $g_{\perp}$ value to that of free electron g-value indicates that the energy gap between the d_{xy} ground state and the nearest excited state (d_{xz},d_{yz}, e) is quite high. This might also be the reason why Cr(IV) (porphyrin) is diamagnetic though it is a d^2 system.

Reduction of Cr(III) porphyrins leads to the formation of Cr(II) porphyrin which irreversibly reacts with dioxygen to form Cr(IV)OP.[25,26,27].

I.4 Manganese porphyrins

In the last five years, considerable amount of work has been done on the synthesis and structural evaluation of oxidation products of Mn(III) porphyrins. Electrochemical oxidation of Mn(III) porphyrins lead to the formation of Mn(III) porphyrin radical cations[4]; chemical oxidation products have been identified as Mn(IV) porphyrin μ -oxo bridged Mn(IV) dimer, Mn(IV) porphyrin adducts of oxidant, Mn(V) nitrido porphyrins. The products of chemical oxidation of Mn(III) porphyrins seem to depend on the nature of the oxidant and the medium.

I.4.1 Mn(III) porphyrin radical cations

Electrochemical oxidation of MnTPPCl, Mn Tetrakis (p-methoxy tetraphenyl porphyrin) Cl and Mn(OEP)Cl have been reported.[4] The one-electron oxidation product for each of these systems ($\simeq$ 1.1V Vs SCE) had been isolated. The pmr spectrum of the oxidised species indicates that the pyrrole protons (α, β, protons) signals are shifted upfield and broadened. ESR spectra of these systems consist of strong absorption at $g = 2$ (linewidth $\simeq$ 300-500G) and a weak and very broad signal around g = 3. A magnetic moment of 4.7BM was obtained for TPPMn(Cl)(ClO_4) which was found to be invariant with temperature in the range -50°C to 29°C. All the oxidation products are formulated as Mn(III) porphyrin radical cations. The g = 2 signal is assigned to the π radical. The broadening of this signal is considered to arise from spin-spin interactions between the d-electrons and the π -electron. Assignment of Mn(III) π radical cation is also consistent with the broadening and loss of intensity of Soret band and increase in the intensity of long wavelength region.

I.4.2 Higher Valent Mn porphyrins

Chemical oxidation of Mn(III) porphyrins has been studied extensively.[29-36] Mn(III) porphyrins have been found to be versatile synthetic oxidation catalysts for alkane oxidation. The activation of C-H bond is accomplished in nature by heme mono oxygenase type of enzymes. Higher valent Mn porphyrins have also been effeciently used to oxidise water thermally and photochemically. Hence the oxidation products of Mn(III) porphyrins are of great importance as unique catalysts for oxidation reactions. Some early papers in the literature contain ambiguous assignments to the oxidation state of Mn in oxidised Mn(III) porphyrins based on insufficient experimental data. Clean synthesis, isolation and structural elucidation have been reported for Mn(IV) (porphyrin) X_2 and (Mn(IV) porphyrin $X)_2O$.[37,38] Oxidation of Mn(III)TPPX in alkaline methanolic solutions by iodosyl benzene or sodium hypochlorite leads to the formation of Mn(IV)$TPPX_2$, where X is OCH_3^-, N_3^- or NCO^-. Oxidation of Mn(III)PX in an inert medium like chloro benzene by iodosyl benzene results in the formation of dimeric species XPMn(IV)-O-Mn(IV)PX, (X = N_3^-, OCN^-). Oxidation of Mn(III)PX by sodium hypochlorite or iodosyl benzene in the presence of excess ammonia results in the formation of Mn(V)NP. The crystal structures of all the three types of species have been reported.

I.4.3 Monomeric Mn(IV) porphyrin[29-40]

ESR of Mn(IV) porphyrins have been reported. ESR spectra were recorded for Mn(IV)P$(NCO)_2$, Mn(IV)P$(N_3)_2$ in dichloromethane solution at 12K.[36] Interestingly, the esr spectrum depends on the nature of the two axial ligands Mn(IV)TPP$(NCO)_2$ exhibits a strong signal at $g = 3.92$ and a resolved ($a_{Mn} = 69G$) structure at $g \simeq 2$. This indicates that the ligand field is axially symmetric and the zero field splitting, $D \gg h\nu$ for the $S = \frac{3}{2}$ system. On the other hand, Mn(IV)TPP$(OCH_3)_2$ yields g values as 5.46, 2.4 and 1.0. The signal at $g = 5.46$ is very strong and resolved ($a_{Mn} = 72G$). This signal indicates highly rhombic character of the $S = \frac{3}{2}$

system. Using the available-theoretical models for the ESR of $S = \frac{3}{2}$ systems, an approximate estimate of $D \simeq 1.7\ cm^{-1}$ has been made for the Mn(IV) porphyrins. In contrast to Cr(III) porphyrins ($S = \frac{3}{2}$) the ZFS value in Mn(IV) porphyrins is quite high. This has been attributed to contraction along the axial bonds in Mn(IV)P due to smaller ionic radius of Mn(IV) ion compared to that of Cr(III) ion. A monomeric Mn(IV) porphyrin containing two molecules of iodosylbenzene has also been reported.[40] A similar esr spectrum ($g = 3.52$, $g = 2$) was reported for the species obtained during γ irradiation of Mn(III)TPPCl containing equimolar amount of TCNE (Tetracyano ethylene). This species has been assigned as Mn(IV)P on the basis of its optical and esr spectra.

A recent study[43-44] on the interconversion of Mn(III)P radical cation and Mn(IV) porphyrin clearly demonstrates the effect of axial ligand on the valence state of Mn. With weak axial ligands like ClO_4^-, Mn(III)P radical cation is favoured. Replacement of perchlorate ion by OCH_3^-, leads to the formation of Mn(IV)P$(OCH_3)_2$.

I.4.4 μ -oxo Mn(IV) porphyrins

It has been established that basic medium is required to generate monomeric Mn(IV)P during the oxidation of Mn(III)P with iodosyl benzene. Instead, if the oxidation performed in a neutral medium like chlorobenzene, PMn(IV)-O-Mn(IV)P dimer is formed. This subtle difference in the synthetic procedure is not clearly discussed in the literature. Camenzind et al[37,45] point out that treatment of Mn(III)TPP(OAC) in dichloromethane with iodosyl benzene leads to very little oxidation in about half-an-hour, but the reaction is instantaneous when sodium methoxide is added to the system. The same authors claim that the Mn(IV)oxo-dimer is formed when the oxidation is done in an inert medium. The exact conditions for the formation of the oxodimer are not very clear but the species has been identified and its crystal structure and magnetic data have been reported.[45] The μ -oxo dimer has -Mn(IV)-O-Mn(IV)-moiety with an effective magnetic moment μ_{eff} = 2BM. No epr signal has been observed down to 8K. This system can oxidise water to H_2O_2 in a thermal or photochemical process. Oxidation of hydrocarbons has also been reported. A report on Mn(V)=0 porphyrins in the literature does not contain adequate data for the assignment of the Mn = 0 vibrations in the IR and the similarity of the optical spectra to μ-oxo Mn(IV) system point to the fact that the species is not Mn(IV) = 0 system but is very likely to be PMn(IV)-O-Mn(IV)P. A μ -oxo Mn(IV) system as an adduct of iodosyl benzene has also been reported (μ_{eff} = 1.5BM). This compound is also epr-silent. The low magnetic moment in the μ -oxo system indicates strong antiferro magnetic coupling of the d-electrons ($J \simeq 250\ cm^{-1}$). Mossbauer study of ^{127}I in the iodosyl benzene adduct have also been reported[48]. The complexes $[(N_3)Mn(IV)TPP]_2O$ and $[(OCN)Mn(IV)TPP]_2O$ are thermally unstable and decompose slowly.[50] When solutions of these systems are allowed to decompose partially and frozen at liquid nitrogen temperature, a 16-line esr spectrum is obtained. The epr spectrum is shown to be very similar to the known mixed valence Mn(III)-O-Mn(IV) systems.[51,52] In equivalence of the Mn atoms have also been observed in the hyperfine couplings. The epr spectra of the mixed valence Mn porphyrins are similar to those observed when spinach chloroplasts are flashed with a pulse of light and frozen.[52] A coupling of $S = \frac{3}{2}$ [Mn(IV)] and $S = 2$ [Mn(III)] leads to a ground state $S = \frac{1}{2}$ in the mixed valence dimer. The theory of the esr of this system is discussed in detail for Mn(III)-O-Mn(IV) dipyridyl systems.[53]

I.4.5 Mn(V) porphyrins

Craig *et al*[54] and Buchler *et al*[55] have independently reported the synthesis of Mn(V) nitrido porphyrin. Treatment of Mn(III)TPP or OEP systems with sodium hypochlorite or iodosyl benzene in the presence of excess of ammonia leads to the formation of $PMn(V)\equiv N$. Optical spectra

($\lambda_{max}^{(nm)}$ = 424, 538, 626nm), crystal structure and magnetic data have been reported. This system is diamagnetic. Mn(V) is a d^2 system and apparently the ground state is non-degenerate and does not have any low lying excited states. A similar situation is observed for PCr(V)$\equiv$N (d^1) which gives a sharp line epr spectrum in solution at room temperature, indicating that the d-orbital energy levels are similar for Mn(V) and Cr(V).

I.4.6 MnP-O_2 complexes[56-59]

Mn(II) porphyrins bind irreversibly to dioxygen. The esr data clearly indicates that Mn exists as Mn(IV) in the dioxygen complex. A typical set of esr parameters are:[56] $D = 2.46\ cm^{-1}$, $E/_D = 0.3291\ cm^{-1}$, A (^{55}Mn)= $52.6 \times 10^{-4}\ cm^{-1}$, B ($^{55}Mn$) = $86.4 \times 10^{-4}\ cm^{-1}$ for MnTPP(O_2) system. A hyperfine coupling for ^{17}O in the O_2 moiety was found to be equal to $2 \times 10^{-4}\ cm^{-1}$. The adduct is accordingly formulated as Mn(IV)P-O_2^{--} . An edge-on geometry for O_2 moiety has been proposed on the basis of EHT calculations.[60] Recent ab initio calculations also support the same view.[61]

I.5 Iron porphyrins[62-95]

Much has been said on the nature of oxidation products of iron porphyrins. A recent review summarises the earlier results upto 1982.[3] The early studies[2,62-65] on the esr and magnetic susceptibility studies on the products obtained on the electrochemical oxidation of iron porphyrins were interpreted on the assumption that the oxidised product is a Fe(IV)P species. More detailed reports have appeared in recent years on the detailed optical, and nmr studies on the oxidation products of Fe(III) porphyrins obtained both by chemical and electrochemical oxidations. Fe(IV) porphyrins are formed when an oxo ligand is present. The species (FeO)P has been identified as Fe(IV) porphyrins.

I.5.1 Electrochemical oxidation of Fe(III) porphyrins

Oxidation of the iron in the iron(III)-porphyrin to Fe(IV)O group is well established for enzymes like catalase and peroxidase where superoxide or peroxide species are involved respectively. There are also other classes of enzymes containing isobacterio chlorin (sirohydro chlorin) which have very low oxidation potentials.[66,67] On the basis of the esr and optical spectra of the oxidised species at room temperature, this species has been identified as Fe(III)P radical cation. In the following paragraphs, the available structural information on each type of oxidised species of Fe(III) porphyrins is summarised.

I.5.2 Fe(III)P radical cation

One electron oxidation of Fe(III) porphyrins is being investigated for the past twenty five years.[65] Early electrochemical studies by Wolberg and Manassen[66] as well as by Felton et al.[62,63] were not very conclusive about the assignment of structure to the species, which was not completely characterised. Chemical oxidations of Fe(III) porphyrins, using iodosylbenzene,[76] chloroperoxy benzoic acid,[93] antimony pentachloride[71] or $Fe(ClO_4)_3$[82] have been reported in recent years. The products of chemical oxidation depend on the nature of oxidising agent. Oxidation product obtained by using iodosylbenzene has been shown to be Fe(IV) species. The product obtained with chloroperoxy benzoic acid has been described as Fe(IV)P π cation radical.[93] Oxidation with $Fe(ClO_4)_3$ or $SbCl_5$ lead to Fe(III)P cation radicals. Electrochemical oxidation in the presence of perchlorate as counter-ion has been studied in detail with Fe(III) porphyrins and $(Fe(III))_2O$.[68,69] The products have been isolated on a synthetic scale and detailed magnetic measurements, Mössbauer and nmr studies have been performed on these systems. Solution magnetic measurements using nmr method has lead to a value of 5.5 BM for $TPP(OCH_3)Fe(ClO_4)$ and the corresponding OEP system over a temperature range of 215-300K. A similar oxidation product obtained by using $SbCl_5$ as oxidant, exhibits a magnetic moment of 5.1 BM over a temperature range 5-300K. Mössbauer data shows increased isomer shifts in comparison with the Fe(III)P, whereas decreased shifts are expected for Fe(IV) species. The oxidised species is esr-silent. In the visible electronic spectrum, Soret band is shifted with diminished intensity and a broad absorption is noticed around 870nm. The oxidised monomeric species yield well-resolved pmr spectra which differ from the parent Fe(III)P spectra in terms of larger phenyl proton isotropic shifts. The large shifts for the phenyl protons which are observed for any transition metal porphyrins had been taken as indicative of the presence of π radical cation. Approximate correlation have been made using the phenyl proton shifts in $(TPP)FeClO_4$ and the mesoproton shifts in $OEPFeCl(ClO_4)$ in assigning the ground state of the unpaired π electron as a_{2u} and a_{1u} respectively. On the basis of above data, the electrochemical oxidation products of FeP had been assigned as Fe(III)P cation radical .

A recent work by C.A. Reed and co-workers report the preparation of analytically pure $FeCl(TPP)SbCl_6$, $Fe(TPP)(ClO_4)_2$ using radical cations of thianthrene and phenoxathiin.[70,71] Detailed magnetic susceptibility measurements and X-ray crystal structure have been reported for these two systems. The temperature dependent-magnetic susceptibility data for FeCl (TPP)$SbCl_6$ has been interpreted as arising from strong antiferro magnetic coupling of $S = \frac{5}{2}$ iron atom and $S = \frac{1}{2}$ porphyrin radical, leading to $S = 2$ ground state. A value of J between -125 to -250 cm^{-1} has been estimated. On the other hand, $Fe(ClO_4)_2TPP$ radical cation exhibits a magnetic susceptibility of 6.50 BM at room temperature. A maximum value of 6.75 BM is reached at 100K. This value is greater than the spin only value for $S = \frac{5}{2}, \frac{1}{2}$ uncoupled system. A ferromagnetic coupling between $S = \frac{5}{2}$ iron and $S = \frac{1}{2}$ porphyrin radical has been postulated to explain the observed susceptibility data, with $J \simeq 40$ cm^{-1}. ESR spectra were not observable for both these systems down to 4.5K. The crystal structure data indicated that the Fe atom is out-of-plane of porphyrin ring in $FeClTPP(SbCl_6)$ and in the plane, in $Fe(ClO_4)_2TPP$. In the later situation the orthogonality of the d-orbitals with $a_{2u} - \pi$ orbital of porphyrin could lead to $S = 3$ state. The overlap in $FeTPPSbCl_6$ could lead to strong antiferromagnetic interaction between unpaired electrons on the metal and the ligand resulting in $S = 2$ state. The magnetic susceptibility data for $FeTPP(ClO_4)_2$ reported by Boersma and Goff[74] (μ = 4.8 BM) differs considerably from the value of 6.75 BM obtained by Gans et al[71]. The latter authors have done the measurement in the solid state using SQUID susceptometer while the former measurement was done using nmr method in solution. At present it is difficult to rationalise the observed difference in the susceptibility for the same compound.

Radical cations of the type $[Fe(III)TPP]^{2+}$, $[Fe(III)OEP]^{2+}$ with Fe in the low-spin state have also been generated and studied by nmr.[72] The low spin systems have been obtained from the corresponding high spin systems generated electrolytically, by adding directly excess of imidazole into the nmr tube. Thus $[Fe(III)TPPIm_2]^{2+}$ and $[Fe(III)OEPIm_2]^{2+}$ had been identified by solution nmr. The magnetic susceptibilities of these two systems obtained by nmr method are 2.8 BM and 3.3 BM respectively, indicating the presence of a triplet state. These systems have been found to be esr silent.

I.5.3 μ-oxo iron porphyrins

One and two-electron oxidation products of μ-oxo iron porphyrins have been reported.[69] The one - electron oxidation product yields a single line esr signal at 77K with g = 2. The doubly oxidised dimer is esr silent. IR spectra of both monomeric and dimeric species show diagnostic absorption at $\simeq$ 1290 cm^{-1} characteristic of porphyrin π-cation radicals. The magnetic susceptibilities of the one- and two-electron oxidation products (ClO_4^- as the counter ion) are respectively 3.2 and 1.7 BM indicating the presence of strong antiferromagnetic exchange in these systems.

Other Fe(III)P radical cations reported involve the ligand sirohydrochlorin (isobacteriochlorin).[66,67] The free base 2,4 dimethyl gem octaethyl isobacteriochlorin (DMOE-iBC) and its metal complexes (Free base : 0.37V vs SCE Zn complex : 0.07V vs SCE) have much lower oxidation potentials than the corresponding porphyrin systems. Oxidation of Fe(II)(DMOE-iBC)(pyridine)(CO) yields a π cation characterised by visible electronic and esr spectrum at room temperature. Fe(II)(DMOE iBC)Cl on one-electron oxidation, yields a radical type visible electronic spectrum and is esr silent. These radical cations are considered to be models for the active sites in sulphite reductase and nitrite reductase. An iron oxophlorin radical system has also been identified by esr.[75]

I.5.4 <u>Fe(IV) porphyrins</u>

A clear identification of Fe(IV)P was probably made for the first time by Chang and Kuo[76] and also by LaMar <u>et al</u>.[77-81] The later group had obtained [Fe(IV)OP base by treating [Fe(III)P-O-O-P Fe(III)] with imidazole type bases at low temperatures (-50 °C). The Fe(IV) species was identified by its typical two-banded visible electronic spectrum and nmr spectrum. The magnetic susceptibility of this species was obtained as 2.9 BM corresponding to low-spin Fe(IV) state (S = 1). The same species was found to be active catalysts involved in the oxidation of triphenyl phosphane in the presence of Fe(II)P oxygen.

Chang and Kuo[76] had obtained a green species on oxidation of Fe(III) starpped porphyrin with iodosylbenzene in neutral medium. This was identified as Fe(IV)OP in the high spin state (μ = 4.9 BM). The optical spectrum of this species was observed to be very similar to that of the active site in catalase enzymes. The nmr spectra of Fe(IV)OP (high spin) and (NMeImFe(IV)OP) (low spin) show significant differences in the contact shift of pyrrole and phenyl protons of porphyrin.

The considerations which govern metal centered-oxidation vs ligand oxidation in Mn-porphyrin apply in the case of Fe porphyrin also. Oxidation of Fe(III)P in the presence of ligands of the type ClO_4^- lead to the formation of π radical cation. If oxo ligands are present then Fe(IV) is the preferred species. It has been shown in recent years that treatment of the radical cation, (Fe(III)P)$(ClO_4)_2$ with OCH_3^- ion leads to the formation of Fe(IV)P$(OMe)_2$. This species has been isolated in the solid form.[82,83]

The nmr, magnetic and Mössbauer data are reported for this system. The dimethoxy system is low spin Fe(IV) (μ = 2.9 BM). But its nmr spectrum is different from that of $[$Base Fe(IV)OP$]$ which is also a low spin Fe(IV). The reasons attributed are that in the former, Fe may be in the plane of P ring, while Fe(IV)O may be a pyramidal system. To clarify the situation further, electrochemical oxidation of Fe(III)P(OH) has been done in CH_2Cl_2 around -70°C to obtain a species characterized as Fe(IV)OP.[84] The same species is also obtained by chemical oxidation with iodosyl benzene in presence of methanol. Further, treatment of Fe(IV)PO with perchloric acid affords the π-radical cation, Fe(III)P$(ClO_4)_2$. Thus, a reasonably clear picture have emerged out of the confusion prevailing over a decade. Fe(IV) porphyrins are also esr silent.

I.5.5 Fe(IV)P radical cation

This species has been postulated as the active center in HRP-compound I.[85-92] Mössbauer data of the HRP-I indicates the presence of Fe(IV).[88] NHR results point to the presence of π-radical cation.[91-92] ESR and ENDOR studies have also been made on this system. These latter studies indicate a free radical system, strongly coupled to a paramagnetic metal center.[97] The overall magnetic susceptibility accounts for $S = \frac{3}{2}$ state. On the basis of these data, the present explanation for HRP-I is that it is Fe(IV)P$^{+\cdot}$ with Fe in the low spin state $(S = 1)$ coupled to a π radical cation $(S = \frac{1}{2})$. Fe(IV)P$^{+\cdot}$ is reported to be formed during the oxidation of Fe(III)P by chlorobenzoic acid in methylene chloride-methanol system at -78°C.[93] This product is epr silent, and its magnetic susceptibility is 4.2 BM. Though this system is distinctly different from Fe(III)P$^{+\cdot}$ in its nmr spectrum, it is not identical to compound I of HRP. Further characterisation of the chemically obtained species is necessary.

An iron porphyrin containing Fe-C bond has been oxidised to Fe(IV) porphyrin.[95] Phenyl Fe(III) (p-tolyl TPP) was oxidised with bromine. The product was identified by nmr data as Fe(IV) porphyrin.

Using a chemical oxidising agent, N-N dimethylaniline-Noxide, a facile oxidation of Fe(III)TPP has been observed.[96] The oxidation product has been assigned as Fe(V)P. No detailed structural assignments are available.

I.6 Nickel porphyrins

One electron oxidation product of nickel porphyrins were reported to undergo valence tautomerism.[98,99] The oxidation product at room temperature was identified as the cation radical while at 77K the colour changed from green to red with a strongly anisotropic esr spectrum ($g_{\perp} = 2.286$, $g_{\parallel} = 2.086$). This species was identified as d^7Ni(III) system. It was also observed that when the oxidation was done using Br_2 as the oxidant no spectral changes occured at low temperatures. When the oxidation had been carried out in the presence of PF_6^- ion, Ni(III) species was observed at low temperatures. A recent resonance Raman study of the system also confirms the above observation. Apparently PF_6^- stabilises Ni(III) whereas Br^- does not.[100]

I.7 Cu porphyrins

Cu(II) porphyrins on oxidation form the radical cations. In solution the oxidised species has two unpaired electrons ($\mu = 2.4$ BM).[101,102] Deuterium nmr of Cu(TPP)$^{+\cdot}$ has also confirmed the presence of radical cation. The crystalline of one-electron oxidation product of Cu(TPP), with $SbCl_6$, is diamagnetic while in solution $\mu = 2.4$ BM.[103] This value matches with that for two non-interacting $S = \frac{1}{2}$ magnetic centers. From the nmr data the ground state for the unpaired π electron in Cu(TPP)$^{+\cdot}$ was assigned as a_{2u}.[104]

Cu(OEP) and Cu(OEC) (octaethyl chlorin) on one-electron oxidation lead to the formation of cation radicals which are esr-silent at ambient temperatures. In frozen solutions at 77°C, dimeric species have been observed with S = 1 state, dimer has one electron each on the Cu atoms and distance between the Cu atoms had been obtained as 3.7 Å from the observed epr spectrum.[105] Another type of oxidised species was detected by epr when a frozen solution of Cu(TPP) was irradiated by γ-rays. This species gave a characteristic triplet state epr spectrum, corresponding to only one Cu center. The radiation induced oxidation has most likely yielded a monomeric Cu radical species.[106]

I.8 Ag porphyrins

Silver(II) porphyrins have unusually low oxidation potentials. The first one-electron oxidation product of Ag(II)OEP and Ag(II)TPP were shown to be diamagnetic and no π- radical spectrum was observed.[107-110] On this basis, the oxidised species has been assigned as Ag(III)P. A recent deuterium nmr study on the same system also confirms this assignment.[111]

A selective review has been presented above on some of the recent work on the oxidation products of transition metal porphyrins as studied by magnetic resonance, optical spectra and magnetic susceptibility measurements. It is clear from the material presented, that no single physical technique is adequate to understand the structural features of the systems discussed. A number of problems still remain to be solved regarding the magnetic properties of oxidised porphyrins. In the work presented in this thesis, an attempt is made to understand the magnetic properties of the oxidation products of some simple transition metal porphyrins, namely vanadyl porphyrins. ESR had been the main technique used, supported by visible absorption and cyclic voltametric data.

REFERENCES

1. Electrochemical and Spectrochemical Studies of Biological Redox Components. Advances in Chemistry Series, Edited by K.M. Kadish (American Chemical Society, Washington D.C., 1982), 201

2. W.D. Hewson and L.P. Hager, in Porphyrins, Edited by D. Dolphin (Acad. Press, N.Y., 1979) Vol. 7, p. 295.

3. C.A. Reed, in Electrochemical and Spectrochemical Studies of Biological Redox Components, Advances in Chemistry Series, Edited by K.M. Kadish (American Chemical Society, Washington D.C., 1982), 201, p.333.

4. H.M. Goff, M.A. Phillippi, A.D. Boersma and A.P. Hansens, in Electrochemical and Spectrochemical Studies of Biological Redox Components, Advances in Chemistry Series, Edited by K.M. Kadish (American Chemical Society, Washington D.C., 1982), 201, p. 356.

