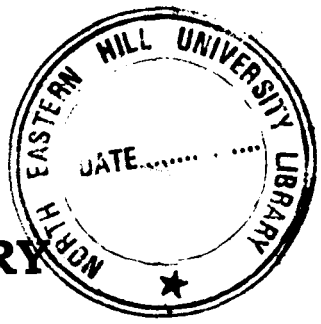
REDOX TUNING OF SOME METALLOPORPHYRINS IN MICELLAR MEDIUM

Thesis Submitted in Fulfillment
Of the Requirement
For the Degree of
Doctor of Philosophy

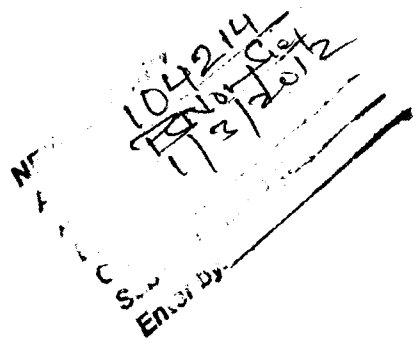
BY

DONBORLANG KHARBHIH



DEPARTMENT OF CHEMISTRY
SCHOOL OF PHYSICAL SCIENCES
NORTH EASTERN HILL UNIVERSITY
SHILLONG – 793022
APRIL 2010

Chemistry



DECLARATION

NORTH EASTERN HILL UNIVERSITY
SHILLONG – 793022
APRIL 2010

I, ***Shri Donborlang Kharbhih****, hereby declare that the subject matter of this thesis is the record of work done by me, that the contents of this thesis did not form basis of the award of any previous degree to me or to the best of my knowledge to any body else, and that the thesis has not been submitted by me for research degree in any other University/Institute.*

This is being submitted to the North Eastern Hill University, Shillong for the Ph.D. Degree in Chemistry.

DONBORLANG KHARBHIH
(CANDIDATE)

27/04/2010

Prof. B. Myrboh
HEAD
DEPARTMENT OF CHEMISTRY
NORTH EASTERN HILL UNIVERSITY
SHILLONG – 793022

Head
Department of Chemistry
North - Eastern Hill University
Shillong - 793022

27/04/10

Dr. A. Lemtur
SUPERVISOR
Reader
Department of Chemistry
North Eastern Hill University
Shillong- 793022

Dr. A. Lemtur
Department of Chemistry
North Eastern Hill University
Shillong - 793022

email: lemtur1@rediffmail.com
Tel. No. 0364 2722618
Fax No. 0364 2550076

CERTIFICATE

This is to certify that the thesis entitled ***"Redox Tuning of some Metalloporphyrins in Micellar Medium"*** *is based on the original work done by* ***Donborlang Kharbhih****, under my supervision in the Department of Chemistry, School of Physical Sciences, North Eastern Hill University, Shillong, Meghalaya. This work has not previously formed the basis for the award of any degree, diploma, fellowship or any other similar title and that it represents entirely an independent work on the part of the candidate.*

27/04/2010

Prof. B. Myrboh
HEAD
DEPARTMENT OF CHEMISTRY
NORTH EASTERN HILL UNIVERSITY
SHILLONG – 793022

Head
Department of Chemistry
North - Eastern Hill University
Shillong - 793022

27/04/10

Dr. A. Lemtur
SUPERVISOR
Reader
Department of Chemistry
North-Eastern Hill University
Shillong- 793022

Place : Shillong.
Date : 27th April, 2010.

ACKNOWLEDGEMENT

First of all, I would like to express my deepest and heartiest gratitude to my supervisor, ***Dr. A. Lemtur,*** *Reader, Department of Chemistry, NEHU, Shillong for his constant help and guidance, inspiration and encouragement throughout the course of this investigation.*

I would also like to express my sincere gratitude to Prof. B.Myrboh, Head, Department of Chemistry, NEHU, Shillong, for all the help rendered to me throughout the course.

I also thank all the faculty members of the Department of Chemistry, NEHU, Shillong for helping me in many ways throughout the course.

I also take this opportunity to thank all the non-teaching staff of the Department for helping me in many ways.

My special thanks go to my wife, Ms. Aicydalyne for all the help and moral support and for always being there for me at all times to lend a helping hand.

I thank my senior and lab mates Dr. A. Tomba Singh, Dr. (Mrs) Cornelia Lyngdoh and Dr. A. Murugan for their constant help and assistance throughout the course.