5. Brian James in Porphyrins, Edited by D. Dolphin, (Acad. Press, N.Y., 1978) Vol. V, p. 207.

6. R.D. Jones, D.A. Summerville and F. Basolo, Chem. Rev., 79, 139 (1979).

7. M.H. Gublmann and A.F. Williams, in Structure and Bonding, (Springer Verlag, Berlin, Heidelberg, 1983), 55, 1.

8. J. Subramanian, in Porphyrins and Metalloporphyrins, Edited by K.M. Smith (Elsevier, Amsterdam, 1975), p. 555.

9. G.R. Luckhurst, M. Setaka and J. Subramanian, Mol. Phys., 32, 1299 (1976).

10. A. Lemtur, B. Chakraborty, T.K. Dhar and J. Subramanian,
J. Phys. Chem., 88, 5603 (1984).

11. G.E. Selyutin, A.A. Shklyaev and V.F. Anufrienko ,
Dokl. Akad. NaukSSR, 255, 390 (1980).

12. M. Hoshino, S. Konishi, M. Imamura, S. Watanabe
and Y. Hama, Chem. Phys. Lett., 102, 259 (1983).

13. J.R. Budge, B.M.K. Gatehouse, M.C. Nesbit and
B.O. West, J. Chem. Soc., Chem. Commun., 8, 370 (1981).

14. J.W. Buchler, K.L. Lay, L. Castle and V. Ulrich,
Inorg. Chem., 21, 842 (1982).

15. J.T. Groves, W.J. Kruper, R.C. Haushalter and
W.M. Butler, Inorg. Chem., 21, 1363 (1982).

16. V. Srinivasan and J. Rocek, J. Am.Chem.Soc.,
96, 127 (1974).

17. J.T. Croves, W.J. Kruper Jr.,J. Chem. Chem. Soc.,
101, 7613 (1979).

18. Yoshihisa Matsuda, Suna Yamasa and Yukito Murakami,
In Organica Chemica Acta, 44, L309 . (1980).

19. J.T. Groves, W.-J. Kruper Jr., J. Am. Chem. Soc.,
101, 7613 (1979).

20. S.I. Arshankow, A.C. Poznjak, Z. Anorg. Allg. Chem.,
481, 201 (1981).

21. J.T. Groves, J. Takahashi and W.M. Butler,
Inorg. Chem., 22, 884 (1983).

22. J.T. Groves, T. Takahashi and W.M. Butler,
Inorg. Chem., 22, 884 (1983).

23. J.T. Groves and Robert C. Haushalter, J. Chem. Soc.,
Chem. Commun., 1165 (1981).

24. J.W. Buchler, C. Dreber, K.L. Lay, A. Raap and K. Gersonde, Inorg. Chem., 22, 879 (1983).

25. R.M. Sellers and M.G. Simic, J. Chem. Soc., Chem. Commun., 401 (1975).

26. K.H. Nill, F. Wagestian and A.P. Feil, Inorg. Chem., 18, 564 (1979).

27. S.K. Cheung, C.J. Grimes, J. Wong and C.A. Reed, J. Am. Chem. Soc., 98, 5028 (1976).

28. R.J. Murray and S.G. Sligor, J. Am. Chem. Soc., 107, 2186 (1985).

29. I. Willner, J.W. Otvos, M. Calvin, J. Chem. Soc., Chem. Commun., 964 (1980).

30. C.L. Hill and B.C. Schardt, J. Am. Chem. Soc., 102, 6374 (1980).

31. D. Mansuy, J.F. Bartoli, L. Chottard, M. Lang, Angew. Chem. Intnl. Edn., 19, 909 (1980).

32. A. Gold, W.Ivey, M. Bowen., Chem. Commun., 293 (1981).

33. C.K. Chang, M.S. Keo, J. Am. Chem. Soc., 101, 3413 (1979).

34. I. Tabushi and N. Koga, Tet. Letts., 1577 (1974).

35. I. Tabushi and N. Koga, Tet. Letts., 305 (1975).

36. I. Tabushi and N. Koga, Tet. Letts., 501 (1978).

37. M.J. Camenzind, F.T. Hollander, C.L. Hill, Inorg. Chem., 22, 3777 (1983).

38. M.J. Camenzind, F.J. Hollander, C.L. Hill, Inorg. Chem., 21, 4301 (1982).

39. Olga Bortolini and Bernard Meuner, J. Chem. Soc., Chem. Commun., 22, 1364 (1983).

40. J.A. Smegal and C.L. Hill, J. Am. Chem. Soc., 105, 2920 (1983).

41. R.F. Ferrante, J.L. Wilkerson, W.R.M. Grahams and W. Wettner, J. Chem. Phys., 67, 5904 (1977).

42. S. Konishi, M. Hoshino and M. Imamura, J. Phys. Chem., 86, 4539 (1982).

43. L.O. Spreer, A.C. Maliyackel, S. Hallbrook, J.W. Otvos and M. Calvin, J. Am. Chem. Soc., 108, 1949 (1986).

44. M. Iwaizumi and H. Komuro, Inorganica Chemica Acta, 111, L9 (1986).

45. B.C. Schardt, F.J. Hollander, C.L. Hill, J. Am. Chem. Soc., 104, 3964 (1982).

46. J.T. Groves, W.J. Kruper, R.C. Haushalter, J. Am. Chem. Soc., 102, 6375 (1980).

47. J.A. Smegal and C.L. Hill, J. Am. Chem. Soc., 105, 3515 (1983).

48. J.A. Smegal, B.C. Schardt and C.L. Hill, J. Am. Chem. Soc., 105, 3510 (1983).

49. T. Birchall, J.A. Smegal and C.L. Hill, Inorg. Chem., 23, 1910 (1984).

50. C.L. Hill, Inorg. Chem., 23, 1984 (1984).

51. S.R. Cooper, G.C. Dismukes, M.P. Klein and M. Calvin, J. Am. Chem. Soc., 100, 7248 (1978).

52. G.C. Dismukes, K. Ferris, P. Watnick, Photobiochem. Photobiophys., 3, 243 (1982).

53. P.M. Plaskin, R.C. Stoufer, M. Mathew and G.J. Palenik, J. Am. Chem. Soc., 94, 2121 (1972).

54. Craig L. Hill and F.J. Hollander, J. Am. Chem. Soc. 104, 7318 (1982).

55. J.W. Buchler, C. Dreher, K.L. Lay, Y.J. Lee and W.R. Scheidt, Inorg. Chem., 22, 888 (1983).

56. Charles J. Weschler, B.M. Hoffman, F. Basolo, J. Am. Chem. Soc., 97, 5278 (1975).

57. B.M. Hoffman, Charles J. Weschler, F. Basolo, J. Am. Chem. Soc., 98, 5473 (1976).

58. B.M. Hoffman, T. Szymanski, T.G. Brown and F. Basolo, J. Am. Chem. Soc., 100, 7253 (1978).

59. I. Tabushi and N. Koga, J. Am. Chem. Soc., 101, 6456 (1979).

60. L.K. Hanson and B.M. Hoffman, J. Am. Chem. Soc., 102, 4602 (1980).

61. A. Dedieu and M.M. Rohmer, J. Am. Chem. Soc., 99, 8050 (1977).

62. R.H. Felton, G.S. Owen, D. Dolphin, J. Fajer, J. Am. Chem. Soc., 93, 6332 (1971).

63. R.H. Felton, G.S. Owen, D. Dolphin, A. Forman, D.C. Borg and J. Fajer, Ann. NY Acad. Sci., 206, 504 (1973).

64. A. Wolberg, J. Manassen, J. Am. Chem. Soc., 92, 2982 (1970).

65. H.B. Dunford and J.S. Stillman, Coord. Chem. Rev., 19, 187 (1976).

66. C.K. Chang and J. Fajer, J. Am. Chem. Soc., 102, 849 (1980).

67. A.I. Scott, A.J. Irwin, L.M. Siegel, J.N. Shoolery, J. Am. Chem. Soc., 100, 7987 (1978).

68. M.A. Phillipi, E.T. Shimomura, and H.M. Goff, Inorg. Chem., 20, 1322 (1981).

69. M.A. Phillipi and H.M. Goff, J. Am. Chem. Soc., 104, 6026 (1982).

70. P. Gans, J.-C. Marchen, C.A. Reed, J.-R. Regnard, Nouv. J. Chem., 5, 203 (1981).

71. P. Gans, G. Buisson, T. Duel, J.-C. Marchen, B.S. Erler, W.F. Scholz and C.A. Reed, J. Am. Chem. Soc., 108, 1223 (1986).

72. H.M. Goff, M.A. Phillippi, J. Am. Chem. Soc., 105, 7567 (1983).

73. E.T. Shimomura, M.A. Phillippi, H.M. Goff, W.F. Schotz and C.A. Reed, J. Am. Chem. Soc., 103, 6778 (1981).

74. A.D. Boersma and H.M. Goff, Inorg. Chem., 23, 1671 (1984).

75. I. Morishima, H. Fuju and Y. Shiro, J. Am. Chem. Soc., 108, 3858 (1986).

76. C.K. Chang and N.S. Kuo, J. Am. Chem. Soc., 101, 3413 (1979).

77. D.H. Chin, A.L. Balch and G.N. LaMar, J. Am. Chem. Soc., 102, 1446 (1980).

78. D.H. Chin, G.N. LaMar and A.L. Balch, J. Am. Chem. Soc., 102, 4344 (1980).

79. D.H. Chin, G.N. LaMar and A.L. Balch, J. Am. Chem. Soc., 102, 5945 (1980).

80. D.H. Chin, Del Gaudio J, G.N. LaMar and A.L. Balch, J. Am. Chem. Soc., 99, 5486 (1977).

81. A.L. Balch, Y.-W. Chan, R.-J. Chang, G.N. LaMar, L. Latos Grazynski and M.W. Renner, J. Am. Chem. Soc., 106, 7779 (1984).

82. John T. Groves, R. Quinn, T.J. McMurry, G. Lang and B. Boso, J. Chem. Soc. Chem. Commun., 21, 1455 (1984).

83. J.T. Groves, R. Quinn, Thomas J. McMurry, M. Nakamura, G. Lang and Brian Boso, J. Am. Chem. Soc., 107, 354 (1985).

84. J.T. Groves and J.A. Gilbert, Inorg. Chem., 25, 123 (1986).

85. H.M. Goff, and M.A. Phillippi, Inorg. Nucl. Chem. Lett., 17, 239 (1981).

86. L.K. Hanson, C.K. Chang, M.S. Davis and J. Fajer, J. Am. Chem. Soc., 103, 663 (1981).

87. I. Morishima, Y. Takamuki and Y. Shiro, J. Am. Chem. Soc., 106, 7666 (1984).

88. T.H. Moss, A. Ehrenberg and A.J. Bearden, J. Biochem., 8, 4159 (1969).

89. T. Harami, Y. Maeda, Y. Morita, A. Trautweirs and U. Gonser, J. Chem. Phys., 67, 1164 (1977).

90. C.E. Schultz, P.W. Devaney, H. Winkler, P.G. Debrunnez, N. Doan, R. Chiang, R. Rutter and L. Hager, FEBS Letts., 103, 102 (1979).

91. G.N. LaMar and J.S. DeRopp, J. Am. Chem. Soc., 102, 395 (1980).

92. I. Morishima and S. Ogawa, J. Am. Chem. Soc., 100, 7125 (1978).

93. J.T. Groves, R.C. Haushalter, M. Nakamura, T.E. Nemo, and B.J. Evans, J. Am. Chem. Soc., 103, 2884 (1981).

94. T.C. Calderwood, W.A. Lee and T.C. Bruice, J. Am. Chem. Soc., 107, 8272 (1985).

95. A.L. Balch and M.W. Renner, J. Am. Chem. Soc., 108, 2603 (1986).

96. M.W. Nee, and T.C. Bruice, J. Am. Chem. Soc., 104, 6123 (1982); 106, 3277 (1984); 107, 2186 (1984).

97. J.E. Roberts, B.M. Hoffman, R. Rutter and L.P. Hager, J. Biol. Chem., 256, 2118 (1981).

98. D. Dolphin, T. Niem , R.H. Felton and I. Fujita, J. Am. Chem. Soc., 97, 5288 (1975).

99. E.C. Johnson, T. Niem and D. Dolphin, Can. J. Chem., 56, 1381 (1978).

100. D. Kim, L.A. Miller and T.G. Spiro, Inorg. Chem., 25, 2468 (1986).

101. J.-H. Fuhrhop and D. Mauzerall, J. Am. Chem. Soc., 91, 4174 (1969).

102. A. Wolberg and J. Manassen, J. Am. Chem. Soc., 92, 2982 (1970).

103. W.R. Sholz, C.A. Reed, J.L. Lee, W.R. Scheidt, and G. Lang, J. Am. Chem. Soc., 104, 6791 (1982).

104. G.M. Godziela and H.M. Goff, J. Am. Chem. Soc., 108, 2237 (1986).

105. C. Mengerson, J. Subramanian and J.-H. Fuhrhop, Mol. Phys., 32, 893 (1976).

106. S. Konishi, M. Hoshino and M. Imamura, J. Am. Chem. Soc., 104, 2057 (1982).

107. K.M. Kadish, D.G. Davis and J.-H. Fuhrhop, Angew. Chem., Int. Ed., 11, 1014 (1972).

108. J.-H. Fuhrhop, K.M. Kadish and D.G. Davis, J. Am. Chem. Soc., 95, 5140 (1973).

109. A. Antipas, D. Dolphin, M. Gouterman and E.C. Johnson, J. Am. Chem. Soc., 100, 7705 (1978).

110. S.E. Jones and H.N. Po, Inorg. Chem. Acta, 42, 95 (1980).

111. G.M. Godziela and H.M. Goff, J. Am. Chem. Soc., 108, 2237 (1986).

CHAPTER II

DETAILS OF EXPERIMENTAL TECHNIQUES

CHAPTER II

DETAILS OF EXPERIMENTAL TECHNIQUES[1-8]

II.1 INTRODUCTION

This section of the Chapter deals with the synthesis of metalloporphyrins used in the present work, purification of solvents and other chemicals used in Cyclic Voltammetric and esr studies. A brief account of the Cyclic Voltammetry is also presented.

II.2 SOLVENTS:[1]

The following solvents were used throughout the experimentation.

(i) Benzene

For extraction and running chromatographic column commercial benzene (drum sample) has been used after twice distillation. For other experimental purposes like optical measurements and recrystallization etc. Spectroscopic grade solvent (Sarabhai M. Chemicals) were used.

(ii) Hexane and Cyclohexane

Commercial drum sample of hexane and cyclohexane have been used after distilling twice.

(iii) Chloroform

Drum sample, distilled twice and dried over $CaCl_2$ has been employed for synthesis, extraction and running columns. For recrystallization and other physical measurements spectroscopic grade was employed.

(iv) Dichloromethane

Drum sample or E. Merck synthetic grade dichloromethane was twice distilled, refluxed over K_2CO_3 (anhydrous) for about 4 hrs and distilled. This sample has been used for synthesis, extraction and column chromatography. For cyclic voltammetric measurements, optical measurements and EPR measurements, the spectroscopic grade solvent distilled once, has been employed.

(v) Methanol and Ethanol

Absolute alcohol has been prepared from the distilled drum sample. These alcohols were used for synthesis, recrystallization etc. A.R. Grade (S.D.'s Fine Chemicals) alcohols were also employed.

(vi) Dimethylformamide (DMF)

DMF (SDS, AR) has been kept over anhydrous $CuSO_4$ overnight, distilled under reduced pressure and kept over activated molecular sieves.

(vii) Benzonitrile

Benzonitrile (SD's Fine Chemicals, LR) has been employed directly for synthesis.

II.3 OXIDISING AGENTS

The following agents were used for oxidation of metalloporphyrins.

(i) Perchloric acid

Perchloric acid (Merck GR) has been used directly.

(ii) Trifluoro acetic acid (TFA)

TFA (Fluka AG) was distilled before use.

(iii) Aluminum Chloride

A solution of aluminum chloride has been made by dissolving aluminum chloride (anhydrous) in distilled, dry and deaerated dichloromethane.

(iv) Boron trifluoride (BF_3) solution

A saturated solution of BF_3 has been made by passing BF_3 gas through distilled and dried dichloromethane.

(v) Antimony pentachloride ($SbCl_5$) solution

2 ml of antimony pentachloride (Fluka AG) has been dissolved in 50 ml distilled, dry and deaerated dichloromethane.

II.4 REAGENTS AND SUPPORTING ELECTROLYTES[2,3]

This reaction describes the methods of preparation of different reagents and complexes which were used during the course of investigation. Some of the reagents were procured commercially.

(i) Vanadyl sulfate[1] (Anhydrous)

Vanadyl sulfate (anhydrous) has been prepared by the action of conc. H_2SO_4 and SO_2 on V_2O_5.

$$V_2O_5 + H_2SO_4 + SO_2 + 5H_2O = 2VOSO_4 \cdot 3H_2O$$

About 2 gms of V_2O_5, 1.3 ml H_2SO_4 (conc.) and about 1 ml of water were mixed thoroughly to form a paste. After keeping overnight, some more water was added and SO_2 gas was passed through the suspension till all V_2O_5 was dissolved. It was then filtered through a sintered funnel. The dark blue filtrate was then slowly concentrated till a crystalline mass was obtained. It was then washed acid-free with 95% ethanol and dried by a suction pump. The bright blue crystalline material was kept in a vaccuum dessicator containing P_2O_5. It is highly hygroscopic.

(ii) Sodium perchlorate[2]

Sodium perchlorate has been prepared by neutralising sodium carbonate (ANALAR) with perchloric acid (LOBA CHEMIE,GR).

After completely neutralising, the volume of the reaction mixture was concentrated and sodium perchlorate has been crystallized out. It was then recrystallized from distilled water several times. The purity of the sample has been tested by running a cyclic voltammogram.

(iii) N-Bromo Succinamide (NBS)[1]

Commercially available N-bromo succinamide has been recrystallized from hot water several times. White crystalline pure N-bromo succinamide has been obtained. Melting point : 170 - 175°C.

(iv) Tetra n-butylammonium perchlorate (TBAB)[1]

A saturated solution of tetrabutylammonium iodied (SISCO, Extrapure) has been prepared in distilled water. To the solution, sodium perchlorate has been added, while tetrabutylammonium perchlorate precipitates out instantly. It has been stirred constantly and filtered fast in order to avoid the liberation of iodine. More sodium perchlorate has been added to the filtrate till white precipitate of tetrabutylammonium perchlorate no longer forms. The precipitates has been suction-filtered and dried by pressing between filter papers. After properly drying, the tetrabutylammonium perchlorate was dissolved in methanol and reprecipitated out by adding distilled water. It was then filtered and dried as before, then recrystallized from methanol. Glassy crystals were formed. The purity of the sample has been tested by running a cyclic voltammogram.

II.5 METALLOPORPHYRIN[4-8]

(i) Protoporphyrin IX-dimethylester[4]

Hemin (from OX blood, CSIR, Biochemicals, New Delhi) was demetalated and esterified. Demetalation, esterification and extraction have been done according to the standard method as reported in the literature[4]. About 2gm of powdered $FeSO_4$ is added. A fast stream of HCl gas is passed through the filtrate of Hemin solution. In order to avoid the excessive generation of heat, the solution is kept in an ice-cooled water. Complete demetalation and esterification are accompanied by a colour change from reddish to pinkish. This can be easily identified by recording an optical spectrum. The absorption band due to Hemin ($\simeq$ 630nm) is replaced by that of protoporphyrin dication (610, 585nm). After cooling, the reaction mixture is extracted with chloroform and washed thoroughly with water. The washing is done fast in order to avoid the hydrolysis of ester by aqueous HCl. After thoroughly washing the reaction mixture with water, the chloroform layer is collected in a conical flask and dried over Na_2SO_4

(anhydrous). After filtering, the solvent is removed by evaporation and the protoporphyrin-IX dimethylester is obtained as residue. For purification, a column of Al_2O_3 (neutral) has been employed. 1:10 $CHCl_3$/Benzene mixture has been used for eluting the porphyrin ester. The green band of chlorin has been seperated from the column and different fractions were tested optically, protoporphyrin IX dimethylester is quite sensitive to light due to the presence of vinyl group. Therefore, during elution the column is wrapped by a dark paper. The porphyrin ester has been crystallized out from chloroform-methanol mixture. The purity of the sample has been checked by proton nmr and by running a TLC against standard PPIXDME (Sigma Chemicals, USA).

$\lambda_{max}^{(nm)}$ 407, 505, 540, 575, 603(s), 630.

(ii) Vanadyl protoporphyrin IX dimethyl ester[5]

Vanadyl protoporphyrin-IX dimethylester has been prepared by using anhydrous $VOSO_4$. In a round bottomed flask fitted with a condenser 50ml of glacial acetic acid, 1.5g of sodium acetate, about 300mg of vanadyl sulfate and 200mg of protoporphyrin-IX dimethyl ester were taken. The mixture was refluxed for few minutes and some pyridine was added. The mixture was refluxed continuously till the metallation occured fully. This was checked by the optical spectra. The mixture was then cooled and extracted with chloroform. The chloroform extract was thoroughly washed with water and 60% formic acid. The chloroform layer was then dried over sodium sulfate (anhydrous) keeping overnight. The chloroform was evaporated to dryness using a rotary evaporator. The crude product was chromatographed using alumina (neutral). Vanadyl porphyrin was eluted by benzene. The product obtained as the pure fraction was then recrystallized from benzene-methanol. Purity of the sample has been tested by TLC.

$\lambda_{max}^{(nm)}$, 410, 500(s), 535, 575 (in chloroform).

(iii) Vanadyl mesoporphyrin IX-dimethylester[5]

The vanadyl complex has been made in the same way as in the case of vanadyl protoporphyrin. Purification has been done by running through a column of silica gel, using benzene as solvent. Vanadyl mesoporphyrin IX-dimethylester has been crystallized out from methanol-benzene mixture. The optical spectrum was taken in $CHCl_3$.

$\lambda_{max}^{(nm)}$, 405, 530, 567.

(iv) Tetrabromo-tetraphenylporphyrin[7,8]

About 1.2gm of purified TPP and about 2.32gms of NBS in $CHCl_3$ were taken in a round bottomed flask fitted with a reflux condenser. The mixture was refluxed for about one hr. The reaction mixture was tested optically and when the bromination occurs, the reaction mixture was kept in a freezer and a few drops of pyridine has been added for neutralising. The solvent has been eliminated and the residue washed with methanol and dried. Brominated porphyrin has been purified by employing a column of silica gel eluting with benzene-cyclohexane mixture. It is then recrystallized from dichloromethane-methanol mixture and dried in a vaccumm dessicator at about 60°.

$\lambda^{(nm)}_{max}$, 437, 534, 575(s), 620, 685.

(v). Vanadyl tetrabromo tetraphenyl porphyrin[6]

The vanadyl complex has been prepared by Adler's[6] method. About 100mg of tetrabromo tetraphenyl porphyrin and about 200mg of vanadyl sulfate (anhydrous) in about 150 ml of DMF have been taken in a round bottomed flask fitted with a reflux condenser. The mixture has been refluxed till metallation occurs. The reaction has been forwarded by adding a few drops of pyridine. Metallation has been checked optically. After complete metallation the reaction mixture has been extracted with benzene and washed thoroughly with water. The benzene fraction has been dried over anhydrous sodium sulfate keeping overnight. By evaporating the solvent, VO tetrabromo tetraphenyl porphyrin has been obtained in the solid form. It is then purified through a column of Al_2O_3 (neutral). The unreacted TPP comes out first from the column and a greenish purple band which contain the vanadyl tetrabromoporphyrin follows. The column has been run using benzene-hexane mixture. The pure vanadyl tetrabromo tetraphenyl porphyrin has been obtained by recrystallization from methanol-benzene mixture.

(vi). Copper tetrabromo tetraphenyl porphyrin[4]

$CuTPPBr_4$ has been prepared by standard method as reported in the literature.[4] About 100mg of $TPPBr_4$ has been dissolved in chloroform in a round bottomed flask and refluxed for about 5 mins. A saturated solution of copper acetate in methanol has been added to the $TPPBr_4$ solution (when it is hot) and allowed to reflux for some more time. Completion of the metallation has been checked by optical spectrum and then the solution was allowed to cool. It is then washed thoroughly with water till all the unreacted copper acetate has been removed. After drying over anhydrous sodium sulfate, the solution is filtered and the solvent is evaporated. Purification has been done by running through a column of basic alumina using benzene/hexane as solvent. The unreacted porphyrin is eliminated as the first fraction. The second fraction contains the pure metalloporphyrin.

Pure $CuTPPBr_4$ crystals has been obtained by recrystallization from benzene-methanol mixture.

$\lambda_{max}^{(nm)}$, 425, 550, 587.

(vii) Zinc tetrabromo tetraphenyl porphyrin[4]

The method of preparation is the same as that for other zinc porphyrins. About 100mg of $TPPBr_4$ in about 100 ml of chloroform is taken in a round bottomed flask and refluxed for about 5 mins. To the hot solution a saturated solution of zinc acetate is added and refluxing is continued for some more time. Completion of metallation has been checked by taking a visible spectrum. The reaction mixture is extracted by adding some more chloroform and washed thoroughly with water so as to remove all the unreacted zinc acetate. The chloroform layer is then dried by adding Na_2SO_4 (anhydrous) and keeping for sometime. It is then filtered and the solvent has been eliminated by evaporation. The metal porphyrin is purified through a column of basic or neutral alumina using benzene/hexane as solvent. Pure crystals has been obtained by recrystallization from benzene-methanol mixture.

$\lambda_{max}^{(nm)}$, 435, 530 (s), 567, 610 (s).

(viii) Nickel tetrabromo tetraphenyl porphyrin[6]

The nickel complex has been prepared by Adler's method[6]. About 100mg of $TPPBr_4$ has been taken in about 200 ml of DMF (Dimethylformamide). Nickel chloride has been added in a little excess and the mixture was refluxed till complete metallation occurs. The metalloporphyrin has been extracted in chloroform, thoroughly washed with water and kept over Na_2SO_4 (anhydrous) overnight. Byevaporating the solvent, the solid $NiTPPBr_4$ has been obtained which was further purified through a column using benzene/hexane as solvent. Pure $NiTPPBr_4$ crystals were obtained by recrystallization from benzene-methanol mixture.

$\lambda_{max}^{(nm)}$, 432, 550, 590.

II.6 INSTRUMENTATION

II.6.1 CYCLIC VOLTAMMETRY

Redox potentials were determined using Mckee-Pederson MP 1502 system. A digigraphic 2000 XY recorder was used for recording the voltammograms. The electrolytic cell comprises of the following: An Elico platinum electrode, type EP 79 (India) was used as a working electrode. A platinum wire sealed in a glass tube connected with a copper wire has been employed as an auxiliary electrode. A saturated calomel electrode (ELICO-type ER 72 P) has been employed as a reference electrode. Throughout the electrochemical investigations (for oxidation) dry CH_2Cl_2 has been used as the solvent. The amount of solvents employed were 5 to 10ml. TBAP (0.1M) has been employed as supporting electrolyte and sodium perchlorate has been employed in the salt bridge. The solvent in the electrolyte cell has been deaerated with oxygen free dry nitrogen gas before any measurement has been done. Calibration of $E_{\frac{1}{2}}$ values and diffusion current were made by using a known concentration of pure ZnTPP in CH_2Cl_2/TBAP (0.1M) medium.

II.6.2 EPR

EPR measurements were done using X band EPR spectrometer, model E 109 (varian) system, employing absorption reference arm. A multipurpose cavity model E-231 has been used. Magnetic field modulation was done at 100 KHz. Some measurements were done using E 104 system also. The EPR data presented in this thesis were obtained from RSIC, Madras, (E 104), Department of Material Science, I.I.Sc., Bangalore (E 109) and (home built), TIFR, Bombay. Measurements at liquid nitrogen temperature were done at Madras and Bangalore and those at liquid He temperature were carried out at TIFR, Bombay. A few measurements towards the later part of the research programme were done with E 109 ESR spectrometer installed in NEHU, Shillong.

Measurements at liquid nitrogen temperature were done using a cold finger dewar and those around liquid He temperature were done using oxford helium flow cryocooler.

REFERENCES

1. A.I. Vogel, A text book of Practical Organic Chemistry, Fourth Edition (ELBS, Longman, London, 1978).
2. Handbook of Preparative Inorganic Chemistry, Edited by G. Brauer (Academic Press, New York, 1965), Vol. II, 1185.
3. Inorganic Synthesis, Editor-in-chief Therald Moellur (McGraw-Hill, 1957), 5, 154.
4. Laboratory methods in porphyrin and metalloporphyrin research, Edited by J.-H. Fuhrhop and K.M. Smith (Elsevier, Amsterdam, 1975).
5. J.G. Erdman, V.G. Ramsey, N.W. Kalenda and W.E. Hanser, J. Am. Chem. Soc., 78, 5844 (1956).
6. A.D. Adler, F.R. Longe, F. Kampas and J. Kemp, J. Inorg. Nucl. Chem., 32, 2443 (1970).
7. E. Samuels, R. Shuttleworth and T.S. Stevens, J. Chem. Soc.(C), Pt. 1, 144 (1968).
8. H.J. Callot, Bulletin de la Societe Chimique de France, Pt 2, 7 (1974).

CHAPTER III

ESR SPECTRA OF DIMERIC SPECIES OBTAINED FROM THE OXIDATION PRODUCT OF VANADYL OCTAETHYL PORPHYRINS

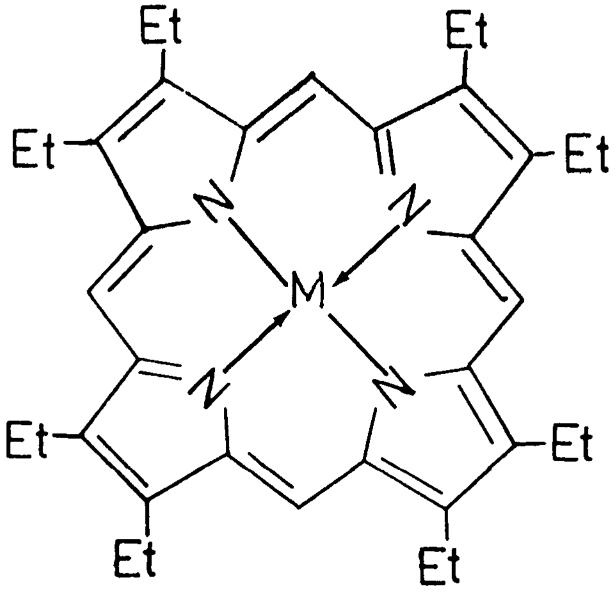
CHAPTER III

ESR SPECTRA OF DIMERIC SPECIES OBTAINED FROM THE OXIDATION PRODUCT OF VANADYL OCTAETHYL PORPHYRIN

III.1 INTRODUCTION

Vanadyl porphyrins being d^1 systems are the simplest among the transition metal porphyrins. One-electron oxidation of vanadyl porphyrins leads to the presence of a single unpaired electron in the ligand pi orbital in addition to the d electron already present. Hence this system affords a simple model for studying the interactions between the metal d electron and ligand pi electron. In this chapter we present the results of low temperature esr studies on the one-electron oxidation product of vanadyl octaethyl porphyrin.