I also acknowledge my sincere thanks to all my research colleagues for helping and encouraging me throughout the course.

I also express my deep sense of gratitude to my parents, brothers and sisters for their patience, love, affection and constant encouragement throughout my academic career.

Above all I thank the Almighty God for all the blessings that He continues to shower upon me throughout my life and I am what I am now is because of Him. I also dedicate this work to Him, for without Him, none of this would have been possible.

DONBORLANG KHARBHIH

CONTENTS

LIST OF TABLES

LIST OF FIGURES

PREFACE

Porphyrin Chemistry is an old chemistry and is an area which is widely research. This is because porphyrins are not only biologically important but also find their way in the field of medicines and material sciences. Thus more porphyrins are synthesized and more new results appear in the literature every day. This provides us an opportunity to venture into this field of research.

Thus, this thesis embodies the new results and information on the Redox Tuning of some Manganese porphyrins, Zinc porphyrins and Copper porphyrins, in surfactant medium which are not reported so far in the literature.

This thesis consists of six chapters. The significance of metalloporphyrins in the biological system and their behaviour in aqueous micellar medium are highlighted in the **Introduction.**

Chapter 1 presents a Brief Review on the Redox Tuning of some Metalloporphyrins in Micellar medium.

Chapter 2 presents all the experimental techniques and measurements employed in the course of this investigation.

Chapter 3 deals with the determination of Critical Micellar Concentration (CMC) by using different methods.

Chapter 4 embodies the UV – Visible studies of some Manganese porphyrins in surfactant medium.

Chapter 5 deals with the Cyclic Voltammetric studies of some Manganese porphyrins in surfactant medium.

Chapter 6 presents The UV – Visible and Cyclic Voltammetric studies of some Zinc and Copper porphyrins in surfactant medium.

INTRODUCTION

Availability of a large number of porphyrin compounds in the literature opens up a wide avenue to study their physico - chemical properties. To a large extent porphyrins are studied as biological model systems. Moreover, porphyrin derivatives attract much more interest in Photo Dynamic Therapy, tumor localization and their importance as therapeutic drugs and targeting agents has been widely recognized. For developing clinically useful porphyrin drugs, it is essential to characterize porphyrin – micelle interactions. Most of the studies of porphyrin in micellar medium are in aqueous medium. Currently, large number of synthetically modified porphyrins are reported in the literature and most of them are not soluble in aqueous medium. Therefore, to study such porphyrins in surfactant/micellar medium, we need to use surfactants which are soluble in organic medium. Such studies may not be attractive and may look more of an adventurous activity.

However, we feel that knowing their behaviour/properties in mixtures of organic solvents will be interesting.

This prompted us to undertake this humble research work. Further, such studies are not readily available in the literature. With this very little information we undertook this investigation with the following objectives:

(i) Water insoluble Porphyrins and Metallo - porphyrins in medical and pharmaceutical fields.

(ii) To explore and to understand the physico – chemical properties of many synthetic water insoluble metalloporphyrins in surfactant medium.

CHAPTER - 1

A BRIEF REVIEW ON THE STUDIES OF PORPHYRINS IN MICELLAR MEDIUM

CHAPTER - 1

Most of the porphyrins studied in micellar medium are usually porphyrins that are soluble in aqueous medium. Therefore, most of the reported works in the literature are mainly the studies of porphyrins soluble in aqueous micellar medium. Advantage of such a system is that it can serve as a biological models for biomembranes[1-3]. The reactivity of a molecule in a micellar environment is more specific[4,5]. It is also known that naturally occurring porphyrins such as Protoporphyrin IX are readily solubilised in aqueous micelles[3]. Some of the studies of porphyrins in aqueous micellar systems /surfactants medium are reviewed in this chapter. A very brief review is presented here (citing only few) for comparison only. This is because we are not using aqueous micelles.

Dynamics of Porphyrin molecules in micelles. Pico – second time – resolved fluorescence anisotropy studies is reported[6]. In this study some Protoporphyrins IX derivatives are taken in aqueous micelles such as SDS, CTAB and TX – 100. It has been found that porphyrins are

solubilised as monomers in TX – 100 and CTAB near the interface. Further, the size of the micelle does not affect the molecular dynamics parameters.

Enhanced aggregation behavior of Antimony (V) porphyrins in poly fluorinated surfactants/clay hybrid micro environment is also reported[7].