The porphyrin ligands that are being used for physicochemical studies broadly fall into two types :[1-6] (i) those which do not have any substituents in the meso positions. Typical examples are octaethyl porphyrin, etioporphyrin, protoporphyrin and many other naturally occuring porphyrins. We shall call these systems as OEP type. (OEP = Octaethyl porphyrin). (ii) those which have alkyl or aryl substituents in the meso positions (TPP type, TPP = meso tetraphenyl porphyrin). In a metalloporphyrin with D_{4h} *symmetry, the two highest occupied pi molecul*



$\mathrm{Et} = C_2H_5$
$\mathrm{M} = \mathrm{VO}$

Fig.III.1. Structures of metalloporphyrin
(Octaethylporphyrin)

orbitals are very close lying, with symmetry labels a_{1u} and a_{2u}. The energy gap between these two orbitals is of the order of 0.5eV or less.[6] Consequently, the relative ordering of these two levels is very sensitive to the nature of the central metal ion. In general it has been observed from the esr studies of metalloporphyrin radical cations, that those belonging to OEP type have a_{1u} ground state (a is the highest occupied pi m.o.) and those belonging to the TPP type have a_{2u} ground state.[2-5] This is only a general observation. In certain situations, for the same system (e.g. Co(III)OEP radical cation) the ground state of the pi radical changes from a_{1u} to a_{2u} when the axial ligand is changed.[7,8] There are only a few exceptions of this type and the above generalisation holds good for a large number of metalloporphyrins. Another important difference between the OEP and TPP systems is that the former undergo extensive aggregation in solutions while the latter do not. With this background we shall discuss the results of our low temperature esr studies on the radical cation of vanadyl octaethyl porphyrin.

At room temperature, vanadyl octaethyl porphyrin, [VO(OEP)] is oxidised to the radical cation in solution.[9,10] The visible electronic spectrum of the species and the redox potential data indicate that oxidation occurs at the ligand pi orbital. The esr spectrum recorded at room temperature indicates that the species is monomeric with S = 1 where one electron is in the vanadium d orbital and the other is in the pi molecular orbital of the porphyrin.[10] Analysis of the linewidth effects using relaxation matrix theory and subsequent simulation of the esr spectrum have led to the conclusion that the major source of the relaxation effects arises from the modulation of the zero field splitting interaction by molecular tumbling motions. From the computer-simulated spectrum, a distance of 4.0Å between the two electrons was obtained. Hence it was considered that a direct measurement of the zero field splitting from the esr spectrum of a frozen solution would be a good check on the results obtained from the linewidth analysis. Hence we had studied the esr spectrum of the radical cation of VO(OEP) at liquid nitrogen temperature and the analysis of this spectrum is presented in this chapter.

III.2 EXPERIMENTAL DETAILS

Radical cation of VO(OEP) was generated by dissolving solid VO(OEP) in trifluoroacetic acid (10^{-3}M) or by adding a few drops of perchloric acid to a solution of VO(OEP) in dichloromethane. ESR spectra of the sample was recorded at liquid nitrogen temperature using a cold finger dewar. Measurements were made using a Varian E-109 'epr spectrometer operating at X band, with 100KHz field modulation. Computer simulations were done on a DEC 10 computer using computer programs described elsewhere.

III.3 RESULTS AND DISCUSSION

The esr spectrum of the radical cation of VO(OEP) at liquid nitrogen temperature is presented in figure III.2. This spectrum appears to arise from a triplet state. But the number of lines are too large to be accounted for by the hyperfine coupling from a single vanadium nucleus. A dimerisation of the VO(OEP) radical cation at low temperatures is not unexpected since the radical cations of Zn, Mg and Cu complexes of OEP are known to dimerise.[11,12] In the case of the radical cations of Zn(OEP) and Mg(OEP) the dimer is diamagnetic since the pi electrons pair up. In the case of the radical cation of Cu(OEP) the dimer has one unpaired electron each on the Cu atomic orbital which are ferromagnetically coupled.[13] Magnetic susceptibility measurements have indicated a value of $J = -2cm^{-1}$ for the exchange integral. We have considered a similar situation for the dimer of the radical cation of vanadyl porphyrin.

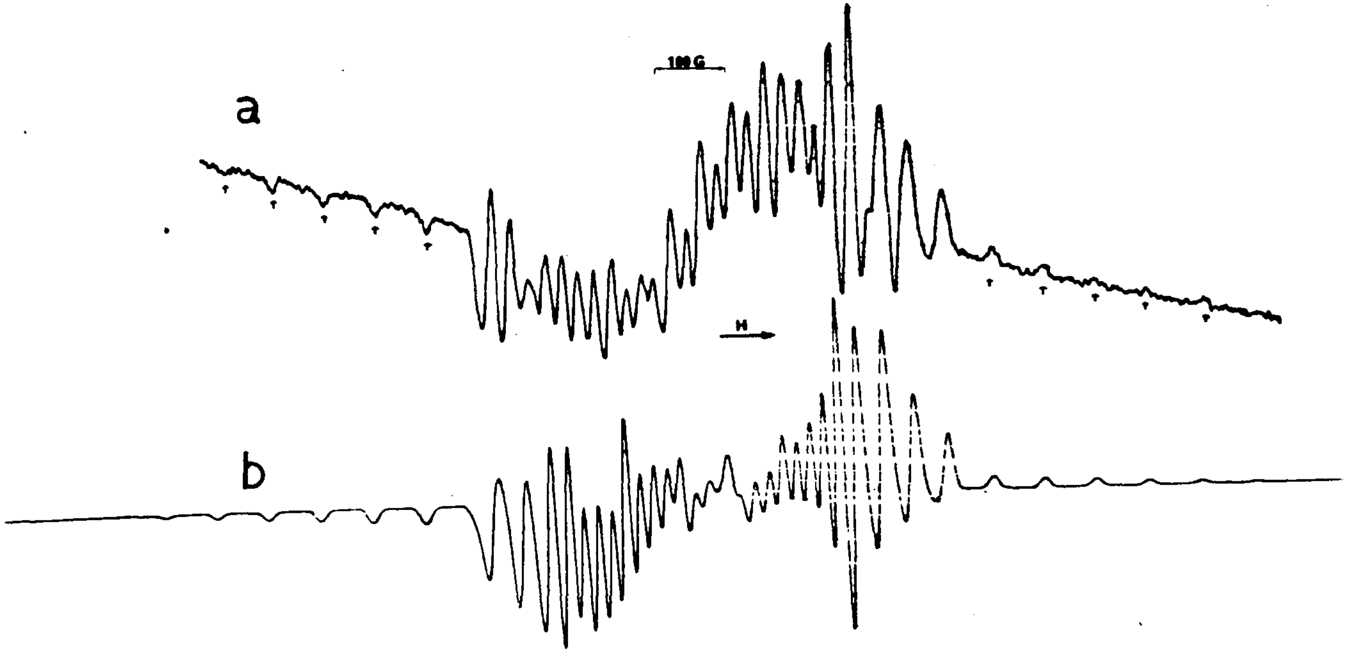


Fig. III. 2(a) ESR spectrum of the radical cation of Vanadyl Octaethylporphyrin in TFA at liquid nitrogen temperature

(b) Computer-simulated spectrum

III.3.1 THEORETICAL BACKGROUND

Diamagnetic dimers are formed from the radical cations of Zn(OEP), Mg(OEP) when these systems are cooled to about -60°C. The equilibrium constants for the dimerisation processes have been obtained for some of these systems.[11,12] From these studies it is apparent that the exchange interaction between the two pi electrons in the dimer is greater than 200 cm^{-1} ($-J > 200\ \mathrm{cm}^{-1}$). This accounts for the strong antiferromagnetic coupling between the two pi electrons in the dimer. Magnetic susceptibility measurements for the dimer of the radical cation of Cu(OEP) leads to a value of $-J = 2\ \mathrm{cm}^{-1}$, between the two d electrons on the Cu atoms.[13] Since the dimer of the radical cation of vanadyl porphyrin is also expected to be similar to that of Cu(OEP) we can make a reasonable assumption that the J values for both these dimers are of equal magnitudes. Thus the vanadyl dimer is treated as S = 1 system with one unpaired electron each on the V ~~Cu~~ orbital. Since both the monomeric units are identical in the dimer this problem can be treated as that of a similar ion dimer with axial symmetry. The customary assumption of parallel d,g and hyperfine tensors is made which is justified by the good agreement of the computer simulated spectrum with the experimental esr spectrum.

The spin Hamiltonian for the dimer can be written as follows:

$$H = H_1 + H_2 + H_{int}$$

where H_1 and H_2 are individual spin hamiltonians for the monomeric species ($S = 1/2$ systems) and H_{int} is the dipolar interaction between the two unpaired electrons. Since J_{dd} is small, the electron electron interaction is considered as purely dipolar. The terms H_1 and H_2 are of the type :

$$H_i = \hat{S}_i \cdot \underset{\sim}{g}_i \cdot \hat{B} + \hat{S}_i \cdot \underset{\sim}{A}_i \cdot \hat{I}_i \quad : \; i = 1,2$$

where the g and A tensors are identical for both the units. The detailed treatment of this problem is well-documented.[14] Using the computer program mentioned in reference 13, we have simulated the esr spectrum of the radical cation of vanadyl porphyrin varying the parameters, g,A and the distance between the two vanadium atoms. The best agreement was obtained for the following values of spin Hamiltonian parameters. $g_{\parallel} = 1.965$, $g_{\perp} = 1.964$, $A_{\parallel}$ (^{51}V) = 2712.4 Mrads^{-1}, $A_{\perp}$ (^{51}V) = 715.78 Mrads^{-1} distance between the metal ions = 4.7Å.

III.3.2 DISCUSSION

The experimental spectrum and the computer-simulated spectrum are presented in figures III.2. The distance between the metal ions in the vanadyl dimer is slightly larger than that obtained for the Cu dimer. This is perhaps due to the slight out-of-planarity of the vanadium atom in vanadyl porphyrins. The ground state of the dimer of VO(OEP) radical cation is governed by three exchange integrals, namely, J_{dd}, $J_{\pi\pi}$ $J_{d\pi}$ $J_{\pi\pi}$, the exchange interaction between the two pi electrons is of the order of $-200\ cm^{-1}$. The exchange interaction between the two d electrons on the vanadium nuclei can be taken to be the same or slightly less than that measured for the Cu analog. ($-2\ cm^{-1}$). The exchange interaction between the d electron and the pi electron is certainly much less than $J_{\pi\pi}$. The analysis of the esr spectrum of the monomeric radical cation of VO(OEP) indicates that the d-pi exchange is larger than microwave frequency. Thus this parameter is also expected to be in the same range as J_{dd}.

III.4 CONCLUSION

It is not possible to observe the esr spectrum of the monomeric radical cation of vanadium OEP at low temperatures. This system dimerises on cooling and the dimeric species is very similar to that obtained for the radical cation of Cu(OEP). The distance between the two vanadium atoms in the dimer has been obtained as 4.7Å by means of computer simulation. The slightly larger distance obtained for the vanadyl dimer than that for the Cu dimer is consistent with the fact that vanadium atom is slightly out-of-plane of the porphyrin ring.

REFERENCES

1. K.M. Smith, in Porphyrins and Metalloporphyrins, Edited by K.M. Smith (Elsevier, Amsterdam, 1975), p. 3
2. J. Fajer, D.C. Borg, A. Forman, D. Dolphin and R.H. Felton, J. Am. Chem. Soc., 92, 3451 (1970).
3. J.-H. Fuhrhop and D. Mauzerall, J. Am. Chem. Soc., 90, 3875 (1968).
4. R.H. Felton, D. Dolphin, D.C. Borg and J. Fajer, J. Am. Chem. Soc., 91, 196 (1969).
5. R.H. Felton, in Porphyrins, Edited by D. Dolphin (Acad. Press, NY, 1978), Vol. V, p. 81.
6. M. Gouterman, in Porphyrins, Edited by D. Dolphin, (Acad. Press, NY, 1978), Vol. III, Chap. 1.
7. D. Dolphin, Z. Muljiani, K. Rousseau, D.C. Borg, J. Fajer and R.H. Felton, Ann. NY. Acad. Sci., 206, 177 (1973).
8. D. Dolphin, A. Forman, D.C. Borg, J. Fajer and R.H. Felton, Proc. Natl. Acad. Sci., U.S.A. 68, 614 (1971).
9. J. Subramanian, in Porphyrins and Metalloporphyrins, Edited by K.M. Smith (Elsevier, Amsterdam, 1975), p. 555
10. G.R. Luckhurst, M. Setaka and J. Subramanian, Mol. Phys., 32, 1299 (1976).
11. J. -H. Fuhrhop, S. Besecke, J. Subramanian, C. Mengerson and D. Riesner, J. Am. Chem. Soc., 97, 7141 (1975).

12. J. -H. Fuhrhop, P.K.W. Wasser, D. Riesner and D. Manzerall, J. Am. Chem. Soc., 94, 7996 (1972).

13. C. Mengerson, J. Subramanian and J. -H. Fuhrhop, Mol. Phys., 32, 893 (1976).

14. T.D. Smith and J.R. Pilbrow, Coord. Chem. Rev., 13, 173 (1974).

CHAPTER IV

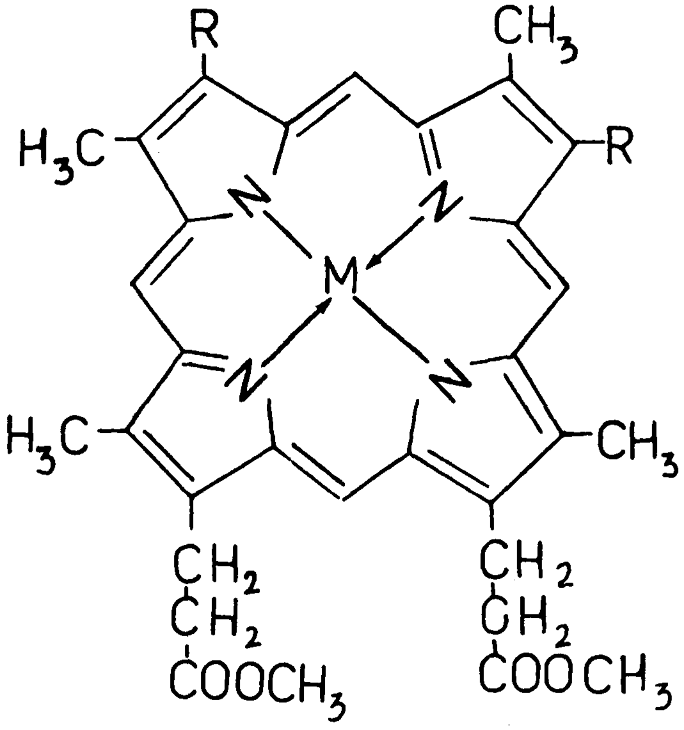
CYCLIC VOLTAMMETRIC STUDIES ON SOME METAL COMPLEXES OF PROTO - AND MESO PORPHYRINS

CHAPTER IV

CYCLIC VOLTAMMETRIC STUDIES ON SOME METAL COMPLEXES OF PROTO- AND MESO PORPHYRINS

IV.1 INTRODUCTION

Electrochemical techniques have been used extensively in porphyrin chemistry.[1-3] Cyclic voltammetry and related techniques have been used to obtain the redox potentials involving various electrode processes like one- and two-electron oxidations and reductions. Controlled potential electrolysis has been used to generate the desired species and study it by various spectroscopic techniques. Thus electrochemistry can be combined with optical spectral studies or by esr and nmr techniques. Techniques have been developed to generate the active species by controlled potential reduction or oxidation in a thin optical cell or in an esr tube.[3] In this manner the active species could be identified spectroscopically and wherever possible such systems have been compared with the products obtained by chemical oxidation or reduction. In some favourable cases, large scale syntheses have been achieved by electrochemical technique. The redox potentials obtained for metalloporphyrins have been used very successfully in rationalising a large volume of chemical or photochemical reactions undergone by



M= VO, Cu, Ni, Zn

R= $-CH{=}CH_2$ for PPIX DME

$-CH-CH_3$ for MPIX DME

CH_3-CH OH for HPIX DME

Fig. IV.1. Structures of metalloporphyrins (Proto-, Meso-, and Hematoporphyrin IX dimethylester) porphyrins. Since both metal-centered oxidation-reductions and ligand centered oxidation-reductions are possible in metalloporphyrins, the electrochemical data on these systems offer considerable challenges to the chemist. In the present work, apart from obtaining the redox potential data for the metal complexes of proto and meso porphyrins, we have obtained evidences for the aggregation of the one-electron oxidation products in some cases.

A brief general summary of the electrochemical behaviour of metalloporphyrins will be presented here for the sake of continuity and also for appreciating the results reported in the present work.

Normally, a metalloporphyrin may possess D_{4h} or C_{4h} symmetry. In a metalloporphyrin the HOMO or the highest occupied molecular orbital (a_{1u}, a_{2u}) is nearly degenerate and the LUMO or the lowest unoccupied molecular orbital (e_g) is truly degenerate. In an oxidation process, electrons are removed from the HOMO levels. This process may occur in the porphyrin ligand system or in the metal system or in both the systems. The central metal atom such as Zn, Cu etc are quite inactive to the redox process. In such cases oxidation or reduction occur in the porphyrin ligand, where as metals such as Fe, Co, Mn etc are quite electro-active and the redox process may

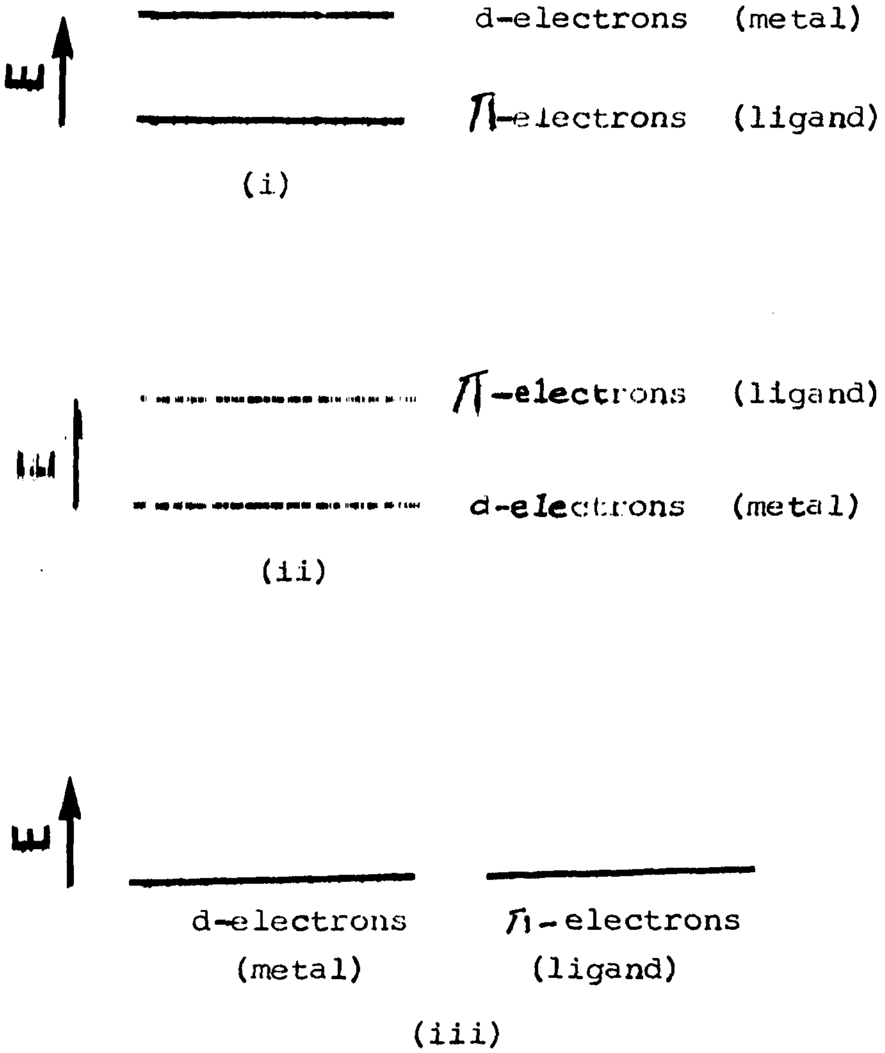


Fig. IV. 2. HOMO representations for metalloporphyrin occur both in the ligand as well as in the metal center. This can be understood by considering the occupied energy levels of π-electrons and d electrons of the metal atom (See figure IV.2). Case (i) contains electro active metal center, therefore, the redox process will occur in the metal. Case (ii) contains non-electroactive metal center, hence the redox process will involve only the ligand system. The situation becomes more complex in the case (iii) where both the ligand and metal are electro active.

The ligand oxidation and reduction processes may be represented as follows;[1] using a metalloporphyrin with bivalent metal

$$M(II)P \xrightarrow[E_{\frac{1}{2}}^{OX}(1)]{-e} M(II)P^{+\cdot} \xrightarrow[E_{\frac{1}{2}}^{OX}(2)]{-e} M(II)P^{++}$$

$$M(II)P \xrightarrow[E_{\frac{1}{2}}^{red}(1)]{+e} M(II)P^{-\cdot} \xrightarrow[E_{\frac{1}{2}}^{red}(2)]{e} M(II)P^{--}$$

$$\Delta_{OX} = E_{\frac{1}{2}}^{OX}(2) - E_{\frac{1}{2}}^{OX}(1) \ ;$$

$$\Delta_{red} = E_{\frac{1}{2}}^{red}(1) - E_{\frac{1}{2}}^{red}(2) \ ;$$

when oxidation-reduction is taking place in the ring, a constancy of Δ_{OX} and Δ_{red} had been observed, $\Delta_{OX} \simeq 0.3eV$, $\Delta_{red} \simeq 0.5eV$. Also the quantity

$\delta = E_{\frac{1}{2}}^{(OX)}(1) - E_{\frac{1}{2}}^{red}(1)$ is constant for a variety of metalloporphyrin (2.0 ± 0.15V) though the absolute magnitude of the potentials vary widely. Independence of Δ_{OX}, Δ_{red} and δ of the metal is explained in terms of negligible mixing of the metal orbitals and the porphyrin π orbitals. The metal ion exerts an inductive Coulombic effect on the ligand π orbitals through σ framework. This influence affects only the absolute values of π energy levels but not the relative values i.e. the difference in the energies between HOMO and LUMO. Using Pariser-Parr Pople π electron energies, the values Δ_{OX}, Δ_{red} and δ have been estimated which agree reasonably well with the corresponding experimental data. When metal-centered oxidation-reduction takes place, this correlation fails. By studying the optical or esr spectra of the oxidised or reduced species one can ascertain whether metal centered redox reaction has taken place or not. Correlation of the redox potentials of metalloporphyrin with metal charge densities, gas phase ionisation potentials and λ_{max} of the metalloporphyrin Q band, have been amde. Such correlation support the inductive effect model. A redox tuning of the porphyrin is possible by changing the metal or the substituents in the ligand.

In the present work we have studied the cyclic voltammetry of Zn, Cu, and VO complexes of proto and meso porphyrins.[5] The redox data obtained from CV studies have not been available at the time the study was undertaken. Our aim in undertaking these studies was to find out the oxidation potentials so that the radical cation of some of the systems could be generated electrochemically. But we have observed that due to aggregation effects, a coating of the oxidised species is formed on the electrode surface which prevents further electrode reaction. A similar observation has been made on these system by Macor and Spiro.[6]

IV.2 BASIC PRINCIPLE OF CYCLIC VOLTAMMETRY[7-11]

Cyclic voltammetry is an electrochemical technique in which current voltage curves were obtained by using a stationary electrode in unstirred solution. The configuration in a cyclic voltammetric cell consists of a working electrode (a platinum disc electrode), an auxilliary electrode (a platinum wire) and a reference electrode (a SCE); The potential at the working electrode is varied with respect to the reference electrode using a triangular wave. The normal sweep rate used in about 100mV/sec. The initial and the final potentials are known as the switching potentials. For any single-step reversible electron transfer process, two peaks are obtained. The average value of the peaks potential corresponding to the half-wave potentials of the electron-transfer process. As an example let us consider the one-electron oxidation of a molecule R

$$R \underset{}{\overset{-e}{\rightleftharpoons}} R^+$$

During the triangular sweep a peak is obtained at a potential E_a corresponding to the process $R \longrightarrow R^+$. In the reverse sweep the species R^+ is reduced back to R thus giving rise to another peak at a potential E_c. The half wave potential at the above reversible reaction is obtained as $E_a + E_c/_2$. The theory of cyclic voltammetry is well documented and only the essential expressions that are used are presented here.[10]

For a reversible process the peak potential can be related to the polarographic half-wave potential, $E_{\frac{1}{2}}$, by the expression

$$E_p = E_{\frac{1}{2}} - 1.11\ (^{RT}/_{nF})$$

$$= E_{\frac{1}{2}} - (0.0285/nF) \qquad \ldots. \qquad (IV.2.1)$$

where n = number of electrons involved in the electrode reaction, T = 298K

and peak to peak difference is

$$E_a - E_c = 0.059/_n\ V \qquad \ldots. \qquad (IV.2.2)$$

at 25 °C

For an irreversible process,

$$E_p - E_{\frac{1}{2}} = -1.857\ (0.026/\alpha n \qquad \text{....} \qquad (IV.2.3)$$

at 25°C

where α = transfer coefficient (its value is normally between 0.3 and 0.7).

or,

$$E_p - E_{\frac{1}{2}} = \pm 0.048/\alpha n_a \text{ V at } 25°C \qquad \text{....} \qquad (IV.2.4)$$

The current for a reversible process is given by Randles-Sevcik equation which is expressed as[10]

$$I_p = 2.69 \times 10^5 n^{\frac{3}{2}} A C D^{\frac{1}{2}} \chi^{\frac{1}{2}} \qquad \text{....} \qquad (IV.2.5)$$

at 25°C.

where χ is the scan rate in volts per second.

and the ratio $I_c/I_a = 1$ .... (IV.2.6)

For an irreversible process, at 25°C

$$I_p = 3.01 \times 10^5 n\ (\alpha n_a)^{\frac{1}{2}} A C D^{\frac{1}{2}} \chi^{\frac{1}{2}} \qquad \text{....} \qquad (IV.2.7)$$

IV.3 EXPERIMENTAL

The preparation of metalloporphyrin, purification of supporting electrolyte and solvents are discussed in detail in chapter II.