Intercalation behaviour of metalloporphyrins in poly fluorinated surfactant/clay hybrid compounds[8] is reported. Intercalation and aggregation behavior of Sb(V) TSPP in sodium saponite clay layer and aggregation mechanisms are discussed. H- and J- type of Sb(V) TSPP dimer formation in the excess area of the hybrid compound is proposed.

Interaction of water – insoluble TPP with micelles probed by UV – Visible and NMR spectroscopy is also reported[9]. The methodology of incorporation of porphyrins (TPP derivatives) into micelles is discussed. To

established that the porphyrins are mono dispersed within the micelles, the soret band is examined. From the UV-Visible and NMR data obtained the mechanism of incorporation of porphyrin within the micelles are proposed. The incorporation depends on the nature of the substituent and the surfactant and the polarity of the substituent. Electrostatic interaction between the porphyrin and the micelle also plays important roles. It is also found that the porphyrin molecules diffused into the micellar solution are mono dispersed.

Electro chemistry of iron Protoporphyrin IX encapsulated in aqueous surfactant micelles is also reported[10]. The binding of the THF to iron porphyrin in SDS micelles stabilizes Fe^{2+} state. This has been characterized by 67mV anodic shift in the voltammogram.

Gandini et. al.[11] have reported the interaction of the $(H_2TPP)^{4-}$ with ionic surfactants: aggregation and location in micelles.

Kinetics of porphyrin metallation reaction in micellar medium is also reported[12].

The incorporation characteristics of tetra aryl porphyrins in bilayers formed from the synthetic surfactant are reported[13]. UV-Visible and Fluorescence studies show that at low concentration the porphyrins are present in the bilayer in monomeric species. The location of these species depends on the nature of substituents on the porphyrin. At higher concentration, aggregation occurs. Aggregation of THPP causes splitting of the B band (soret band) into two bands one of which is lower in intensity.

Aggregation behaviour of ($THPPH_2$) in the inner core and on the surface of CTAB micelles is also reported[14]. Absorbance Vs. Concentration plot below the 1.0×10^{-5} $molL^{-1}$ obeys the Beer's law but does not follow Beer's law beyond 1.0×10^{-5} mol L^{-1} indicating occurrence of porphyrin aggregation. The aggregation is reflected in the line width of the soret band. The line width of the soret band narrows

down. At higher concentration, the soret band position is also shifted and does not obey the Beer's law indicating an aggregation of $THPPH_2$ on the outer surface of CTAB micelles. From the narrowing of the width of the soret band and the blue shift of the soret band it has been suggested that the aggregation is face-to-face H - type aggregation.

Porphyrins in reverse micelles, the effect of the side – chain length on the aggregation has been studied by studying triplet – state life time[15]. Longer excited life time indicating dominating monomer while shorter excited life time indicating aggregation. The high amphiphilic nature of porphyrins promotes the firm embedding of the porphyrin molecules in the interfacial region of reverse micelles. Such embedding may prevent the porphyrins from aggregation and exists as monomers in the reverse micelles.

Protonation of amphiphilic porphyrins in SDS micellar solution is also repoorted[16]. The amphiphilic porphyrin taken is 5, 10, 15, 20-tetra (4-hydroxy phenyl)

porphyrin. Titration with HCl shows red shift of the band at 652nm to 691nm with an isosbestic point at 445nm. On the other hand titration with NaOH shows regeneration of free base and the band at 652nm disappears and an isosbestic point occurs at 432nm. Thus a microphase transition is observed.

REFERENCES

1. J.H. Fendler, *Science*, **223**, 886 (1984).

2. J.H. Fendler, *Annu. Rev. Phys. Chem.*, **35**, 137 (1984).

3. S. Majumdar, S. Mitra, *Struct. Bonding*, **81**, 115, (1993).

4. R.G. Weiss, V. Ramamurthy, G.S. Hammond, *Acc. Chem. Res.*, **26**, 530 (1993).

5. K. Kalyansundaram, *Photochemistry in micro heterogeneous systems*, Acad. Press, New York, 1991.

6. N.C. Maiti, S. Majumdar and N. Periasamy, *J. Phys. Chem.*, **99**, 10708 – 10715 (1995).

7. L.A. Lucia, T. Yui, R. Sasai, S. Takagi, K. Takagi, H. Yoshida, D.G. Whitten and H. Inoue, *J. Phys. Chem. B*, **107**, 3789 – 3797 (2003).