IV.4 RESULTS AND DISCUSSION

IV.4.1 Cyclic voltammetry of zinc protoporphyrin

The cyclic voltammetry of zinc protoporphyrin has been investigated with a view to understand the aggregation processes taking place in this system. There is a considerable difference in the appearance of the cyclic voltammogram of Zn protoporphyrin and zinc tetraphenyl porphyrin (Figures IV.3 and IV.4). The first oxidation peak on the anodic side is split and the second oxidation peaks are not observable. When this investigation was undertaken, the only oxidation potential data available was that of polarographic measurements made by Stanienda and Biebl.[12] These authors have reported only the first oxidation potential and no mention has been made on the aggregation tendencies. More recent work by Macor and Spiro[6] contains cyclic voltammetric studies on Zn, Ni, Co, Fe, Cr and Mn protoporphyrin dimethylester.[6] These authors report considerable film formation at the platinum electrode surface. They have observed that for ligand centered oxidations, the intensities of cyclic voltammetric peaks diminish during continuous runs and almost disappear. This occurs since the thick film on the electrode surface prevents further electrochemical oxidation of the species in solution. These authors have not presented any detailed analysis of the cyclic voltammograms but a study of the film material on the electrode

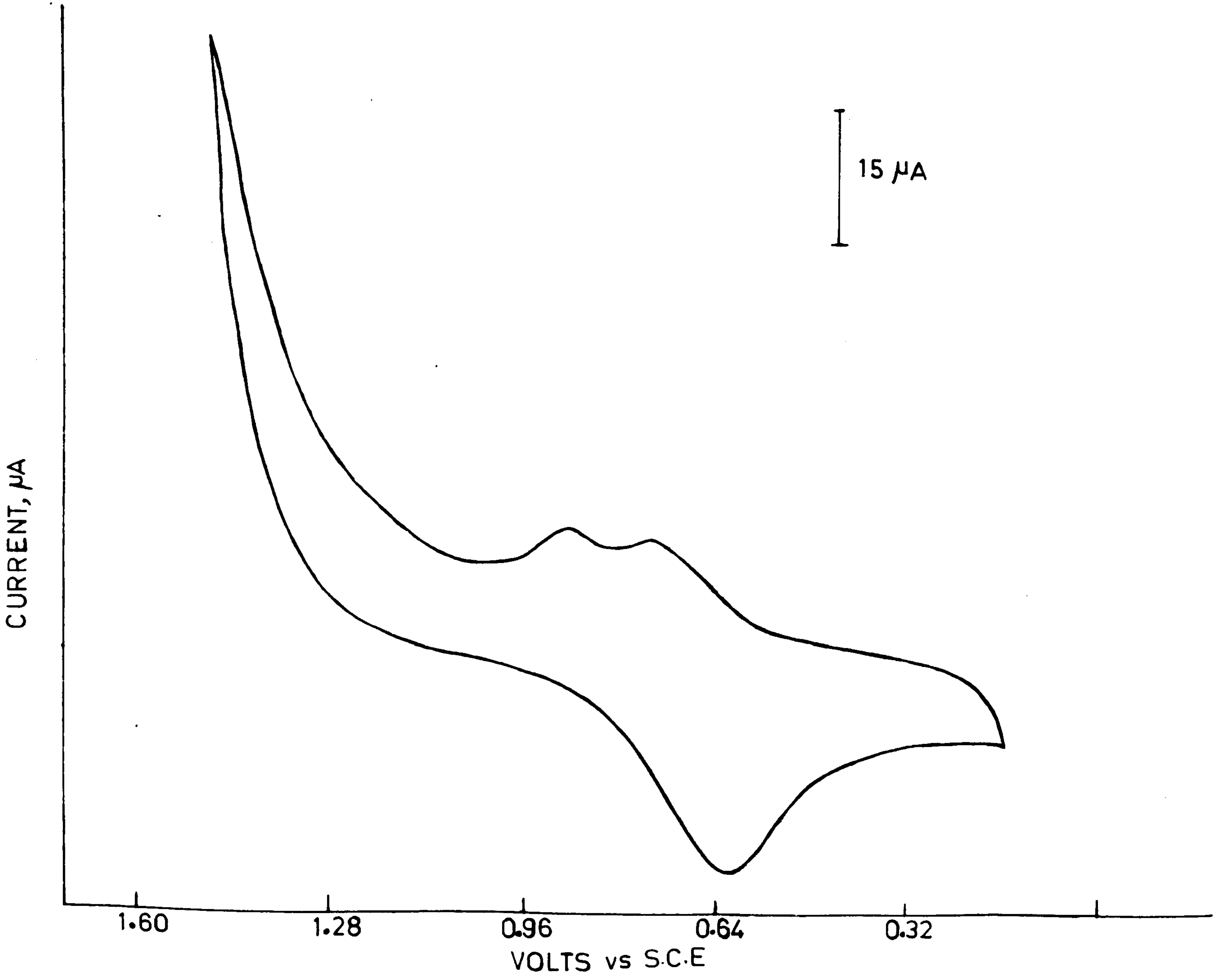


Fig.IV.3. Cyclic Voltammogram of Zinc protoporphyrin IX dimethylesters

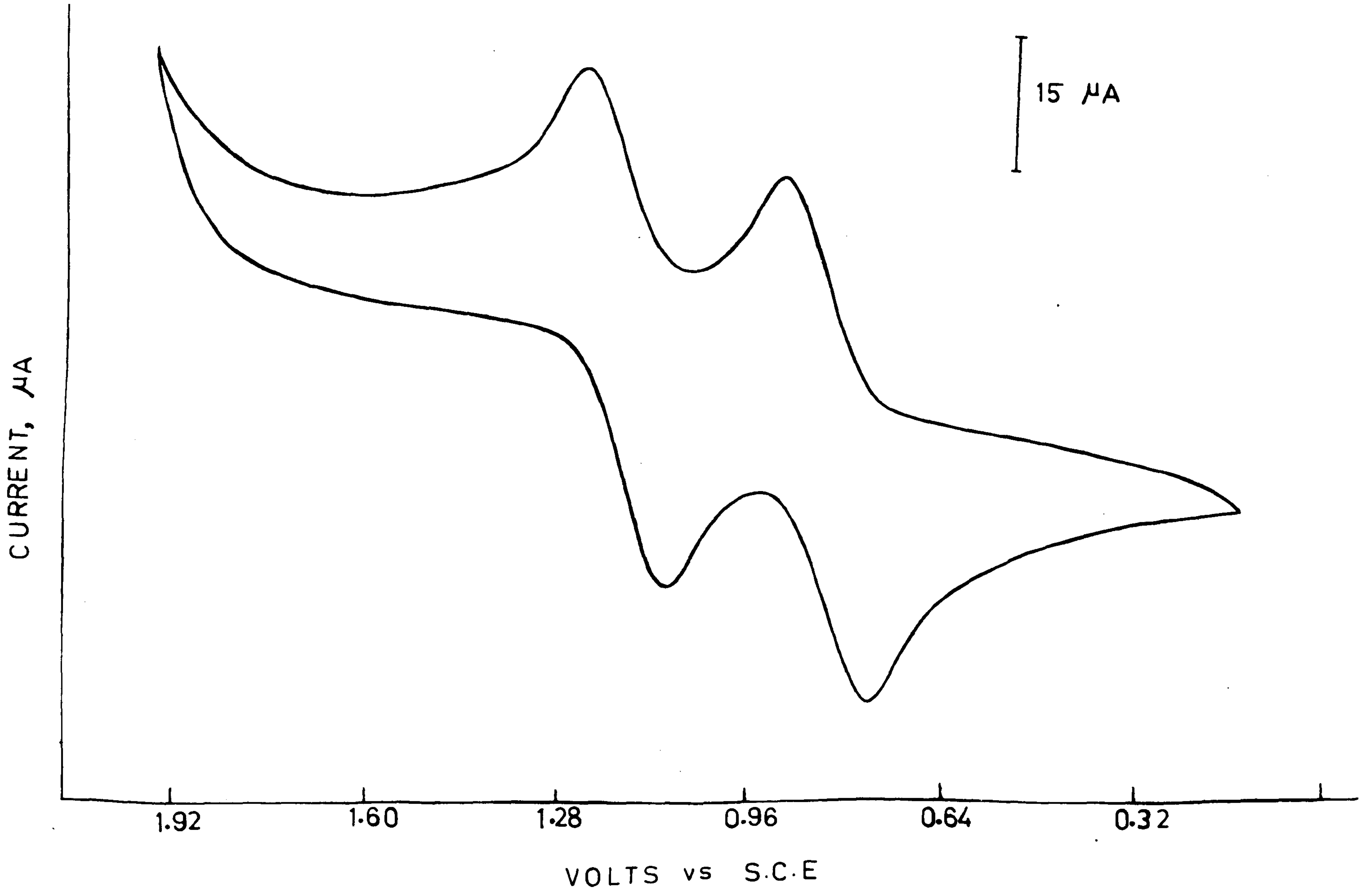
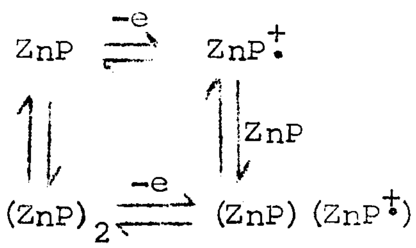


Fig.IV.4. Cyclic Voltammogram of ZnTPP

by visible absorption and laser Raman spectroscopy is presented. They had arrived at the conclusion that when the ligand oxidation is taking place, the vinyl groups in the protoporphyrin are activated and lead to polymerisation reactions which result in the formation of the film. These authors have also reported only one oxidation potential for zinc protoporphyrin (0.75 V vs SCE).

In the present investigation, we have also observed film formation at the electrode surface and the region where the first oxidation is expected, two peaks are observed. No peaks are observed in the region for second oxidation process. The two peaks observed in the anodic sweep are separated by 153 millivolts. In the reverse cathodic process only a single broad peak is observed. If we consider that aggregation is restricted to dimers in solution, (though in the solid state polymerisation is possible) we can assign the two peaks to the first oxidation potentials for the monomeric species and dimeric species respectively. We tentatively assign the lower of the two potentials to the first oxidation potentials of the dimer, since the removal of an electron from a pi system delocalised in the dimer is expected to be easier than that from a monomer. Thus we can envisage the following equilibrium in solution.



A recent work on the cyclic voltammetric study on dimeric crown ether porphyrin has clearly pointed to the different oxidation potentials for monomeric and dimeric species.[13] A difference of 150 to 200 millivolts between the oxidation potentials of the monomer and dimer. Though Macor and Spiro have reported negligible film formation for free base protoporphyrin, we have noticed a splitting of the first oxidation peak which is much less pronounced than that observed for the zinc and other metal complexes.

IV.4.2 Cyclic voltammetry of Copper and Vanadyl protoporphyrins

The cyclic voltammograms of Cu and vanadyl protoporphyrins are presented in Figures IV.5 and IV.6). The half-wave potential data obtained from the cyclic voltammetric systems are presented in table IV.1 . The splitting of each oxidation peak is not well-resolved in these systems but considerable broadening of the peaks and film formation at the electrode surface have been observed. An estimate of the first oxidation potentials of the monomer and dimer have been made though the error involved in

TABLE IV.1

Cyclic voltammetric data for proto- and Meso porphyrin systems at room temperature

Solvent : CH_2cl_2

Concentration : 10^{-3}M

Supporting electrolyte : TBAB

Sweep rate : 100 m v/s

System	Reference Electrode	Oxidation potential in volts				$E_{1/2}$ in volts	Reversibility
		$E_{1/2}$(I)	$E_{1/2}$(II)	$E_{1/2}$(III)	$E_{1/2}$(IV)		
VOPPIX DME	SCE	0.694	1.173	1.591[E_p^a(III)]		0.479	dimerisation
ZnPPIxDME	"	0.565	0.785[E_p^a(II)]				"
CuPPIxDME	"	0.543	1.398[E_p^a(II)]				"
VOMeso	"	0.94	1.22			0.28	Reversible
VOMeso (higher Concentration)	Ag/Agcl	0.636	0.974	1.282	1.449		dimersation
ZnTPP	SCE	0.785	1.093			0.082	Reversible

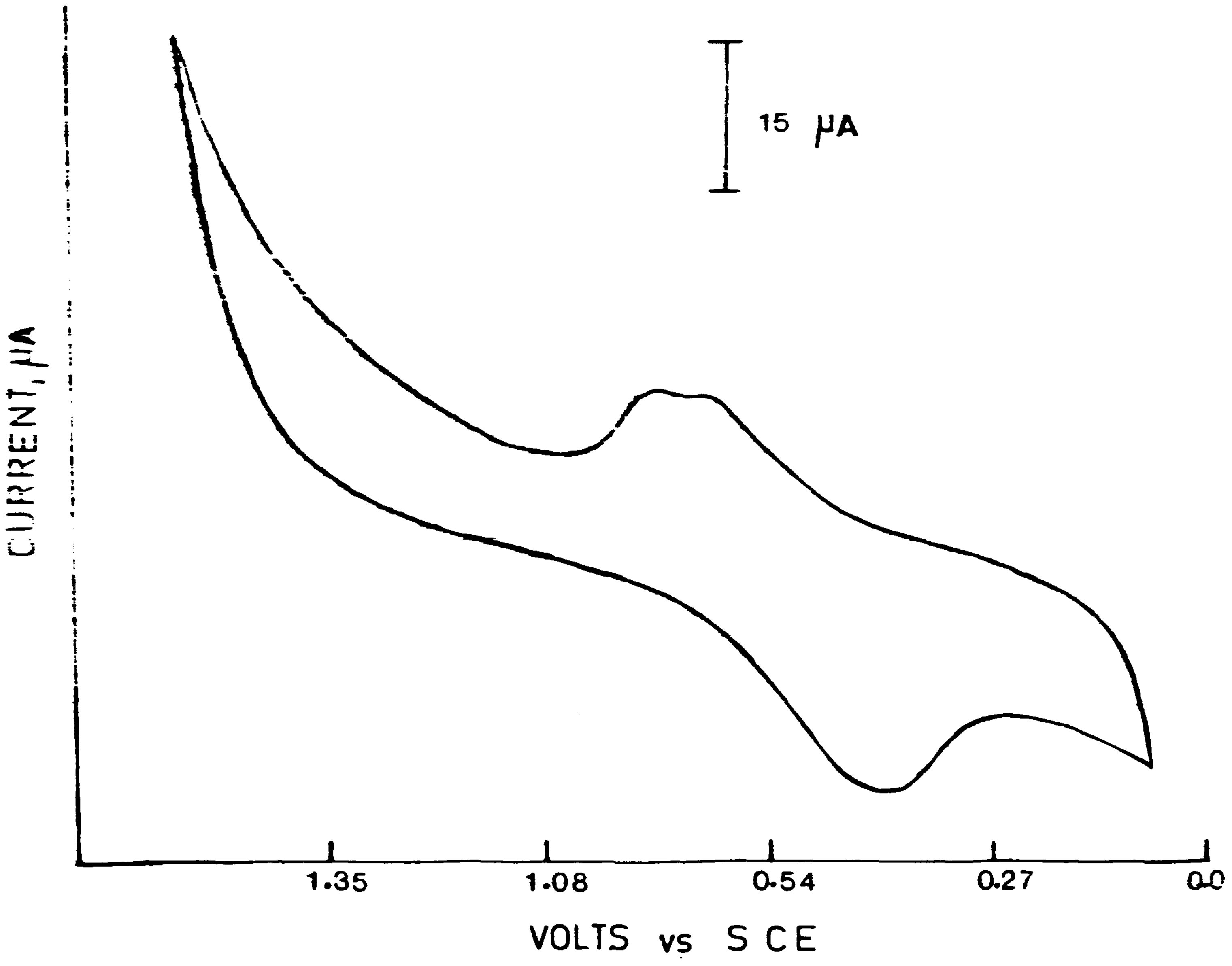


Fig.IV.5. Cyclic Voltammogram of Copper protoporphyrin IX dimethylester

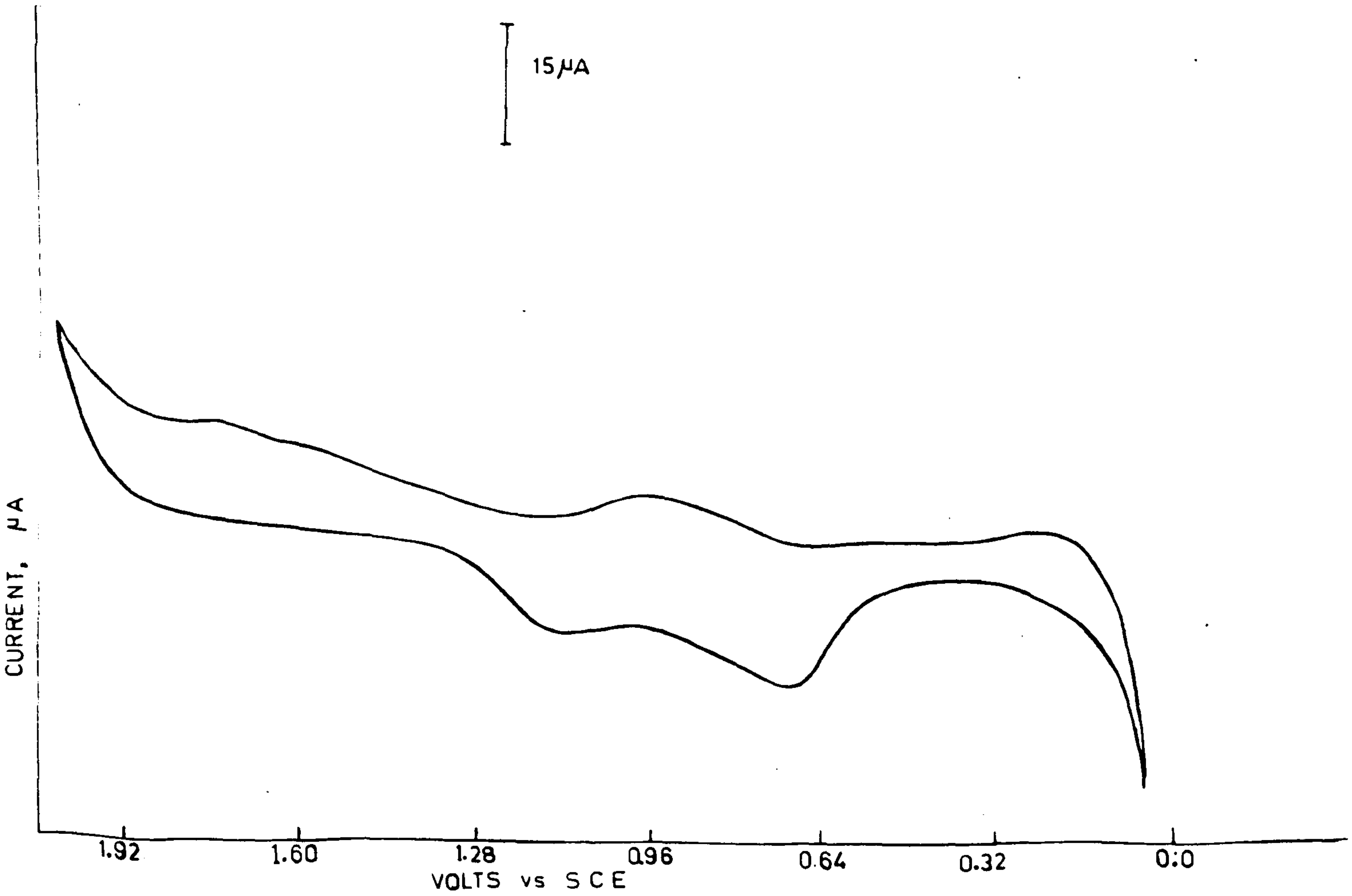


Fig.IV.6. Cyclic Voltammogram of Vanadyl protoporphyrin IX dimethylester these estimates may be higher than those for zinc protoporphyrin. In all the three cases, namely zinc, copper and vanadyl protoporphyrins the area under the split peaks are approximately equal indicating nearly equal concentrations of monomer and dimer. Further evidence for the existence of dimeric species in solution is presented in the next chapter where the esr spectra of oxidation products of vanadyl proto and meso porphyrins are discussed.

IV.4.3 Voltammetry of vanadyl meso porphyrin

VO meso porphyrin gives clear information on the existence of monomer dimer equilibrium when the cyclic voltammograms are recorded at different concentration ranges. On the lower side of 1 millimolar concentration, the first and second oxidation peaks and the reverse cathodic peaks are clearly seen. The cyclic voltammogram is very similar to that of VOTPP though the peaks are slightly broader than those in the case of the latter. Thus we can assign this cyclic voltammogram as arising out of predominantly monomeric species. At concentration in the range of 0.005 to 0.01M different types of cyclic voltammograms are observed. (figures IV.7 and IV.8(a) and IV.8(b)). In figure IV.8, the first and second oxidation peaks for the monomer and the aggregated species in solution are clearly seen. The first and second oxidation potentials for

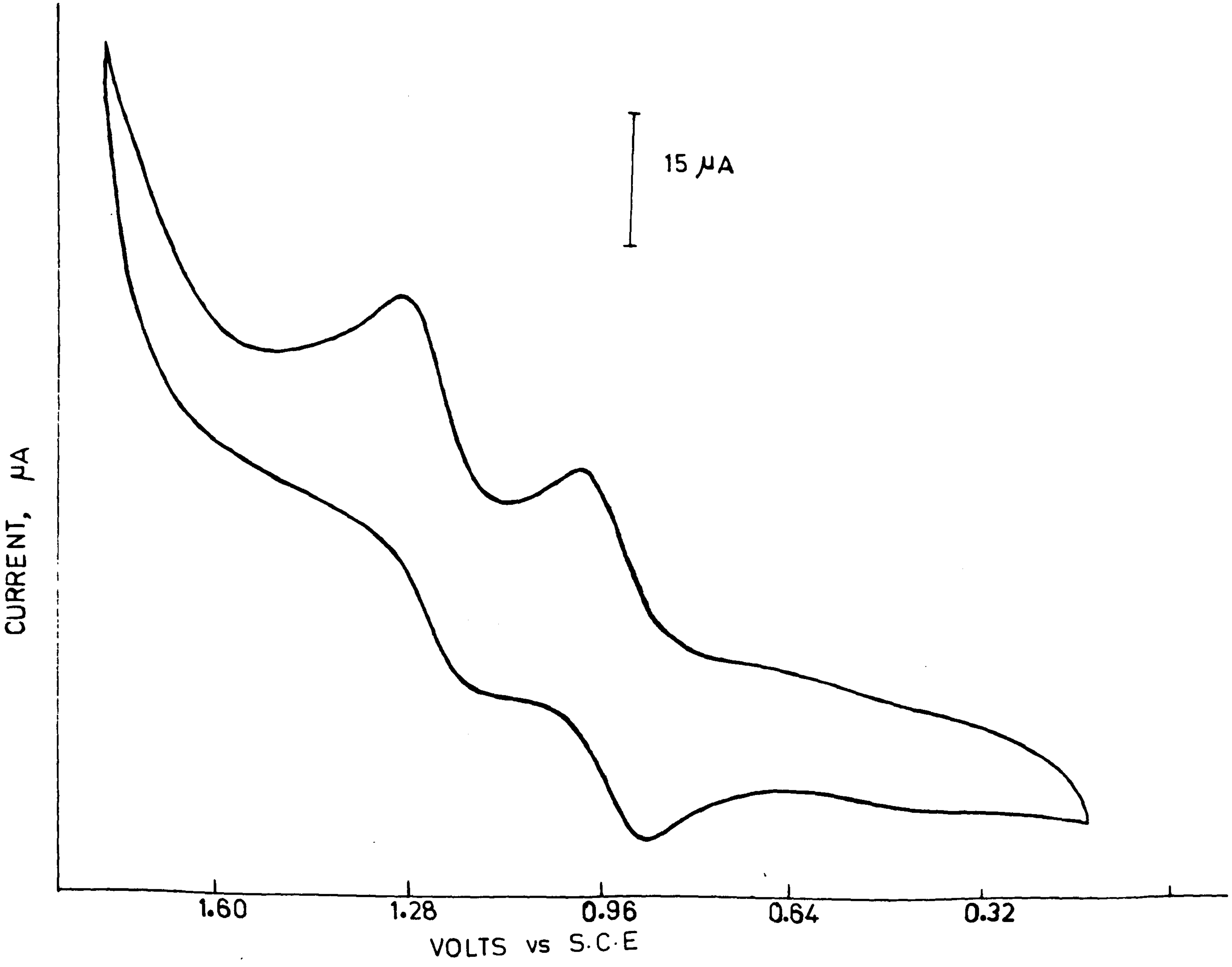


Fig.IV.7. Cyclic Voltammogram of Vanadyl mesoporphyrin IX dimethylester at concentration around 10^{-3}M

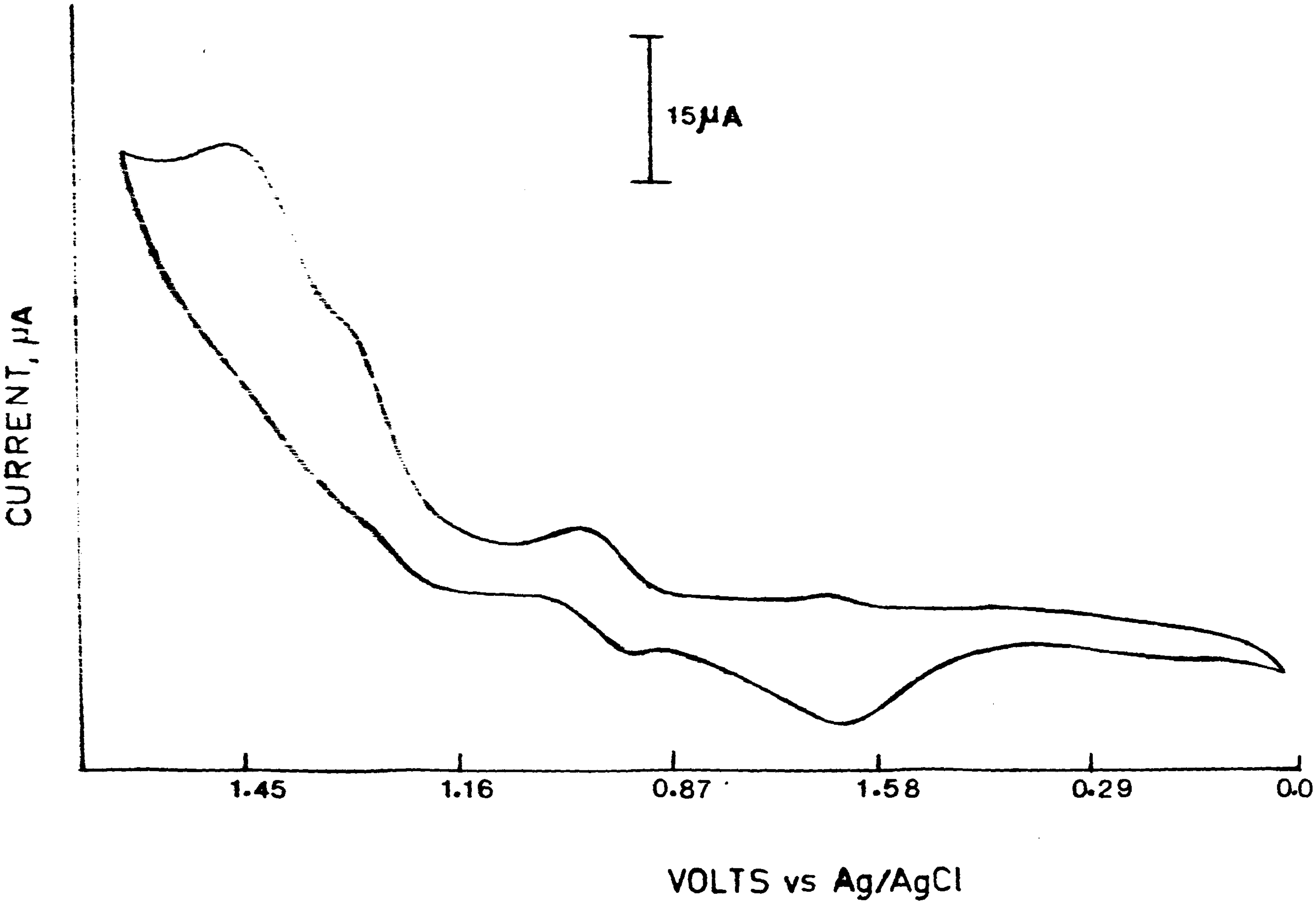


Fig. IV.8(a). Cyclic Voltammogram of Vanadyl mesoporphyrin IX dimethylester of concentration around 10^{-2}M (Ag/AgCl as reference electrode)

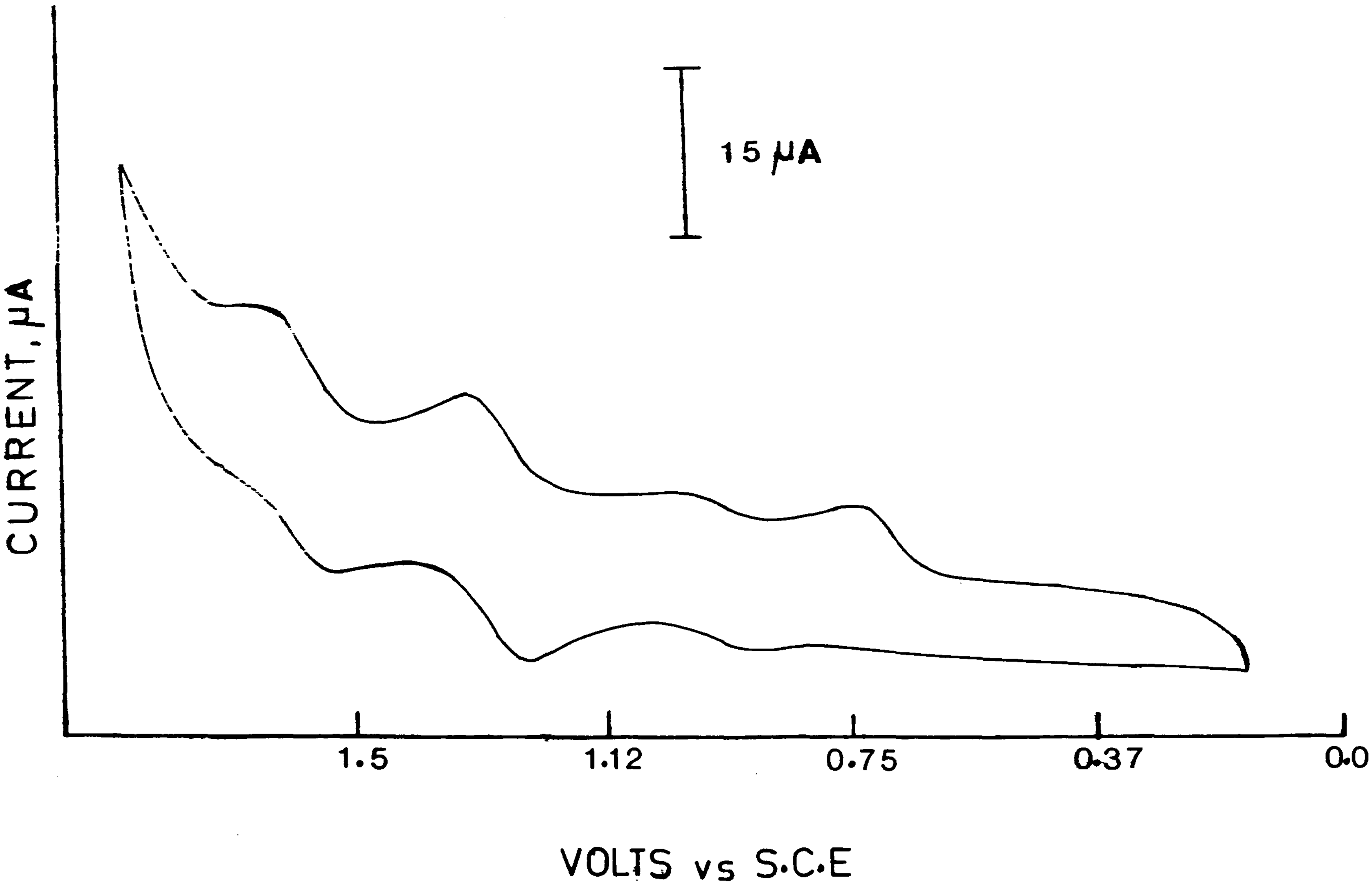


Fig. IV.8(b). Cyclic Voltammogram of Vanadyl mesoporphyrin IX dimethyl ester of concentration around 10^{-2}M (Volts vs S.C.E) the monomer and the aggregated species (assumed as dimer) are presented in table IV.1.

IV.4.4 Cyclic voltammetry of iron hematoporphyrin

Metallohematoporphyrins which are closely related to proto and meso porphyrins also undergo extensive aggregation in solution. The cyclic voltammogram of iron(III) hematoporphyrin presented in figure IV.9, supports this view. No quantitative identification of the peaks for the monomer and dimer had been attempted in this case.

IV.5 CONCLUSION

The cyclic voltammetric studies on Zn, Cu and vanadyl protoporphyrins vanadyl mesoporphyrin and iron hematoporphyrin have indicated clearly that aggregated species exist in solutions in equilibrium with the monomeric species. Wherever possible, the first and second oxidation potentials for the monomer and the aggregated species have been obtained from the cyclic voltammograms.

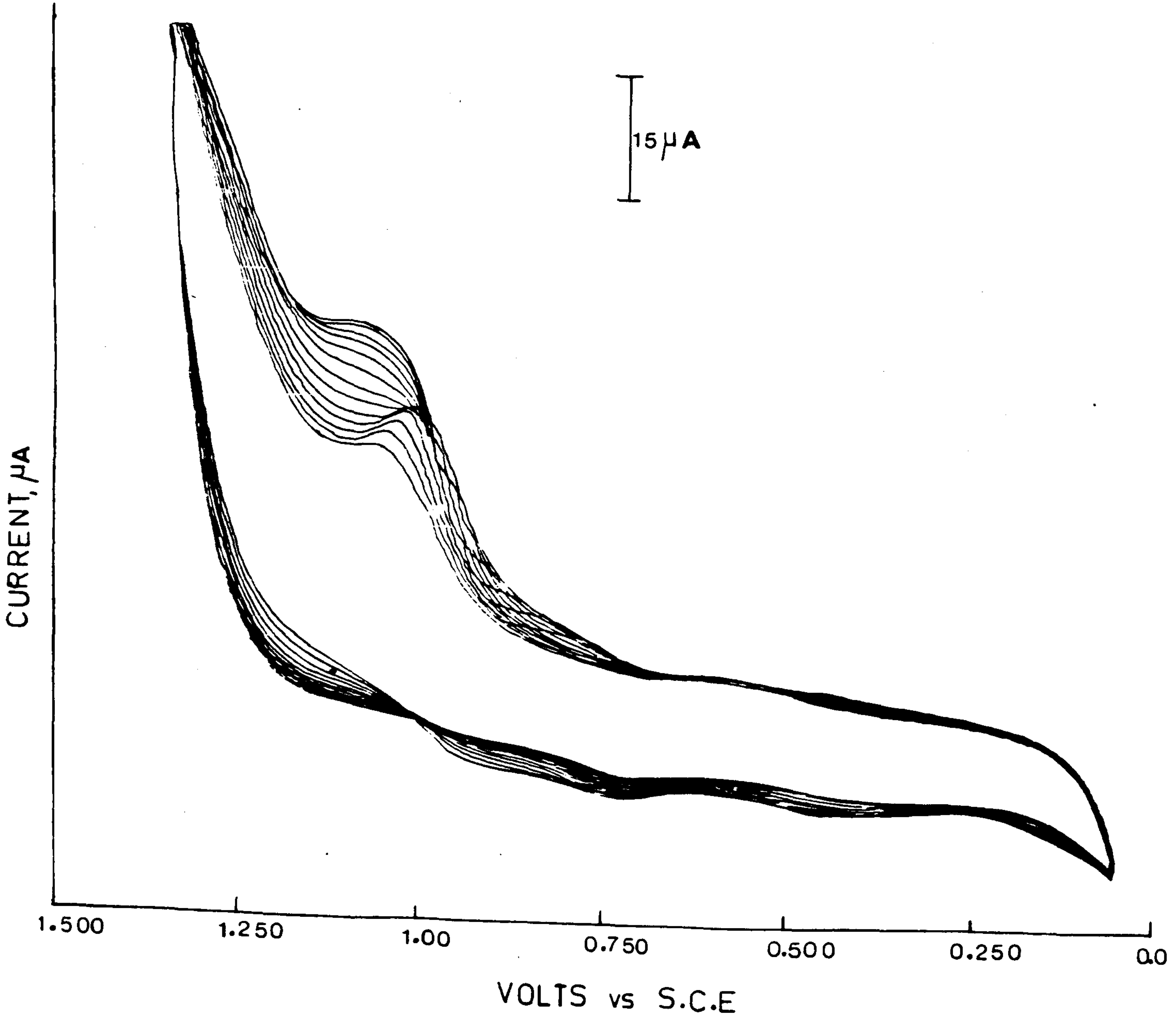


Fig. IV.9. Cyclic Voltammogram of Iron(III) hematoporphyrin IX dimethylester

REFERENCES

1. R.H. Felton, in The Porphyrins, Edited by Dolphin (Academic Press, New York, 1979), Vol. V., p. 53.
2. D.G. Davis, in The Porphyrins, Edited by Dolphin (Academic Press, New York, 1979), Vol.V, p 127.
3. Electrochemical and Spectrochemical Studies of Biological Redox Components. Advances in Chemistry Series, Edited by K.M. Kadish (American Chemical Society, Washington D.C., 1982), 201.
4. J.-H. Fuhrhop, K.M. Kadish and D.G. Davis, J. Am. Chem. Soc., 95, 5140 (1973).
5. A. Lemtur, B. Chakraborty, T.K. Dhar and J. Subramanian, J. Phys. Chem., 88, 5603 (1984).
6. K.A. Macor and T.G. Spiro, J. Am. Chem. Soc., 105, 5601 (1983).
7. G.A. Mabboti, J. Chem. Edn., 60, 697 (1983).
8. P.T. Kissinger and W.R. Heineman, J. Chem. Edn., 60, 702 (1983).
9. G. Cauquis, V.D. Parker, in Organic Electrochemistry, Edited by M.M. Baizer (Marcel Dekker, New York, 1973), p. 93.
10. J.A. Plambeck, Electroanalytical Chemistry (Wiley Interscience, New York, 1982).
11. A.J. Bard and L.R. Faulkner, Electrochemical Methods, (John Wiley, NY, 1980).
12. A. Stanienda and G. Biebl, Z. Phys. Chem., (Frankfurt and Main) (N.S.) 52, 254 (1967).
13. C.B. Maya and V. Krishnan, Inorg. Chem., 24, 3253 (1985).

CHAPTER V

ESR STUDIES ON THE OXIDATION PRODUCTS OF VANADYL PROTO - AND MESO PORPHYRINS

CHAPTER V

ESR STUDIES ON THE OXIDATION PRODUCTs OF VANADYL PROTO- AND MESO PORPHYRINS

V.1 INTRODUCTION

It has been established clearly that when vanadyl octaethyl porphyrin is oxidised a radical cation is formed.[1,2] Similar results have been obtained for vanadyl etioporphyrin also. We report in this chapter the esr studies on the oxidation products of vanadyl proto- and meso porphyrins. The one-electron oxidation product of vanadyl protoporphyrin, [VO(PROTO)] has shown aggregation effects even in solution at room temperature. While the corresponding species from vanadyl mesoporphyrin, [VO(MESO)] is monomeric like that of VOOEP at concentrations in the range of 10^{-3} molar, at higher concentrations, it shows aggregation effects in solution.[3] We present here esr evidence for the above conclusions, which are amply supported by the cyclic voltammetric studies presented in the previous chapter.

V.2 EXPERIMENTAL DETAILS

The details on the synthesis of vanadyl proto- and meso porphyrin have been presented in Chapter II. Oxidations were done in dry dichloromethane using a few drops of a solution of antimony pentachloride (0.01 molar) in dry dichloromethane. Dissolution of the vanadyl porphyrin in pure trifluoroacetic acid also led to the formation of the radical cations. These systems are quite stable at least for a day. In general, the radicals were generated just before running the esr spectra. The solutions were maintained in argon or nitrogen atmosphere. Optical spectra were also recorded for the radical cations. Electrochemical oxidation at controlled potentials were also done in the case of vanadyl meso porphyrin. A simple beaker type of electrochemical cell (same as that used for cyclic voltammetric study) was used for the electrogeneration and the radical cation solution was transferred into the esr tube by pressurising the cell with nitrogen gas. Computer simulations were done using computer programs reported earlier.[4]

The reversibility of oxidation of vanadyl porphyrin in trifluoroacetic acid was checked in the following way: The optical spectra of the oxidised species was recorded (figure V.1) . . The solution of VO(PROTO) in trifluoroacetic acid was transferred to a 100 ml flask and nitrogen gas was passed to remove the trifluoroacetic acid. The solid containing some trifluoroacetic acid was

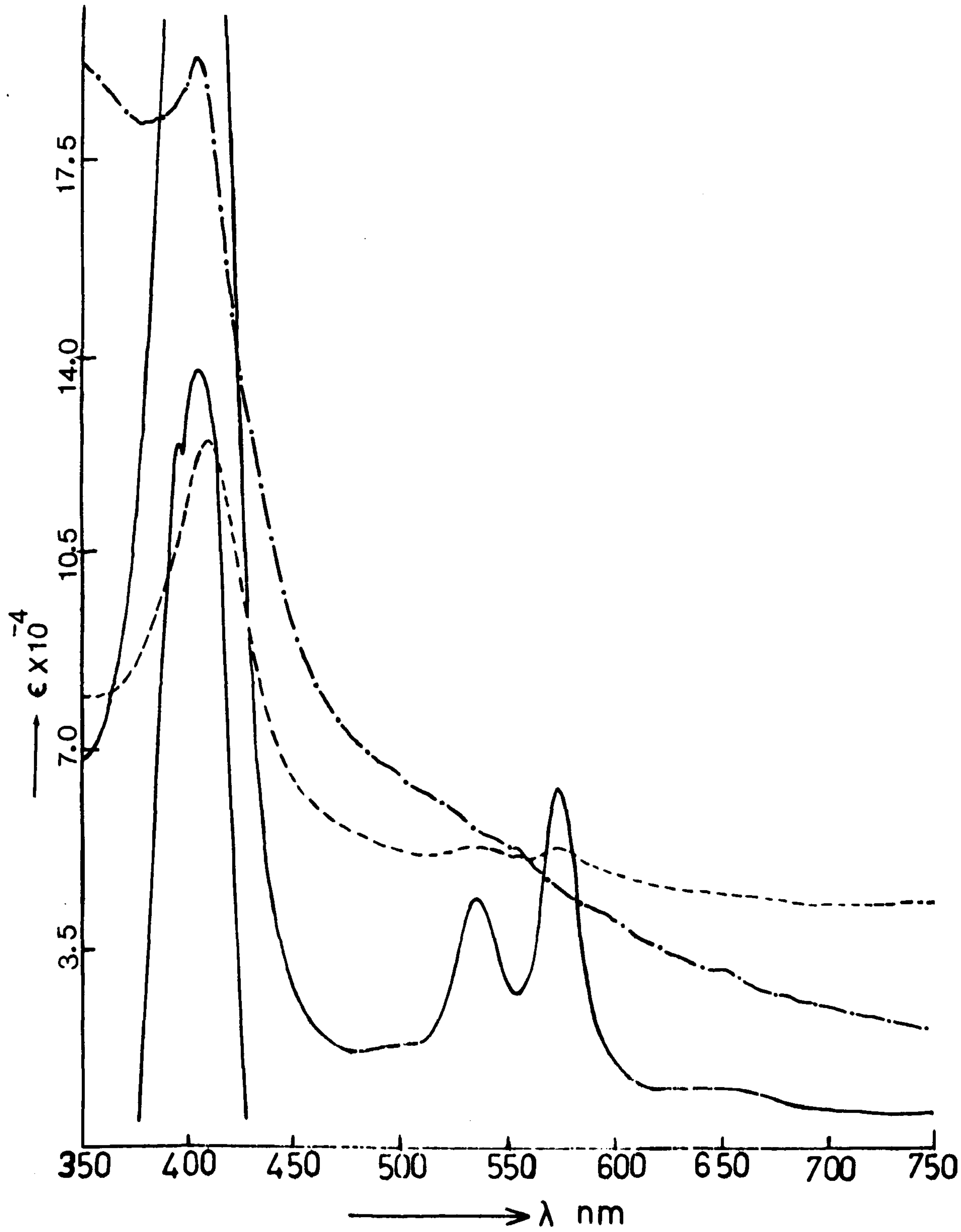


Fig.V.1. (—) Visible absorption spectrum of VOPPIXDME in acetonitrile (10^{-5}M), (–.–) VOPPIXDME in TFA, and (....) VOPPIXDME in acetonitrile with traces of perchloric acid dissolved in dichloromethane and traces of triethylamine were added to reduce the porphyrin radical cation. The optical spectrum of the solution was taken immediately, which corresponded to the parent unoxidised VO(PROTO). The solution was then evaporated, reextracted with dichloromethane, washed with water and dried. The solvent was then removed and the TLC of the resultant solid showed the presence of VO(PROTO) with a small amount (10%) of the demetalated porphyrin. In this manner we have confirmed that the vinyl and ester groups are present in the system after rereduction with triethylamine. Additional confirmation also comes from the observation of a red shifted Soret band for VO(PROTO) which is characteristic of vinyl or formyl substituents in the porphyrin periphery.^{5} The band at the same wavelength is observed before oxidation and after oxidation in TFA-reduction with triethylamine sequence. Hence we have concluded that apart from small extent of demetalation the porphyrin moiety is not affected by treatment with TFA under the experimental condition. It is of course imperative that the optical and esr measurements be made as soon as the oxidation is performed. That oxidation indeed occurs is also confirmed by the esr spectral data. A simple oxo protonation does not lead to the optical spectrum of the type shown in figure V.1). We have confirmed this aspect by treating VO(TPP) with trifluoroacetic acid and recording the visible absorption and esr spectra at room temperature. Only minor changes occur in the ^{51}V hyperfine coupling and the g value on the addition of TFA to a solution of VO(TPP).

V.3 RESULTS AND DISCUSSION

V.3.1 ESR SPECTRUM OF THE RADICAL CATION OF VANADYL PROTOPORPHYRIN AT ROOM TEMPERATURE

The oxidation product of vanadyl protoporphyrin has an unusual esr behaviour compared to VO(OEP) or vanadyl mesoporphyrin.[3] At concentrations, in the range of 10^{-4} molar no esr spectrum is observed in solution. When the concentration is increased to 10^{-3} molar, an esr spectrum containing fifteen lines with a broad background signal is noticed. It is difficult to get a well-resolved spectrum in this case. The best possible spectrum was obtained by dissolving VO(PROTO) in trifluoroacetic acid in the concentration range 10^{-3} molar. The fifteen line spectrum with a spacing of about 40 gauss is indicative of hyperfine coupling from two equivalent ^{51}V nuclei. This could arise from three possible situations: (i) a dimer formed by two molecules of unoxidised vanadyl porphyrin. (ii) a dimer from two molecules of oxidised species (iii) a dimer from one molecule of the oxidised species and one molecule of the unoxidised species. Highly concentrated solutions of vanadyl protoporphyrin in the absence of any oxidising agent do not give rise to fifteen line spectrum. This observation rules out the first possibility. In the second situation, the unpaired electrons on the porphyrin are likely to pair up (the pairing energy is of the order of 15 Kcal/mole[6]) thus leaving one unpaired electron each on the vanadium orbital. This system is then basically the same as situation (i) and one may not be able to observe an esr spectrum in solution due to strong dipolar broadening. Further, even if it is observed, one expects a spacing between the hyperfine lines equal to one half of the hyperfine coupling of ^{51}V observed in unoxidised vanadyl porphyrin. The observed spacing in the present case is about one-third of what is obtained for unoxidised VO(PROTO). The following simple first order treatment of the spin Hamiltonian would indicate that the spectrum arises from situation (iii). The reduction of the hyperfine coupling to one-third of its original value is suggestive of the fact that there are three unpaired electrons undergoing fast exchange compared to esr time scale. On this basis we propose that the species in solution is formed from a radical cation of VO(PROTO) with $S = 1$ and an unoxidised molecule of VO(PROTO) with $S = \frac{1}{2}$. Thus the dimeric species has three unpaired electrons with $S = \frac{3}{2}$ or $S = \frac{1}{2}$. The equivalence of the two ^{51}V nuclei indicates that the unpaired pi electron is delocalised on both the molecules. In this regard, the dimeric species resembles the dimer obtained on oxidation of chlorophyll system, wherein the delocalisation of the unpaired electron over both the chlorophyll molecules has been postulated.[7] Recent papers on chlorophyll aggregation have also pointed out that the aggregation can involve more than two chlorophyll molecules.[8,9] In the present study, the observation of hyperfine interaction with only two ^{51}V nuclei confirms the presence of only dimers in solution. The isotropic spin Hamiltonian for the dimer can be written as :

$$H = g_1 \beta B(S_z^{(1)} + S_z^{(2)}) + g_2 \beta B S_z^{(3)} + a(\hat{I}^{(1)} \cdot \hat{S}^{(1)} + \hat{I}^{(2)} \cdot \hat{S}^{(2)}) + J_1 \hat{S}^{(1)} \cdot \hat{S}^{(2)} + J_2 (\hat{S}^{(1)} \cdot \hat{S}^{(3)} + \hat{S}^{(2)} \cdot \hat{S}^{(3)}) \quad \ldots \quad (V.1)$$

The indices 1 and 2 refer to the electrons in the two vanadium orbitals and 3 refers to the unpaired pi electron. If J_1 and J_2 are quite large compared to the microwave frequency, then one observes an average 'a' value in solution. Under this condition, if one uses the basis functions for $S = \frac{3}{2}$ state, with the above Hamiltonian, we obtain the allowed transition $\left|\frac{3}{2}, \frac{1}{2}\right\rangle \leftrightarrow \left|\frac{3}{2}, -\frac{1}{2}\right\rangle$ with the energy to first order given by

$$E = g\beta B/\hbar \;+\; (a/3)\,(m_I^{(1)} + m_I^{(2)}) \qquad \ldots \quad (V.2)$$

If we use $S = \frac{1}{2}$ state for the three spin system, the expected hyperfine coupling is 2a/3. (The spin Hamiltonian is solved to first order using $S = \frac{1}{2}$ and $S = \frac{3}{2}$ basis functions in the appendix). The experimental and a computer-simulated spectrum (stick plot) using equation (2) are presented in figures V.2a and V.2b. The computer simulation includes second order hyperfine couplings. The spacing between the lines is taken as one-third (3mT) of the ^{51}V coupling in the unoxidised VO(PROTO) (8.8mT). The esr spectrum of the frozen solution of this species at liquid nitrogen temperature was also recorded. This spectrum appears to contain a superposition of the esr spectra of unoxidised monomeric VO(PROTO) and the oxidised species. Hence a complete analysis of this spectrum could not be made. The spectrum corresponding to the oxidised species was however, found to be the same as that obtained from the oxidation product of vanadyl mesoporphyrin at high concentrations (10^{-2} molar) at liquid nitrogen temperature. A detailed analysis of this spectrum is presented in the next section.

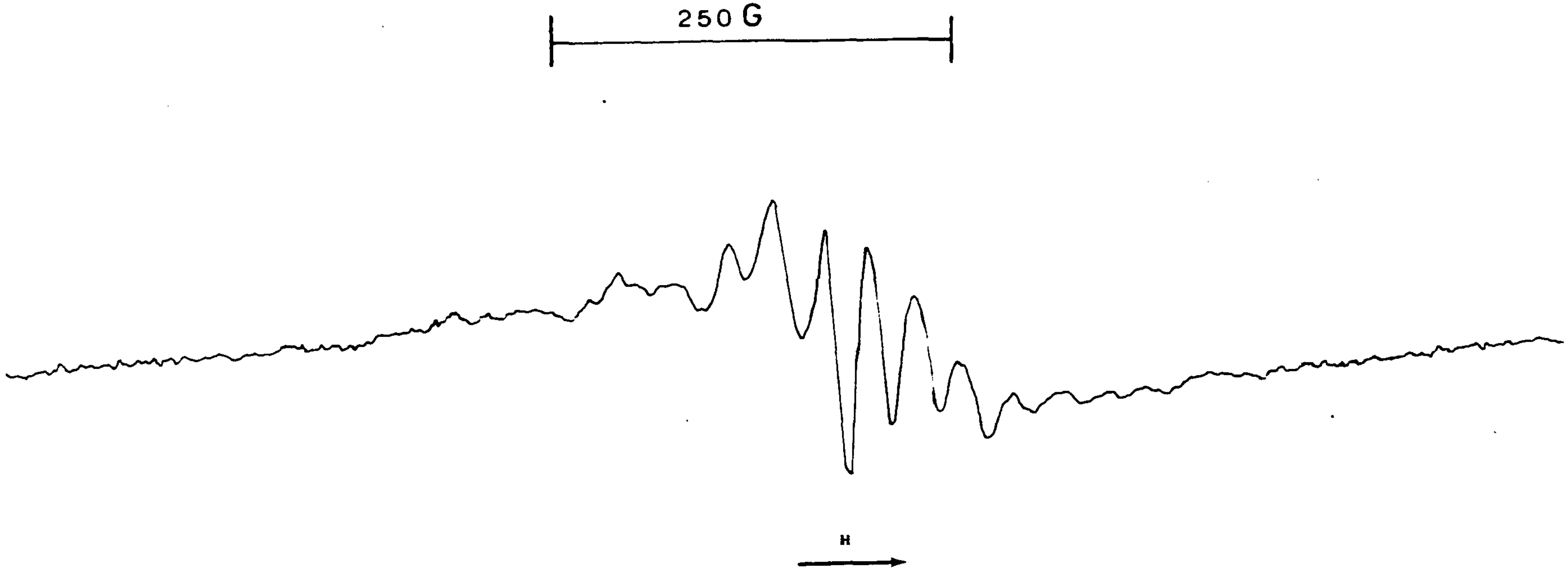


Fig.V.2(a). ESR spectrum of Vanadyl protoporphyrin IX dimethylester oxidised with TFA at room temperature

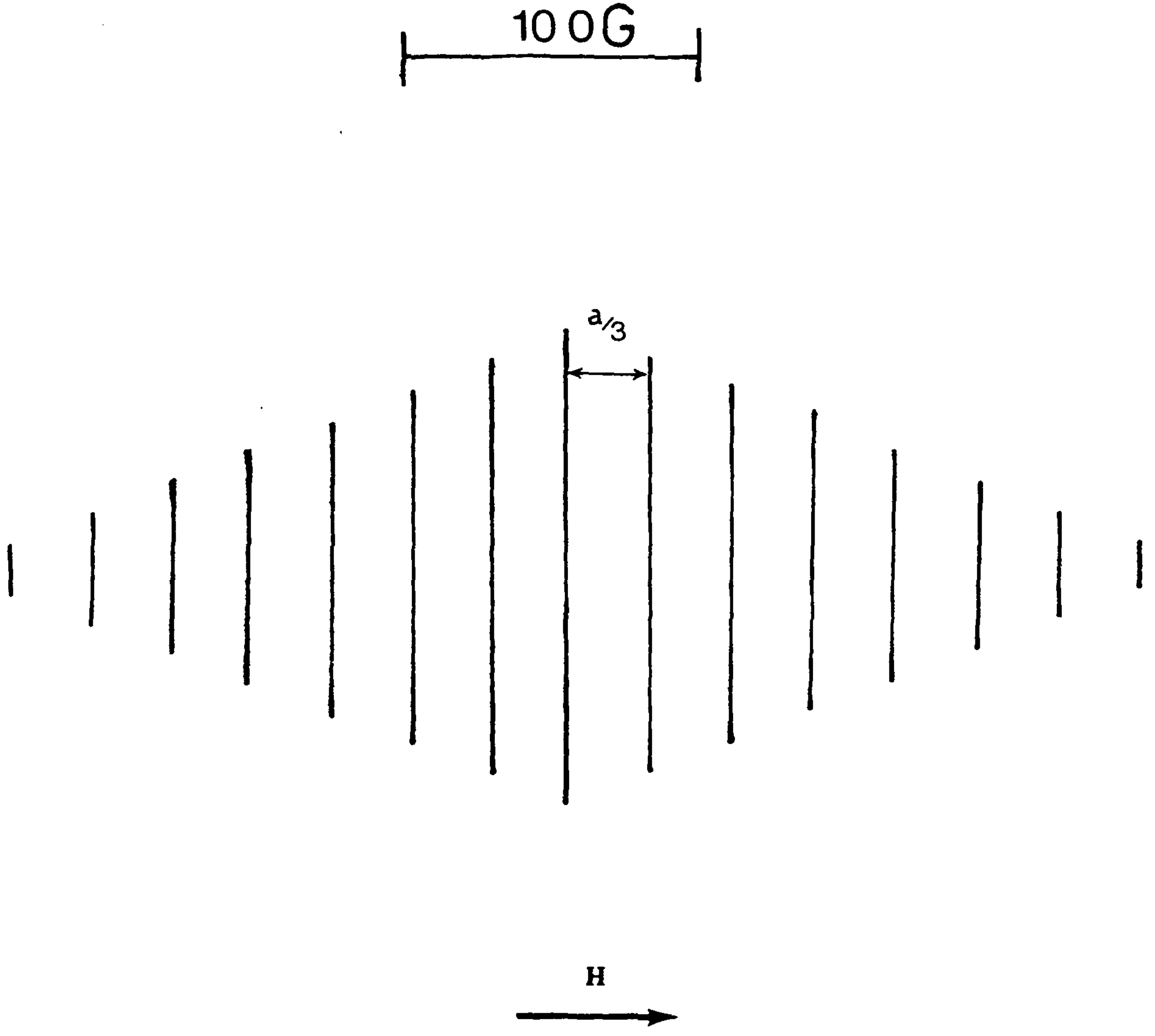


Fig.V.2(b). Stick plot of Vanadyl protoporphyrin IX dimethylester oxidised with TFA at room temperature using a/3 = 528.4 M rad s^{-1}