8. Matsuoka, T. Yui, R. Sasai, K. Takagi, H. Inoue, *Mol. Cryst. Liq. Cryst.* **341**, 333, (2000).

9. N. Vermathen, E.A. Louie, A.B. Choderl, S. Ried and U. Simomis, *Langmuir,* **16**, 210-221 (2000).

10. D.K. Das and O.K. Medhi, *Indian J. of Chem.*, **37A**, 980-984 (1998).

11. S.C.M. Gandini, V.E. Yushmanov, I.E. Borissevitch and M. Tabak, *Langmuir*, **15**, 6233-6243 (1999).

12. V.H. Rao and V. Krishnam, *Inor. Chem.*, **24**, 3538 – 3541 (1985).

13. J.H. Vaesch, M.C. Feiters, A.M. Peters and R.J.M. Nolte, *J. Phys. Chem.*, **98**, 5541-5551 (1994).

14. C. MA, Y.H. Zhang, C.S. Fu and Q.S. Li, *Chinese Chem. Letts.*, **11(10)**, 929 – 930 (2000).

15. J.H. Yu, Y.X. Weng, X.S. Wang, L. Zhang, B.W. Zhang and Y. Cao, *Chinese Chem. Letts.*, **14(8)**, 844 – 847 (2003).

16. X.H. Zhao and Y.H. Zhang, *Chinese Chem. Letts.*, **15(10)**, 1205 – 1208 (2004).

CHAPTER - 2

EXPERIMENTAL SECTION

CHAPTER – 2

2.1. INTRODUCTION:

This chapter deals with the general experimental techniques involving purification of solvents and reagents, preparation of supporting electrolyte, synthesis of porphyrins and metalloporphyrins, determination of CMC, descriptions of the UV – Visible spectrophotometric measurements and Cyclic Voltammetric instrumentation.

2.2. PURIFICATION OF SOLVENTS AND REAGENTS:

2.2.1. Dichloromethane :

Dichloromethane was refluxed with anhydrous K_2CO_3 for about 2 hours and then distilled and stored over molecular sieves (Linde-4A).For UV - Visible spectroscopy and Cyclic Voltammetric measurements, Dichloromethane of spectroscopic grade was used.

2.2.2. **Chloroform** :

Chloroform was purified by passing through a column of basic alumina and then the eluate was distilled twice before using. For recrystallization and other physical measurements, spectroscopic grade solvent was used.

2.2.3. **Methanol** :

Drum samples were refluxed over anhydrous CaO for about 2 hours and distilled with iodine and Mg turnings twice before using. For physical measurements, spectroscopic grade solvents were used.

2.2.4. **Pyrrole** :

Pyrrole was purified by distillation under reduced pressure from KOH pellets and stored in a dark sealed vessel.

2.2.5. **2-Methoxybenzaldehyde**:

2-Methoxybenzaldehyde was distilled and used.

2.2.6. 4-Methoxybenzaldehyde:

4-Methoxybenzaldehyde was distilled and used.

2.2.7. 1-Naphthaldehyde:

1-Naphthaldehyde was distilled and used.

2.2.8. 2-Methylbenzaldehyde:

2-Methylbenzaldehyde was distilled and used.

2.2.9. 3-Methylbenzaldehyde:

3-Methylbenzaldehyde was distilled and used.

2.3. 4-Methylbenzaldehyde:

4-Methylbenzaldehyde was distilled and used.

2.3.1. Reagent grade SDS, TX – 100, Cetyl trimethyl ammonium bromide(CTAB), Triethylamine, Manganese acetate, Zinc acetate, Copper acetate, Sodium acetate, BF_3-etherate, p-Chloranil, DDQ, Sodium carbonate, Perchloric acid, Tetrabutylammonium bromide, etc. were used as received.

2.4. PREPARATION OF SUPPORTING ELECTROLYTE [1,2]:

Preparation of supporting electrolyte, Tetrabutylammonium perchlorate (TBAP) involves two steps as follows:

i) Preparation of Sodium perchlorate:

Sodium perchlorate was prepared by neutralization of Sodium carbonate with Perchloric acid. The volume of the reaction mixture was reduced by concentrating it in a water bath and then allowed to cool when crystals of sodium perchlorate separate out. The crystals were filtered out and recrystallized several times from distilled water.

ii) Preparation of Tetra-n-butylammonium perchlorate (TBAP):

A saturated solution of tetrabutylammonium bromide was prepared in distilled water. To this solution, sodium perchlorate crystals were added when

crystals of TBAP separates out instantly. Constant stirring is done till precipitation of TBAP is completed. The crystals of TBAP were filtered out, washed several times with distilled water and then recrystallized twice from methanol. Glassy crystals of TBAP were formed and the purity of the product was check by running a Cyclic Voltammogram.