V.3.2 ESR SPECTRA OF VANADYL MESOPORPHYRIN AT ROOM AND LOW TEMPERATURES

Extensive broadening of the esr lines in VO(PROTO) and the presence of more than one species at liquid nitrogen temperature, have prevented a detailed analysis of the esr spectra of the oxidised form of VO(PROTO). Aggregation is not as predominant in VO(MESO) as it is in the case of VO(PROTO). Monomeric species at room temperature and dimeric species similar to that observed for VO(OEP) at low temperatures have been characterised for VO(MESO) in the concentration range of 10^{-3} molar or less. In the concentration range of 10^{-2} molar aggregated species similar to that observed for VO(PROTO) are observable which give rise to well-resolved esr spectra. Hence a more quantitative analysis of the esr spectra could be possible in this situation than what could be done in the case of VO(PROTO).VO(MESO) could be oxidised to the radical cation by oxidation with antimony pentachloride in dichloromethane or by dissolution in trifluoroacetic acid. The esr spectrum of the radical cation thus obtained is presented in figure V.3. This spectrum is very much similar to that of the esr spectrum of VO(OEP) obtained under similar conditions. Electrochemical generation of the radical cation also led to the same spectrum. At liquid nitrogen temperature, a dimeric species (dimer A) is formed

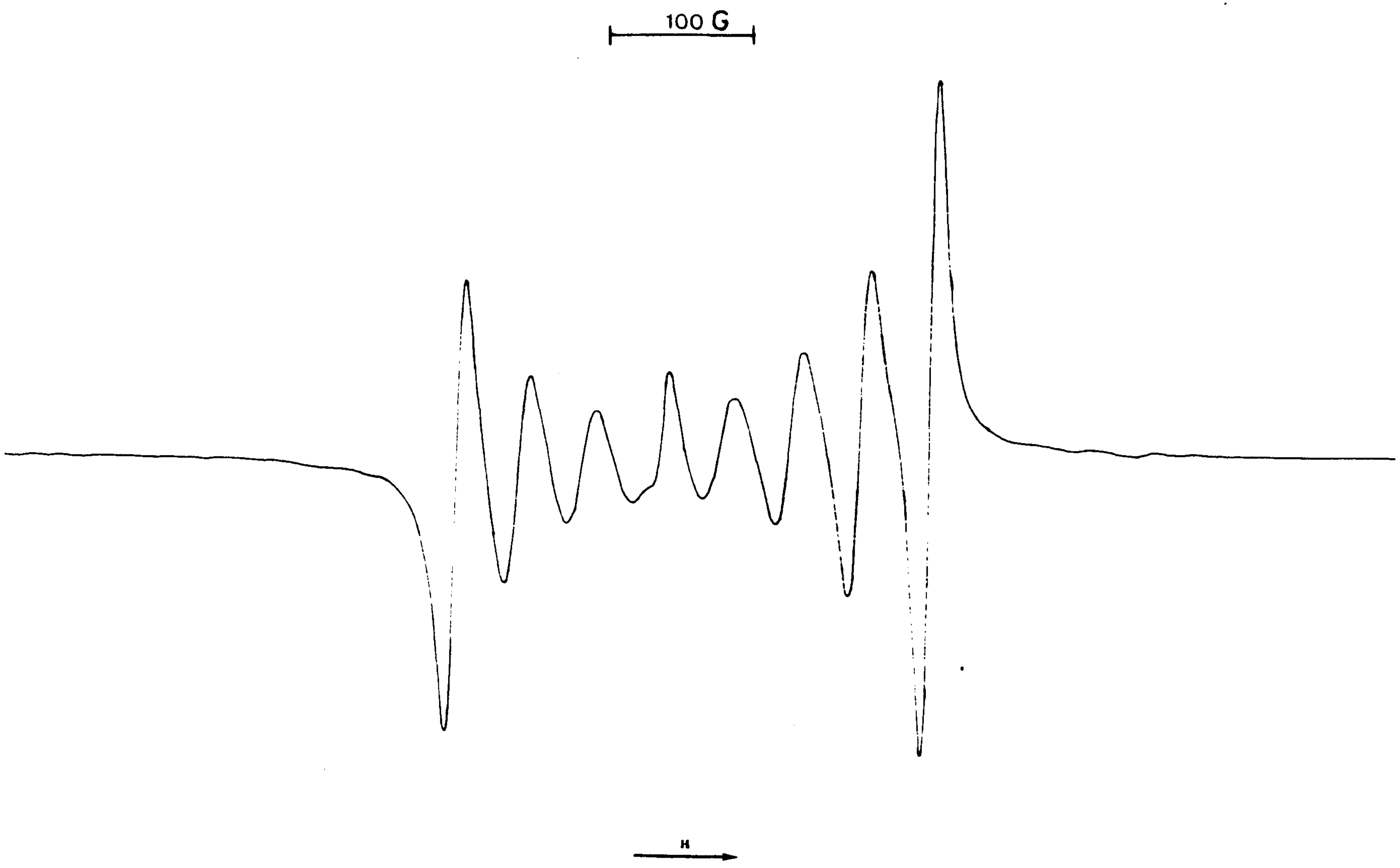


Fig.V.3. ESR spectrum of Vanadyl mesoporphyrin IX dimethylester oxidised with $SbCl_5$ at room temperature

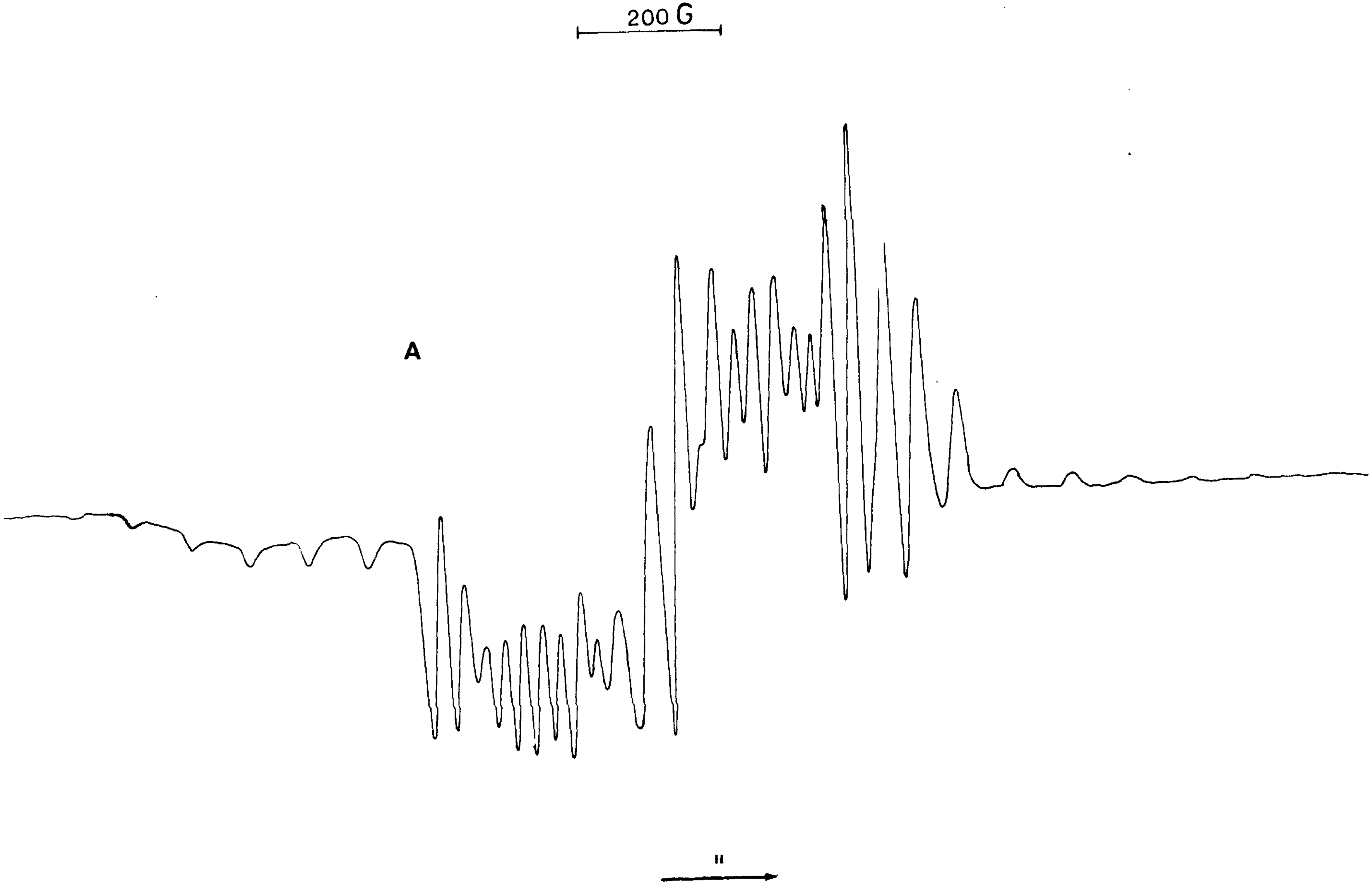


Fig.V.4. ESR spectrum of Vanadyl mesoporphyrin IX dimethylester oxidised with TFA at liquid nitrogen temperature (dimer A) from two molecules of the radical cation (figure V.4) in the same manner as that observed for VO(OEP), discussed in chapter III. A computer simulation of the esr spectrum at liquid nitrogen temperature indicated that the parameters are essentially unaltered from those observed for the dimer from VO(OEP) radical cation.

The esr spectrum of dimer A changes dramatically when the concentration of VO(MESO) is increased to about tenfold. The esr spectrum does not look like a triplet state spectrum. The spectrum consists of fifteen lines and appears to be nearly isotropic. This could arise either from an $S = \frac{1}{2}$ system or from $\pm (\frac{1}{2})$ manifold of $S = \frac{3}{2}$ system. In order to identify the species, we have also taken into account the results of cyclic voltammetric studies discussed in detail in chapter IV. Since the presence of a dimer has been indicated by the cyclic voltammetric data we shall assign this dimer as dimer B to distinguish it from the dimer A. The esr spectrum of this species is similar to that obtained for VO(PROTO). The low-temperature esr spectrum of VO(PROTO) consists of a superposition of dimer B spectrum and that of unoxidised monomeric VO(PROTO). Hence we assign that dimer B arises from the species represented as $[VO(MESO)][VO(MESO)]^{+\cdot}$, a formulation similar to the one made for the oxidised product of VO(PROTO). Thus dimer B must be a $S = \frac{3}{2}$ species. The esr

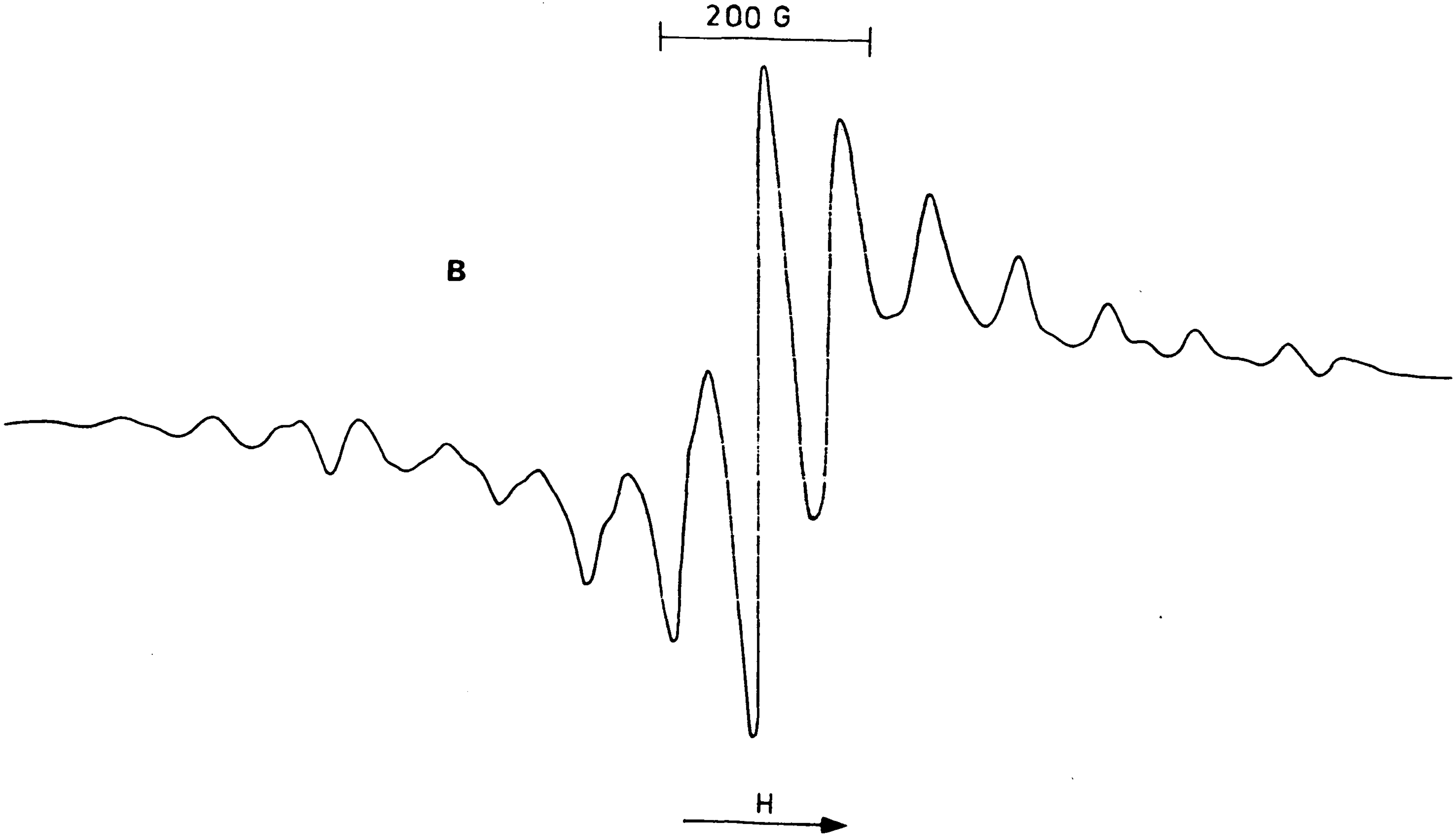


Fig.V.5(a). ESR spectrum Vanadyl mesoporphyrin IX dimethylester oxidised with TFA at liquid nitrogen temperature (dimer B)

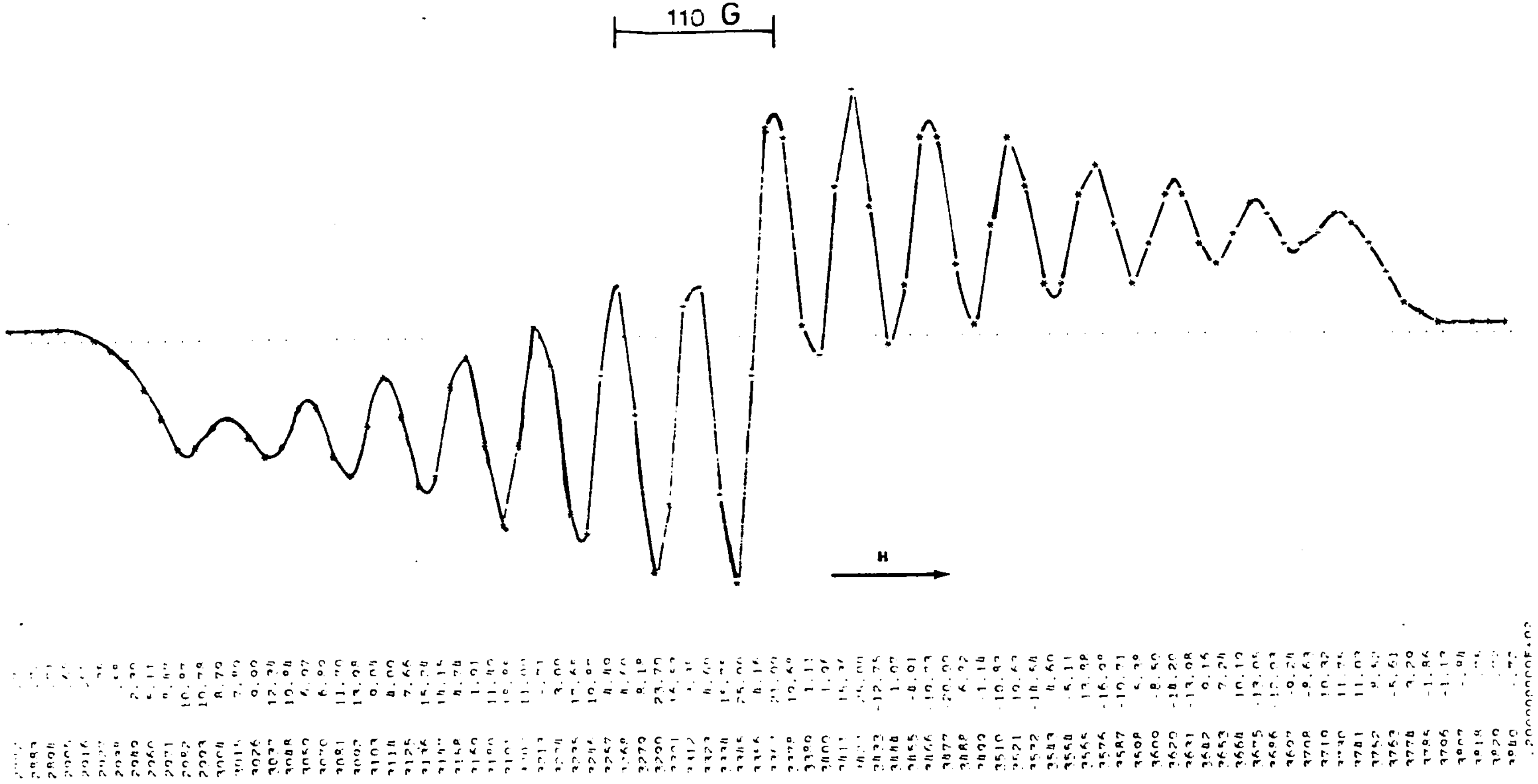


Fig.V.5(b). Computer-simulated ESR spectrum of oxidised Vanadyl mesoporphyrin IX-dimethylester with TFA at lquid nitrogen temperature (dimer B) transition could arise from the $S = \frac{1}{2}$ manifold of $S = \frac{3}{2}$ state. If the zero field splitting for the $S = \frac{3}{2}$ system is very small one may not observe more than one transition in the region of $g = 2$. If the zero-field splitting is very large (larger than microwave frequency) one should observe a strong transition at $g = 4$ and a weak transition at $g = 2$. Since the latter situation is not obtained, we can say that the zero-field splitting is very small and is not measurable from the esr spectrum. Assuming an effective spin of $S = \frac{1}{2}$ we have simulated the esr spectrum. The simulated spectrum indicates that the g and A values are very nearly isotropic. ($g_{\perp} = 1.913$, $g_{\parallel} = 1.911$, $A_{\perp} = 740.222$ MradS^{-1}, $A_{\parallel} = 807.51$ MradS^{-1}). The average hyperfine coupling constant A (isotropic) for dimer B obtained at liquid nitrogen temperature is somewhat larger than the corresponding value at room temperature (84 MHz or 527.788 MradS^{-1}) for VO(PROTO). Thus the species identified as dimer B is considered to arise from one molecule of VO(MESO) radical cation and one molecule of unoxidised species. (Figures V.5a and V.5b). Oxidation of VO(MESO) with $SbCl_5$ in dichloromethane leads to a different type of situation compared to that in the case of trifluoroacetic acid. At room temperature with 10^{-3}M solutions of VO(MESO) a monomeric radical cation is obtained just in the same way as in trifluoroacetic acid. Cooling this solution to liquid nitrogen temperatures leads to type-A dimer esr spectrum. The concentration of antimony pentachloride is about five fold in excess of that of VO(MESO). When tenfold or larger excess of $SbCl_5$ are used a new type of esr spectrum (figures V.7a and V.7b) is obtained. This spectrum seen both at liquid nitrogen and liquid helium temperatures though it is quite broad at liquid nitrogen temperature. The esr spectrum looks like that of a triplet state spectrum but is different from that of dimer A spectrum. Only a single ^{51}V coupling is discernable. A similar spectrum has been reported for VO(Etioporphyrin) oxidised with $SbCl_5$, though an analysis of this spectrum has not been done. An esr spectrum corresponding to a triplet state containing one ^{51}V coupling could arise only from a monomeric radical cation of VO(MESO) which has been hitherto observed only at room temperature. A spin Hamiltonian for this system could be written as

$$H = \beta\,(\hat{S}_1 \cdot \underset{\sim}{g}_1 \cdot \hat{B} + \hat{S}_2 \cdot \underset{\sim}{g}_2 \cdot \hat{B}) + \hat{S}_1 \cdot \underset{\sim}{A} \cdot \hat{I} + \hat{S}_1 \cdot \underset{\sim}{D} \cdot \hat{S}_2 + J\,\hat{S}_1 \cdot \hat{S}_2 \qquad \ldots \quad (V.3)$$

This spin Hamiltonian is similar to the one adopted to interpret metal-free radical-interaction in spin label bound metal complexes.[10,11] In these system, $J \simeq 0$ or of the

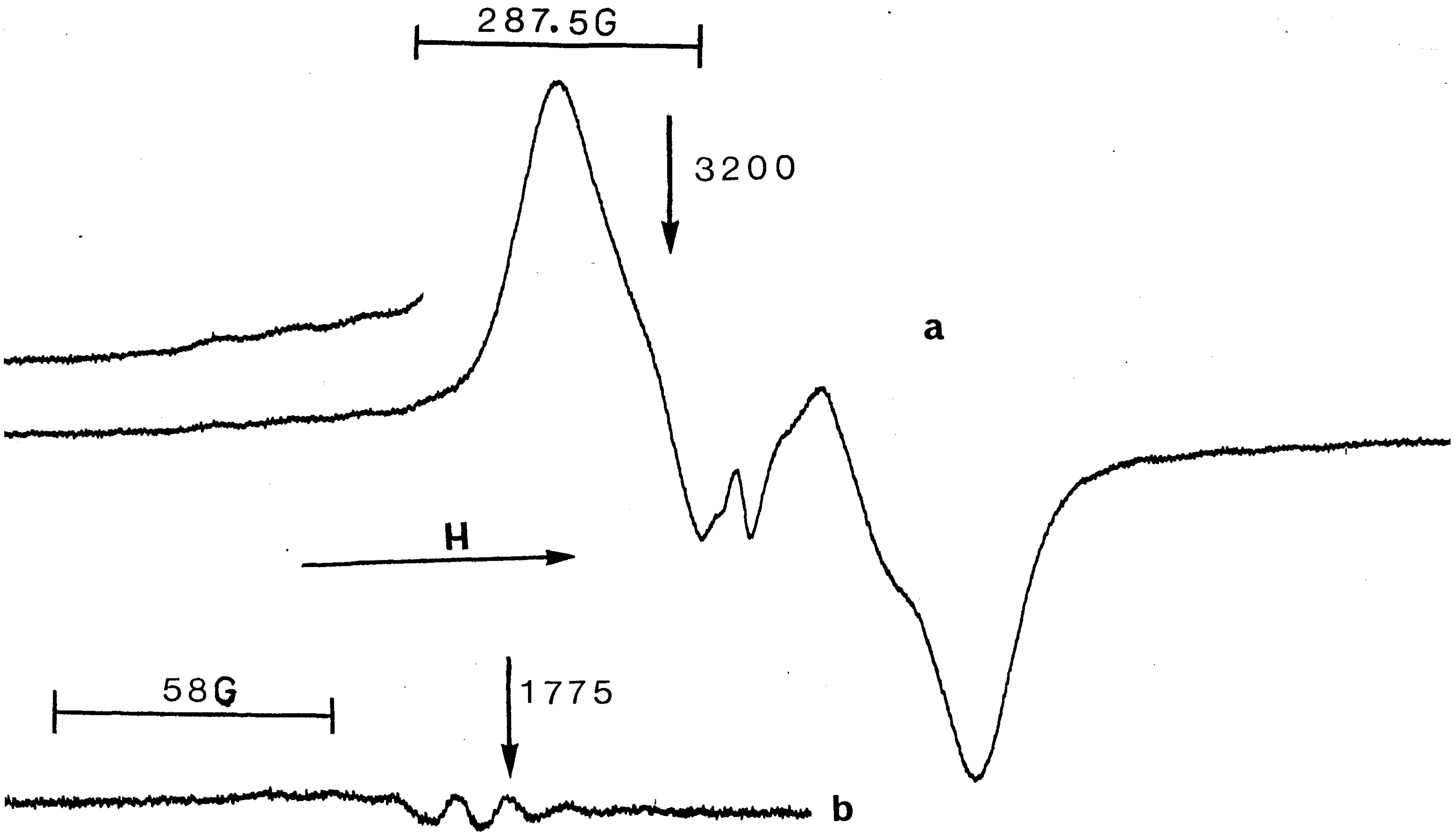
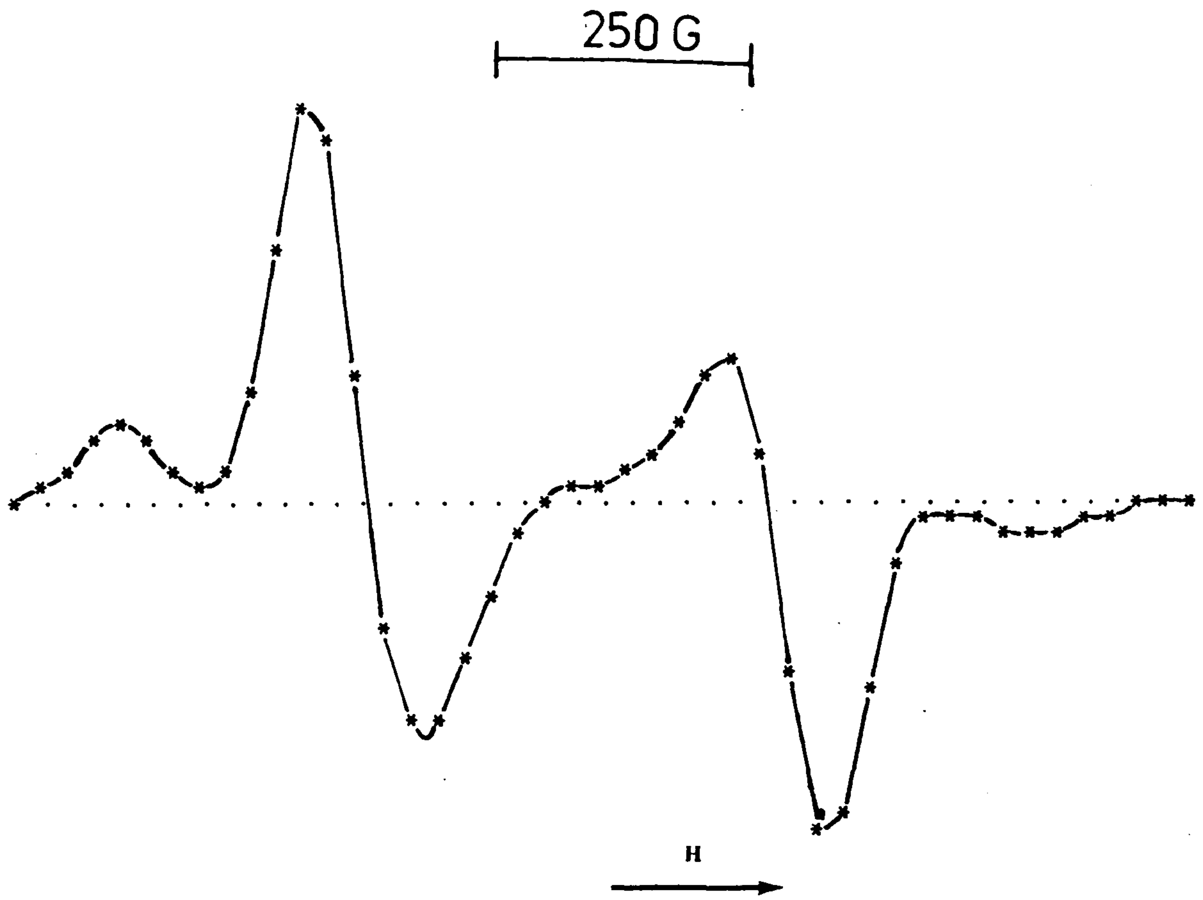


Fig.V.6(a). ESR spectrum of Vanadyl mesoporphyrin IX dimethylester oxidised with $SbCl_5$ at liquid Helium temperature; (a) g = 2 region (b) half-field region



```
2775      -.23
2800      -.85
2825     -2.20
2850     -3.88
2875     -4.65
2900     -3.82
2925     -2.28
2950     -1.32
2975     -2.17
3000     -6.68
3025    -16.02
3050    -25.00
3075    -22.90
3100     -7.95
3125      7.67
3150     14.27
3175     13.55
3200     10.00
3225      5.82
3250      2.45
3275       .45
3300      -.60
3325     -1.27
3350     -2.08
3375     -3.30
3400     -5.40
3425     -8.30
3450     -9.27
3475     -3.05
3500     10.52
3525     21.20
3550     20.13
3575     11.55
3600      4.35
3625      1.23
3650       .55
3675       .90
3700      1.60
3725      2.15
3750      2.00
3775      1.27
3800       .55
3825       .15
3850       .02
3875       .00
 .100000000E+02
```

Fig.V.6(b).Computer-simulated ESR spectrum of oxidised Vanadyl mesoporphyrin IX-dimethylester with $SbCl_5$ at liquid Helium temperature order of 10^{-4} cm^{-1}. In the case of VO(MESO) radical cation, however, $J \gg h\nu$ where ν is the microwave frequency, in otherwords $J > 0.3$ cm^{-1}. In view of the strong exchange, we can consider that both the electrons experience an average environment. An approximate Hamiltonian for the system can be written for this system under strong exchange condition as follows

$$H = \hat{S} \cdot \underset{\sim}{g} \cdot \hat{B} + \hat{S} \cdot \underset{\sim}{A} \cdot \hat{I} + \hat{S} \cdot D \cdot \underset{\sim}{\hat{S}} + J \cdot \hat{S}_1 \cdot \hat{S}_2 \qquad \ldots \quad (V.4)$$

considering only the dipolar interaction as the contributing factor to ZFS interactions. Here S is the total spin angular momentum operator and g is the average g tensor for the d-electron and the π electron. In order to find the approximate magnitude of the zero field splitting term, we have ignored the nuclear spin coupling and diagonalised the Hamiltonian for each orientation under axial symmetry, which is indicated by the esr spectrum. The powder spectrum was thus obtained for the system and an estimate of D value was made from this simulations then hyperfine coupling terms were included as perturbation terms and the powder spectrum was calculated for the best values of D and A the hyperfine couplings. Though this approach is rather crude it gives a reasonable fitting to the experimental spectrum. The value of D has been obtained as 1200 MHz. Considering an axially symmetric Hamiltonian with zeeman and zero field interaction only, we have

$$H = \beta H \cdot g \cdot \hat{S} + D_{\perp} (S_x^2 + S_y^2) + D_{\parallel} (S_z^2) \qquad \ldots \qquad (V.5)$$

In terms of D and E, the Hamiltonian is (E = 0)

$$\beta H g \cdot \hat{S} + D (S_z^2 - \frac{1}{3} (S + 1) S).$$

where $D = \frac{3}{2} D_{\parallel}$ or $D_{\parallel} = \frac{2}{3} D = 800$ MHz. If we assume the same principal axes for g and D tensor then, the symmetry axis is perpendicular to the porphyrin plane. The inter electron axis is in the plane of the porphyrin ring. Hence if we express the ZFS tensor along the inter electron axis (Z') $D_{x'x'} = D_{y'y'} = - \frac{1}{2} D_{z'z'}$. The quantity $D_{\parallel}$ is along an axis perpendicular to the inter electron axis and hence

$$D_{\parallel} = D_{x'x'} = D_{y'y'} = - \frac{1}{2} D_{z'z'}$$

$$D_{z'z'} \text{ (in MHz)} = 1.298\ g^2/R^3$$

Where the inter electron distance R is expressed in Angstrom units using a value of $D_{z'z'} = 1600$ MHz, we get a value for R as 3.2Å, we have assumed here the entire ZFS interaction arises from dipolar coupling between the two electrons. This assumption is justified, since the exchange interaction between the two electrons is only of the order of 1 cm^{-1}. An approximate estimate of the distance of the unpaired pi electron from the center could be made by using the pi m.o wavefunction for the HOMO of porphyrin. Using a_{1u} and a_{2u} orbitals we can estimate the distance as

$$R = \sum_{i}^{\text{all atoms}} C_i^2 R_i \qquad \ldots \text{(V.6)}$$

Where C_i^2 is the square of the mo coefficient for the ith atom in the a_{1u} or a_{2u} orbital and R_i is the distance of the ith atom from the center of porphyrin. Using the formula, we obtained the value of R as 3.30 for a_{1u} and 3.21 for a_{2u} orbitals which are the two highest occupied m.o's for a metalloporphyrin with D_{4h} or C_{4v} symmetry. Thus the estimate for the inter-electron distance in the radical cation of VO(MESO) is in reasonable agreement with molecular orbital picture. The value of R obtained from linewidth studies reported for VO(OEP) (3.87Å) is however, larger than the present estimate.

There is a report in the literature[12] on a monomeric vanadyl porphyrin radical species obtained by γ-irradiation of VO(TPP) in chlorinated solvents. The esr spectrum of this species consists of a strong transition at half-field region including hyperfine structure from a single ^{51}V nucleus. The transition at g = 2 region was not seen since in this region, strong lines from the unoxidised porphyrin were observed. In our studies, though we have observed half-field lines, these lines are very weak in intensity compared to the transition in g = 2 region. It appears that the radical species obtained by irradiation is different from the species generated by chemical oxidation reported in the present work.

V.4 CONCLUSION

VO(PROTO) and VO(MESO) lead to various types of species on one-electron oxidation. Monomeric radical cation, dimer of the radical cation and a dimer consisting of one molecule of radical cation and one molecule of unoxidised vanadyl porphyrin had been identified. The monomeric radical cation has also been obtained in the solid state at low temperatures. The esr results of VO(MESO) and VO(PROTO) corroborate well with the cyclic voltammetric data on these systems.

REFERENCES

1. J. Subramanian, in Porphyrins and Metalloporphyrins, Edited by K.M. Smith (Elsevier, Amsterdam, 1975), p. 555.

2. G.R. Luckhurst, M. Setaka and J. Subramanian, Mol. Phys., 32, 1299 (1976).

3. A. Lemtur, B. Chakraborty, T.K. Dhar and J. Subramanian, J. Phys. Chem., 88, 5603 (1984).

4. C. Mengerson, J. Subramanian and J.-H. Fuhrhop, Mol. Phys., 32, 893 (1976).

5. K.M. Smith, in Porphyrins and Metalloporphyrins, Edited by K.M. Smith (Elsevier, Amsterdam, 1975), p. 3.

6. J.-H. Fuhrhop, P.K.W. Wasser, D. Riesner and D. Mauzerall, J. Am. Chem. Soc., 94, 7996 (1972).

7. M.W. Druyan, J.R. Norris and J.J. Katz, J. Am. Chem. Soc., 95, 1682 (1973).

8. J.A. Betti, R.E. Blankenship, L.V. Natarajan, L.C. Dickenson and R.C. Fuller, Biochem. Biophys. Acta, 680, 194 (1982).

9. K.M. Smith, L.A. Kehres and J. Fajer, J. Am. Chem. Soc., 105, 1387 (1983).

10. S.S. Eaton, K.M. More, B.M. Sawant, P.M. Boymel and G.R. Eaton, J. Mag. Res., 52, 435 (1983).

11. S.S. Eaton and G.R. Eaton, Coord. Chem. Rev., 26, 207 (1978).

12. M. Hoshino, S. Konishi, M. Imamura, S. Watanabe and Y. Hama, Chem. Phys. Lett., 102, 259 (1983).

CHAPTER VI

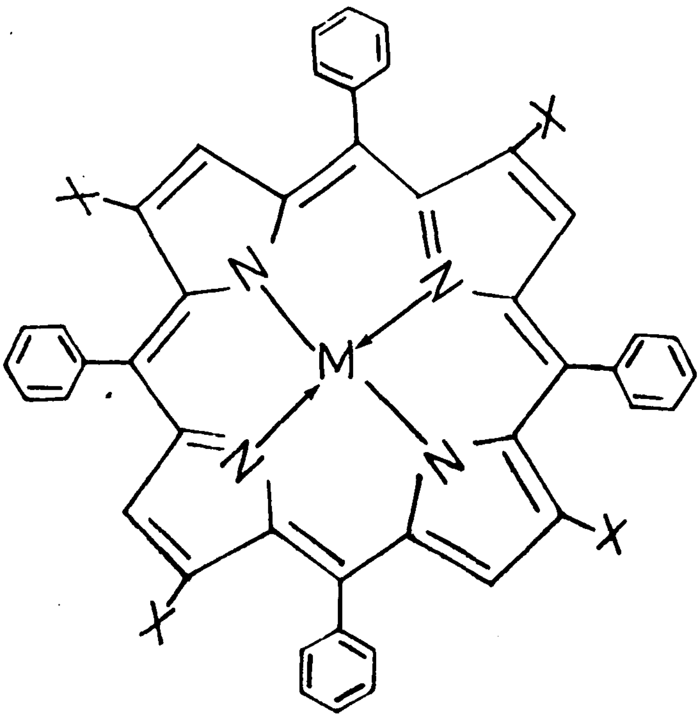
CYCLIC VOLTAMMETRIC STUDIES ON SOME METAL COMPLEXES OF TETRABROMO MESO TETRAPHENYL PORPHYRIN

CHAPTER VI

CYCLIC VOLTAMMETRIC STUDIES ON SOME METAL COMPLEXES OF TETRABROMO MESOTETRAPHENYL PORPHYRIN

VI.1 INTRODUCTION

The redox potentials of metalloporphyrins can be tuned to one's requirement by modifying the substituents in the periphery of the metalloporphyrin.[1,2] Substituents could be introduced in the ortho or para positions of the phenyl rings in the meso positions or in the α and β positions in the pyrrole ring. A number of studies have been reported on the redox potentials of phenyl substituted meso tetraphenyl porphyrin.[3,4] The redox potentials have been correlated with the Hammet constants of the substituents.[3,4] The effect of substituents on the phenyl ring on the redox potential is only moderate since the phenyl ring is twisted out of the plane of the porphyrin ring to some extent. When the substituent is in the beta position the effect on the redox potential is quite marked. Very few studies on the redox potentials of such systems are available.[5,6] The results indicate that with electron withdrawing substituents the shift in the reduction potentials is quite large compared to that in the oxidation potential. As an example, for tetra cyano TPP the oxidation potential for the copper complex is shifted



M = VO, Cu, Zn, Ni
X = Br

Fig.VI.1. Structure of metalloporphyrin (MBr_4TPP system) from 1.06V [for Cu(TPP)] to 1.41V while the corresponding first reduction potential is shifted from -1.35V to -0.35V. This has been interpreted on the basis that the sites for oxidation and reduction are different.

The redox potential data are available for some metal complexes of porphyrins with mono substituents in the beta position and with symmetric tetracyano TPP.[5,6] We have in the present work attempted cyclic voltammetric studies on some metal complexes of symmetric tetrabromo substituted TPP. Only the oxidation potentials have been obtained and wherever possible the optical and esr spectra of the one-electron oxidation product have been recorded for the possible assignment of the product obtained on oxidation.

VI.2 EXPERIMENTAL DETAILS

The synthesis of symmetric tetrabromo TPP and its metal complexes is discussed in detail in chapter II. The procedure for cyclic voltammetric studies is the same discussed in chapters II and IV. Dichloromethane and tetra n-butylammonium perchlorate were used as solvent and supporting electrolyte respectively. Cyclic voltammetric studies were done on the following systems: Zn(II), Cu(II), Ni(II) and VO(II) complexes of tetrabromo TPP.

TABLE VI.1

Cyclic voltammetric data for Br_4TPP systems at room temperature.

Solvent : CH_2cl_2

Concentration : $10^{-3}M$

Supporting Electrolyte : TBAB

Reference electrode : SCE

Sweep rate : 100 m v/s

System	Oxidation potential in volts						$E_{1/2}$	Reversibility
	$E_p^a(I)$	$E_p^c(I)$	$E_{1/2}(I)$	$E_p^a(II)$	$E_p^a(II)$	$E_{1/2}(II)$		
$CuBr_4TPP$	0.980	0.860	0.920	1.296	1.220	1.258	0.338	Rev.
$NiBr_4TPP$	0.880	0.764	0.822	1.240	1.092	1.166	0.344	Rev.
$VoBr_4TPP$	1.264	1.184	1.224	1.454	1.372	1.413	0.189	Rev.
$ZnBr_4TPP$	0.866	0.754	0.810	1.172	1.008	1.090	0.280	Rev.

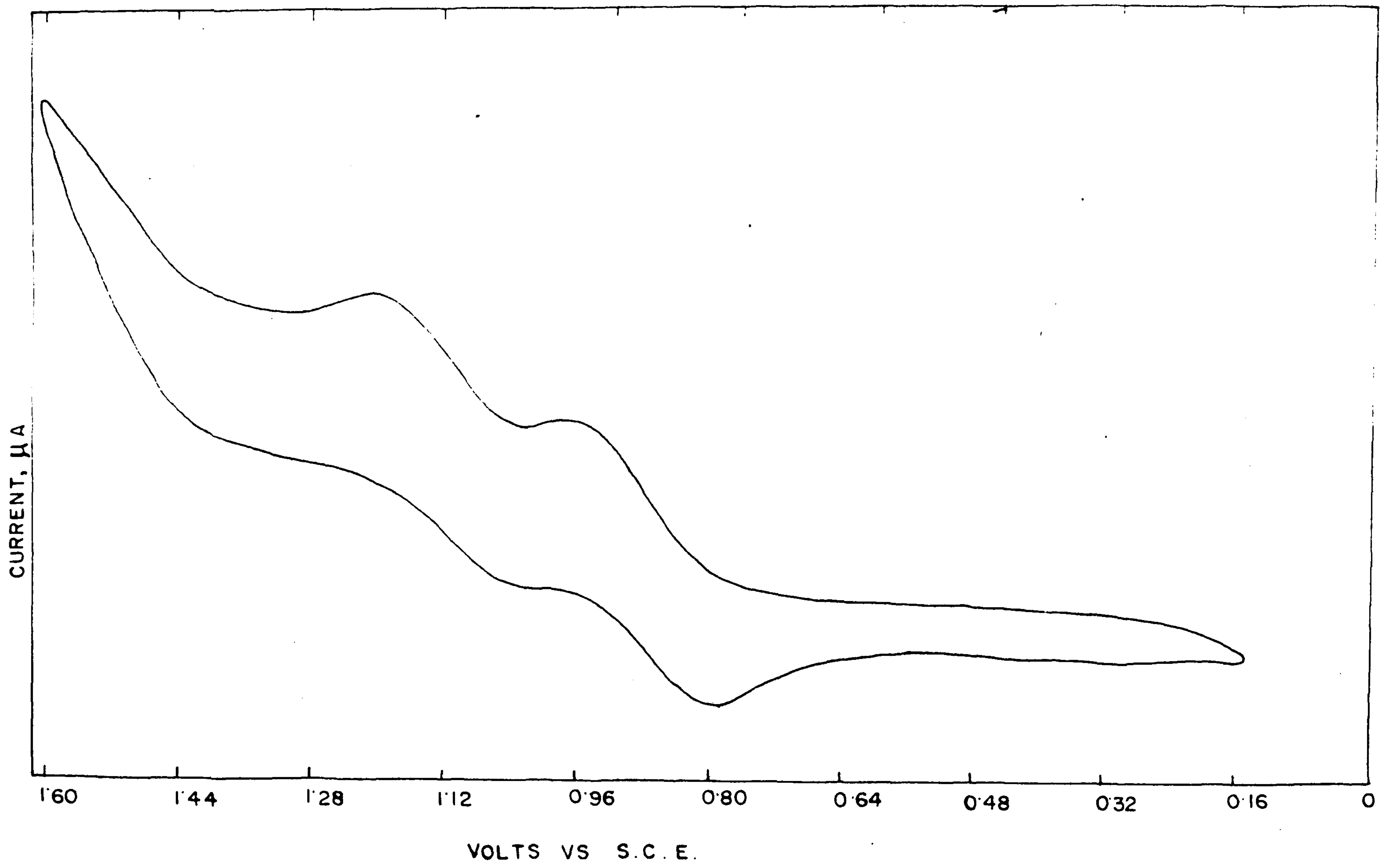


Fig.VI.2. Cyclic voltammogram (oxidation steps) of $Zn(Br_4TPP)$ in CH_2Cl_2 at room temperature.
Sweep rate 100 mv/s.

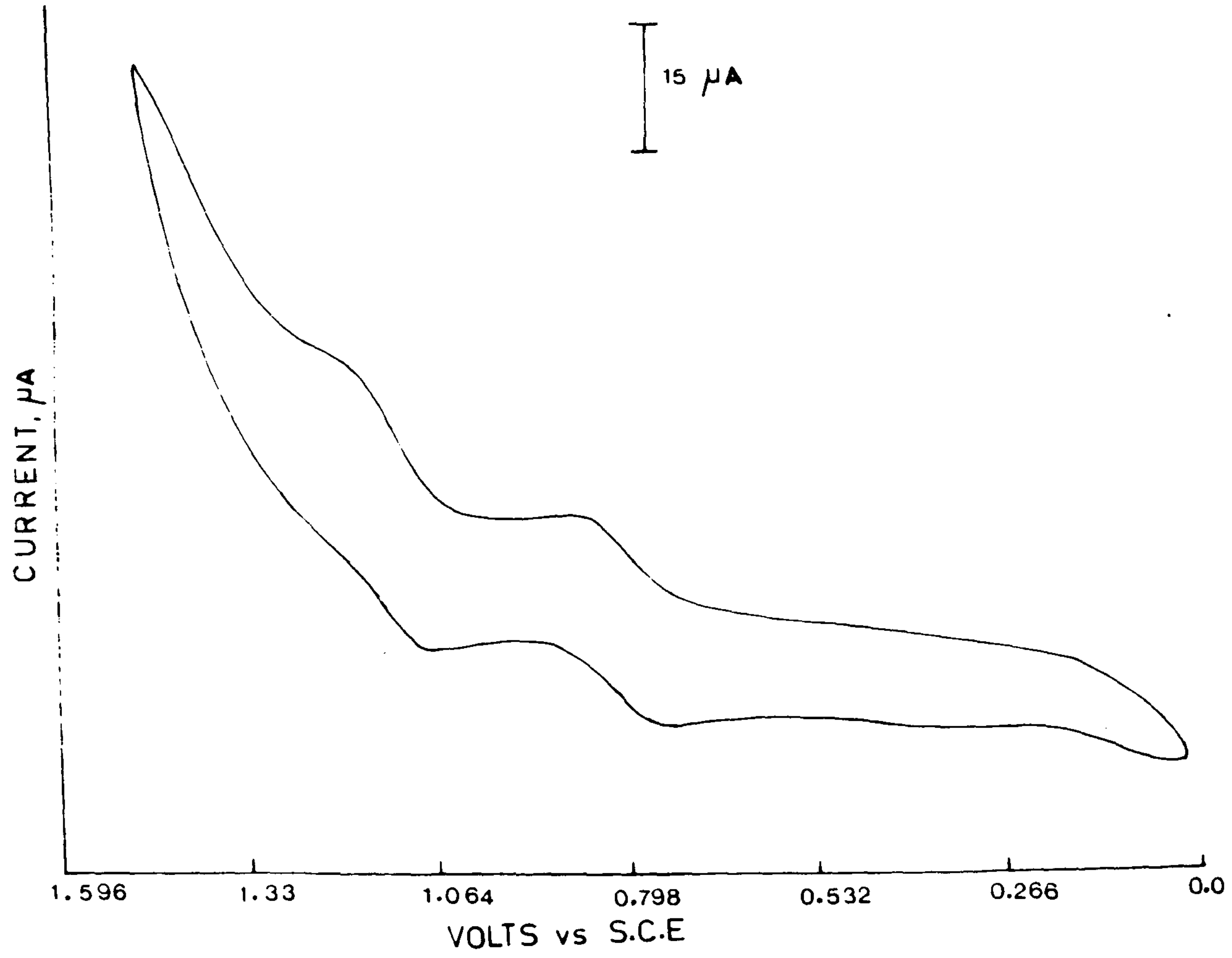


Fig.VI.3. Cyclic voltammogram of $CuBr_4TPP$

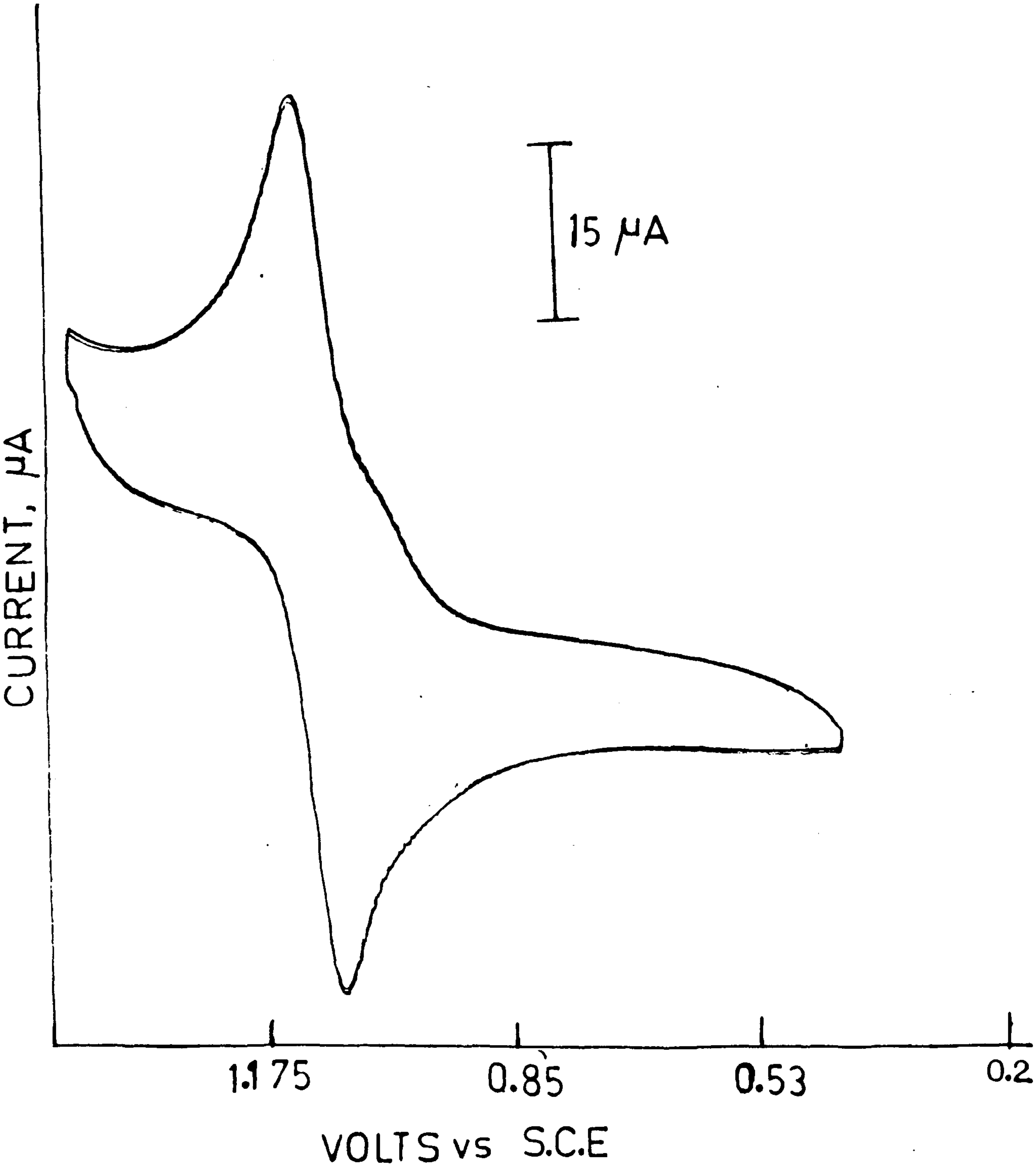


Fig.VI.4. Cyclic voltammogram of $NiBr_4TPP$

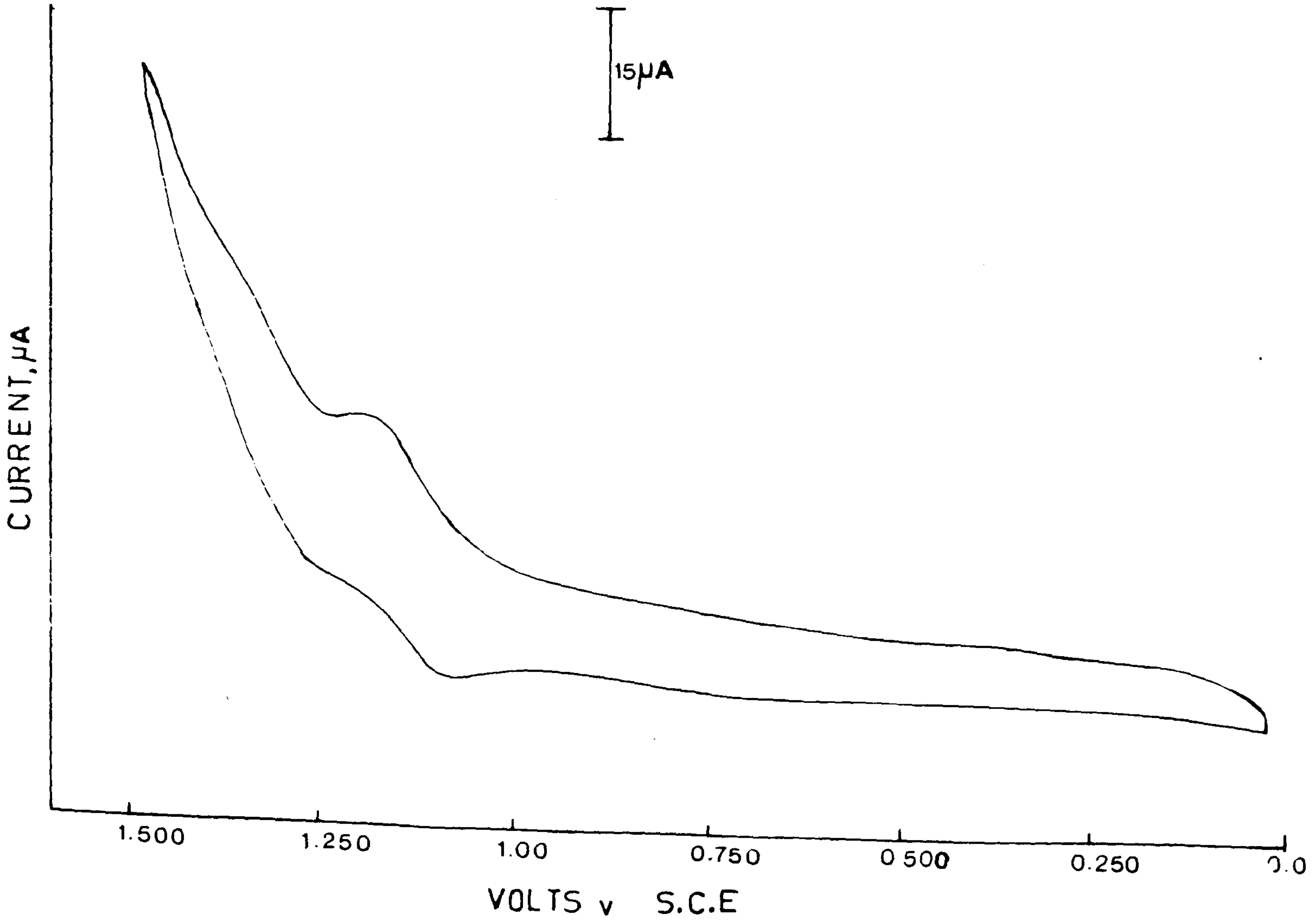


Fig.VI.5. Cyclic Voltammogram of $VOBr_4TPP$

VI.3 RESULTS AND DISCUSSION

The cyclic voltammograms are presented in figures VI.2, VI.3, VI.4, VI.5. The half-wave potentials for the metalloporphyrins studied in the present work are listed in table VI.1. The half-wave potentials of the corresponding TPP and tetracyano TPP systems are also presented for comparison. The tetrabromo system is expected to lead to a significant change in the pi acidity of porphyrin system. But the oxidation potentials indicate no significant change from the unsubstituted TPP. The oxidation potentials however lie in the intermediate range between those of TPP systems and tetracyano TPP systems. The difference between the first and second oxidation potentials is in the range 20 to 30 millivolts which is indicative of oxidation at the porphyrin site. We have also attempted to identify the first oxidation product by optical and esr spectroscopy. Oxidation of Zinc and Nickel tetrabromo TPP leads to the formation of radical cations as indicated by esr spectra (see figures VI.6 and VI.7). The oxidation was done using antimony pentachloride as oxidising agent. Interestingly we have observed that the esr spectrum of the radical cation of Zn(II) tetrabromo TPP is quite different from that of the corresponding system from Zn(TPP). Zn(TPP) on oxidation with antimony pentachloride yields a twelve-line spectrum with a spacing of about 1.4 Gauss. Normally one expects a

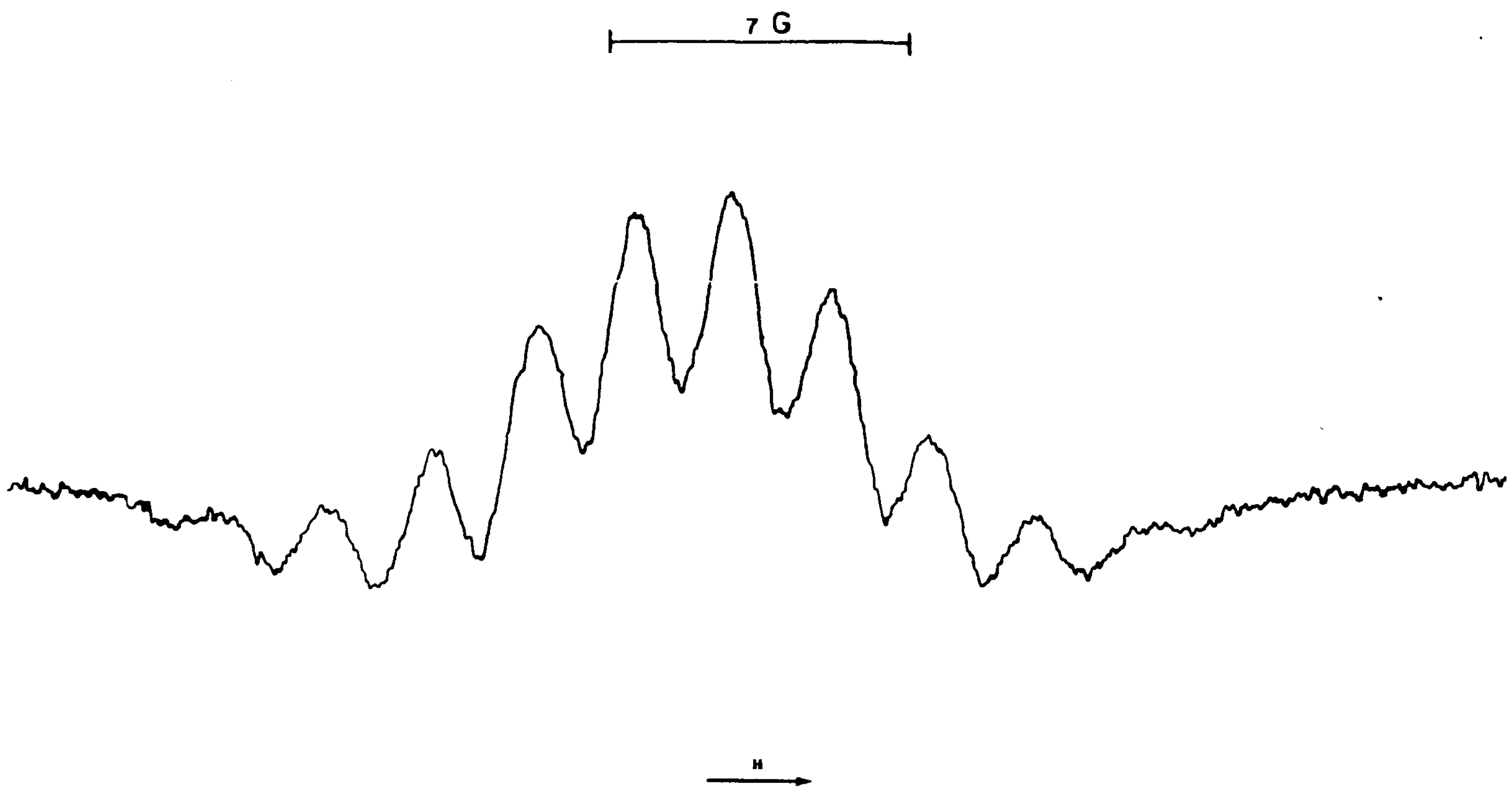


Fig.VI.6.(a). ESR spectrum of oxidized ZnTPP with $SbCl_5$ at room temperature

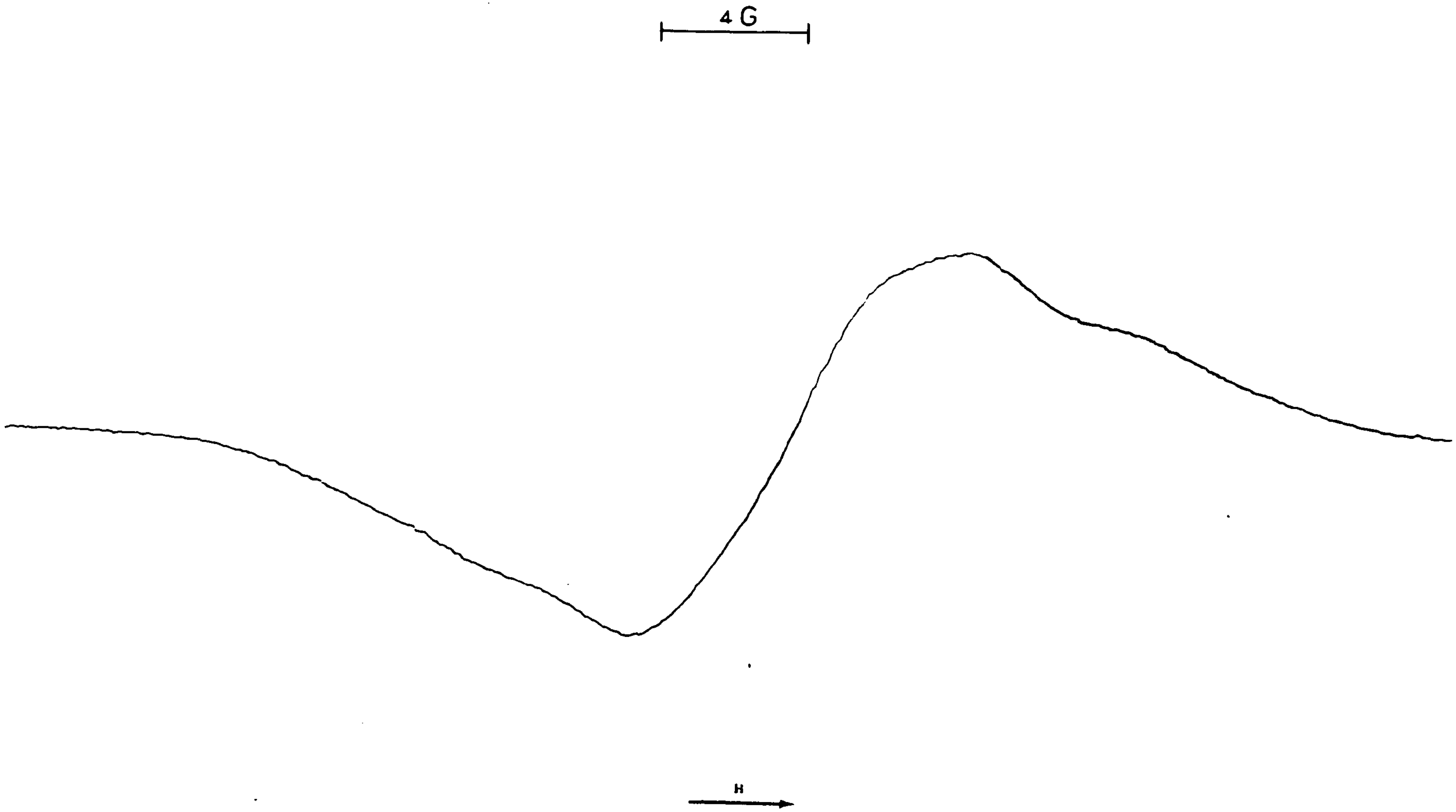


Fig.VI.6.(b). ESR spectrum of oxidized $ZnBr_4TPP$ with $SbCl_5$ at room temperature nine line spectrum which arises from the coupling of four equivalent nitrogen atoms. The twelve line spectrum may be interpreted as arising from four equivalent nitrogen atoms and one nucleus having spin 3/2 having the same coupling as the nitrogen. This nucleus could be a chlorine atom coming from the antimony pentachloride ion which is present as the counterion. In the case of Zn(II)tetrabromo TPP, we do not observe well-resolved lines. A broad three hump-pattern is observed in this case with an approximate spacing of four gauss. The contributing nuclei to the hyperfine structure could be the four nitrogen atoms, the four bromine atoms and the chlorine atom from counterion. Since there are too many parameters for adjustments we have not attempted any simulation of this spectrum.

The oxidation of Ni tetrabromo TPP is also assigned on the ligand. The esr and optical spectra of the species obtained on oxidation of the nickel complex with antimony pentachloride are presented in figures VI.7 and VI.8 respectively. The spectra indicate only the presence of a free radical species.

The oxidation potentials for vanadyl tetrabromo TPP occur at about 200 millivolts higher than the corresponding values of vanadyl TPP. The difference between the first and second oxidation potentials indicate that oxidation occurs in the ligand site as expected for vanadyl porphyrins.

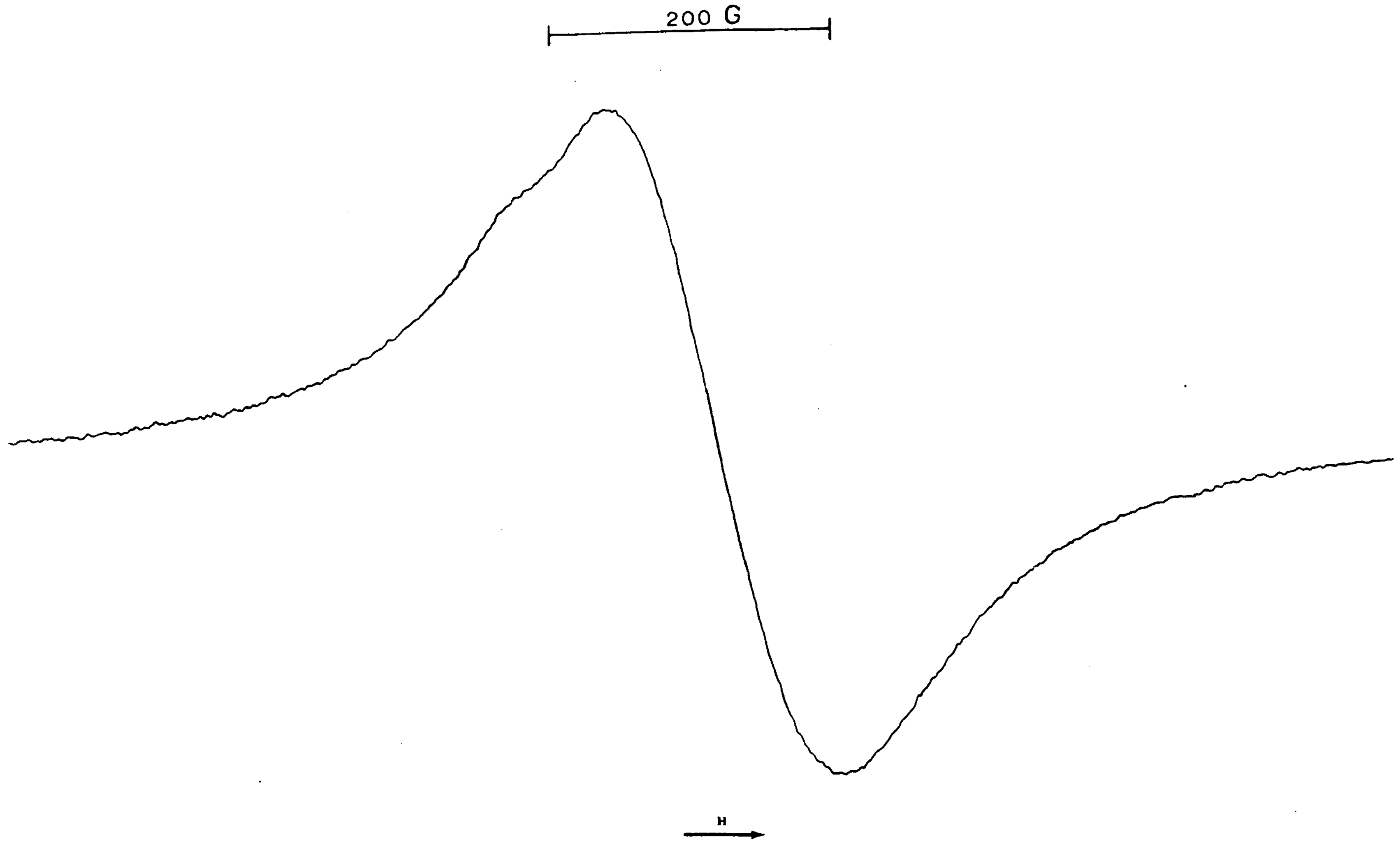


Fig.VI.7. ESR spectrum of $NiBr_4TPP$ with $Sbcl_5$ at room temperature

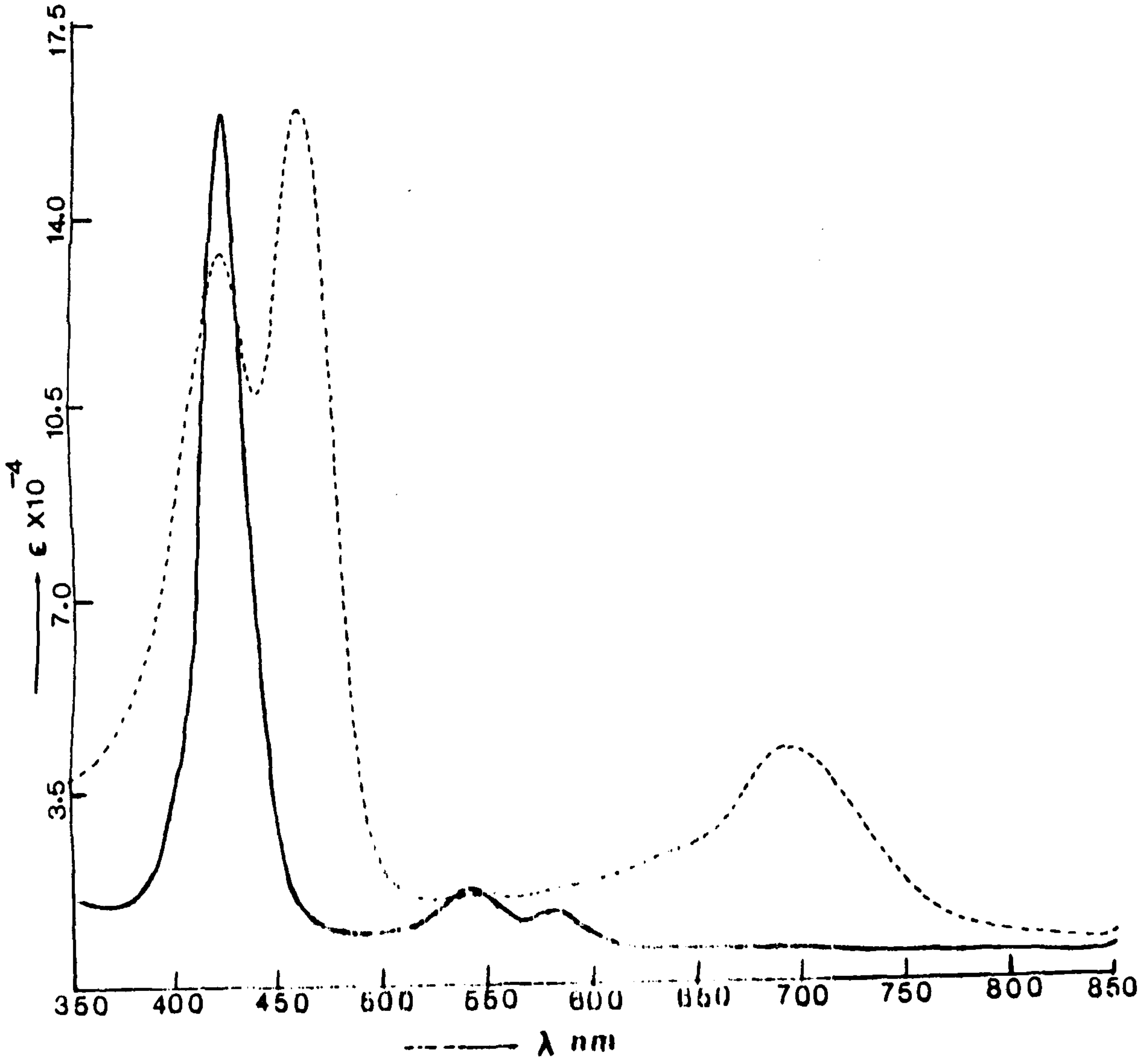


Fig.VI.8. (——) visible absorption spectrum of NiBr$_4$TPP in CH$_2$cl$_2$ (10^{-4}M), (----) visible absorption spectrum of NiBr$_4$TPP in CH$_2$cl$_2$ oxidized with Sbcl$_5$

VI.4 CONCLUSIONS

The foregoing cyclic voltammetric studies indicate that tetrabromo substitution increases the oxidation potentials of metalloporphyrins only to a marginal extent, compared to the tetracyano system. In general it has been observed that electrophilic substituents in the beta positions of the porphyrin ring changes the redox potentials significantly as compared with substitution on the phenyl ring in the meso positions. In the present cases, however, the effect of tetrabromo substitution on the oxidation potentials is only marginal.

REFERENCES

1. R.H. Felton, in the porphyrins, Edited by Dolphin (Academic Press, New York, 1979), Vol. V, p. 53.
2. L.A. Bottomley, L. Olson and K.M. Kadish, in Electrochemical and Spectrochemical Studies of Biological Redox Components, Advances in chemistry series, Edited by K.M. Kadish (American Chemical Society, Washington DC, 1982), 201, p. 279.
3. K.M. Kadish and M.M. Morrison, J. Am. Chem. Soc., 98, 3326 (1976).
4. K.M. Kadish and M.M. Morrison, BioInorg. Chem., 3, 480 (1977).
5. A. Girandeau, H.J. Callot and M. Gross, Inorg. Chem., 18, 201 (1979).
6. A. Girandeau, H.J. Callot, J. Jordan, I. Ezhar and Maurice Grass, J. Am. Chem. Soc., 101, 3857 (1979).

SUMMARY

SUMMARY

This thesis entitled "ESR AND ELECTROCHEMICAL STUDIES ON THE OXIDATION PRODUCTS OF SOME METALLOPORPHYRINS" discusses the results of investigations on the electron spin resonance and electrochemical studies on the oxidation products of some transition metal porphyrins. It consists of six chapters.

A brief review is presented in Chapter I on the structural studies (with emphasis on esr data) on the oxidation products of Ti, V, Cr, Mn, Fe, Ni and Cu porphyrins. This review provides a background material to give a proper perspective for the results of the investigations presented in subsequent chapters on the oxidation products of vanadyl porphyrins.

The details of the experimental procedures adopted in this thesis are presented in Chapter II.

The esr spectrum of the radical cation of vanadyl-octaethylporphyrin at liquid nitrogen temperature is presented in Chapter III. The esr spectrum indicates the presence of hyperfine coupling from two ^{51}V nuclei. Hence a dimer formation is indicated by the esr spectrum. The dimer has a triplet ground state in which the two unpaired π electrons pair up while the electrons on the vanadium atoms are ferromagnetically coupled. This dimer

is similar to that obtained from the radical cation of Cu(II) octaethylporphyrin. Assuming that the zero field interaction arises mainly from the dipolar coupling between the electrons on the vanadium atom, as has been done in the case of CuOEP, the esr spectrum has been computer-simulated to obtain the spin Hamiltonian parameters. The distance between the two unpaired electrons and hence between the two vanadium atoms has been obtained as 4.7Å.

The results of the cyclic voltammetric studies on Zn and VO complexes of proto and mesoporphyrins are presented in Chapter IV. The highlights of the experimental results are Zn and vanadyl protoporphyrin exist predominantly as dimers in solution in the concentration range 10^{-3}M. Vanadyl mesoporphyrin is monomeric in the same concentration range and both monomer and dimer exist in equilibrium at a concentration range 10^{-2}M. Oxidation pontentials have been obtained for both the monomer and dimer in the case of VO mesoporphyrin. The difference between the oxidation potentials of the monomer and dimer is about 150 millivolts.

The results of cyclic voltammetric studies presented in Chapter VI are substantiated by the detailed esr studies on the oxidation products of VO proto- and mesoporphyrins, which form the contents of Chapter V. An one-electron oxidation product of the dimer of VO (protoporphyrin) was identified in solution at room temperature from a study of the esr spectrum. This system has three unpaired electrons (one each on the vanadium atom and one unpaired π electrons per two molecules). The esr spectrum obtained at room temperature from this system has been shown to arise from $M_S = \pm \frac{1}{2}$ states of $S = \frac{3}{2}$ manifold. VO mesoporphyrin yields monomeric radical cation on one-electron oxidation at room temperature in the concentration range 10^{-3}M. At higher concentrations, a dimer similar to that obtained for VO protoporphyrin is formed. ESR spectrum of the dimer with $S = \frac{3}{2}$ state has been obtained at 77°K and is analyzed for the spin Hamiltonian parameters.

A monomeric radical cation of VO-mesoporphyrin has been identified around 10K. The parent compound has been oxidised with at least tenfold excess of antimony pentachloride. This system yields a typical triplet state-esr spectrum with a single ^{51}V hyperfine coupling. The distance between the unpaired π electron and the electron on the vanadium atoms has been obtained as 3.7Å, from the esr spectrum.

Cyclic voltammetric data on some of the metal complexes of tetrabromotetraphenyl porphyrin are presented in Chapter VI. It has been noticed that the oxidation potentials are only marginally affected by the substituents in the β positions, in contrast to the reduction potentials which are considerably shifted under similar conditions. Wherever possible esr and optical data had been used to assign the oxidation products.

APPENDIX

APPENDIX

The isotropic Hamiltonian for the three-spin system is given by eq. VI. The spin functions for the $S = \frac{3}{2}$ manifold are the following:

$$\left|\tfrac{3}{2},\tfrac{3}{2}\right> = \alpha(1)\ \alpha(2)\ \alpha(3)$$

$$\left|\tfrac{3}{2},\tfrac{1}{2}\right> =$$

$$(1/3^{\frac{1}{2}})\left[\alpha(1)\,\alpha(2)\,\beta(3) + \alpha(1)\,\beta(2)\,\alpha(3) + \beta(1)\,\alpha(2)\,\alpha(3)\right]$$

$$\left|\tfrac{3}{2},-\tfrac{1}{2}\right> =$$

$$(1/3^{\frac{1}{2}})\left[\alpha(1)\,\beta(2)\,\beta(3) + \beta(1)\,\alpha(2)\,\beta(3) + \beta(1)\,\beta(2)\,\alpha(3)\right]$$

$$\left|\tfrac{3}{2},-\tfrac{3}{2}\right> = \beta(1)\ \beta(2)\ \beta(3) \qquad \text{(A1)}$$

Using these functions and the Hamiltonian of eq 2, we get the eigenvalues, to first order, as

$$E_1 = (3/2)g\beta B/\hbar + a(m_I^{(1)} + m_I^{(2)}) + (1/4)J_1 + (1/2)J_2$$

$$E_2 = (1/2)g\beta B/\hbar + (1/6)a(m_I^{(1)} + m_I^{(2)}) - (1/12)J_1 - (1/6)J_2$$

$$E_3 = -(1/2)g\beta B/\hbar - (1/6)a(m_I^{(1)} + m_I^{(2)}) - (1/12)J_1 - (1/6)J_2$$

$$E_4 = -(3/2)g\beta B/\hbar - a(m_I^{(1)} + m_I^{(2)}) + (1/4)J_1 + (1/2)J_2$$

$$\text{(A2)}$$

where $g = (1/3)(2g_1 + g_2)$.

One observes the transition in solution.

$\left|\tfrac{3}{2},\tfrac{1}{2}\right> \leftrightarrow \left|\tfrac{3}{2},-\tfrac{1}{2}\right>$, which is independent of J_1 and J_2 with

$$\Delta E = g\beta B/\hbar + (a/3)(m_I^{(1)} + m_I^{(2)}) \qquad \text{(A3)}$$

On the other hand, if we use the spin functions in the $S = \frac{1}{2}$ manifold, we expect the following results:

$$\left|\frac{1}{2},\frac{1}{2}\right\rangle =$$

$$(1/6^{\frac{1}{2}})\left[\alpha(1)\beta(2)\alpha(3) - 2\alpha(1)\alpha(2)\beta(3) + \beta(1)\alpha(2)\alpha(3)\right]$$

$$\left|\frac{1}{2},-\frac{1}{2}\right\rangle =$$

$$(1/6^{\frac{1}{2}})\left[\alpha(1)\beta(2)\beta(3) - 2\beta(1)\beta(2)\alpha(3) + \beta(1)\alpha(2)\beta(3)\right]$$

The eigenvalues to first order are

$$E_1 = (1/2)g\beta B/\hbar + (1/3)a(m_I^{(1)} + m_I^{(2)}) + (1/12)J_1 - (1/3)J_2$$

$$E_2 = (-1/2)g\beta B/\hbar - (1/3)a(m_I^{(1)} + m_I^{(2)}) + (1/12)J_1 - (1/3)J_2$$

(A4)

and

$$E = g\beta B/\hbar + (2/3)a(m_I^{(1)} + m_I^{(2)}) \qquad \text{(A5)}$$

where $g = (4/3)g_1 - (1/3)g_2$.

Thus, we expect a spacing of (2/3)a for the hyperfine coupling if the system is in the $S = \frac{1}{2}$ state.