2.5. SYNTHESIS OF PORPHYRINS:

2.5.1. meso-5,10,15,20 – Tetrakis(2-methoxyphenyl) porphyrin:

meso - 5,10,15,20 – Tetrakis (2-methoxyphenyl) porphyrin, [T(2-OMeP)P] was prepared by the method of Wagner and Lindsey[3]. In a 500mL round bottom flask fitted with a reflux condenser and a nitrogen bubbler,2-Methoxybenzaldehyde (0.485mL, 2.98mmol) and pyrrole (210μL, 2.98 mmol) were dissolved in 300mL of distilled chloroform. After purging the solution with nitrogen gas for 5 minutes, the reaction was initiated by adding catalytic amount of

BF_3-etherate (120 μL of 2.5M stock solution). The reaction mixture was then stirred at room temperature for 1 hour. The progress of the reaction was monitored by taking aliquots of the reaction mixture at regular intervals, oxidizing with *p*-chloranil, followed by absorption spectrophotometry[4]. At the end of 1 hour, *p*-Chloranil (0.7327g, 2.98mmol) was added in powder form and the reaction mixture was gently refluxed (61°C) for 1 hour. The completion of the reaction was monitored by UV –Vis spectroscopy and ^1H NMR spectroscopy. The mixture was evaporated to dryness and the crude product was washed with methanol until the filtrate was clear. It was then purified by silica gel column chromatography using dichloromethane as the eluent. The purity of the product was checked by TLC and UV – Visible absorption spectra.

λ_{max} (nm) (in chloroform): 414, 513, 546, 588, 642.

2.5.2. meso-5,10,15,20–Tetrakis(4-methoxyphenyl) porphyrin:

meso - 5, 10, 15, 20 – Tetrakis (4 - methoxy phenyl) porphyrin, [T(4-OMeP)P] was prepared by the method of Wagner and Lindsey[3] by taking 4-Methoxybenzaldehyde and pyrrole as described above.

λ_{max} (nm) (in chloroform): 421, 518, 556, 593, 649.

2.5.3. meso-5,10,15,20–Tetrakis(1-naphthyl) porphyrin, (TNP):

TNP was prepared by the method of Wagner and Lindsey[3] as described above by taking 1-Naphthaldehyde and pyrrole.

λ_{max} (nm) (in chloroform): 423, 515, 548, 589, 644.

2.5.4. meso-5,10,15,20 – Tetrakis(2-methylphenyl) porphyrin:

Meso - 5, 10, 15, 20 – Tetrakis (2 -methylphenyl) porphyrin, [T(2-MeP)P] was prepared by the method as described in the literature[5] by refluxing the reaction mixture containing 3mL of freshly distilled pyrrole and 5.02mL of 2-Methylbenzaldehyde in 250mL of reagent grade Propionic acid for 30 minutes. The reaction mixture was cooled to room temperature and kept standing for 6 days. The solid material was collected, washed with methanol and purified by column chromatography using dichloromethane as an eluent. The purity of the product was checked by TLC and UV-visible spectra.

λ_{max} (nm) (in dichloromethane): 484, 514, 549, 588, 645.

2.5.5. meso-5,10,15,20 – Tetrakis(3-methylphenyl) porphyrin:

Meso - 5, 10, 15, 20 – Tetrakis (3 -methylphenyl) porphyrin, [T(3-MeP)P] was prepared by the method as described above for [T(2-MeP)P].

λ_{max} (nm) (in dichloromethane): 484, 514, 549, 588, 645.

2.5.6. meso-5,10,15,20 – Tetrakis(4-methylphenyl) porphyrin:

Meso - 5, 10, 15, 20 – Tetrakis (4 -methylphenyl) porphyrin, [T(4-MeP)P] was prepared by the method as described in the literature[6-8].

λ_{max} (nm) (in dichloromethane): 486, 516, 512, 552, 649.

2.6. SYNTHESIS OF METALLOPORPHYRINS:

2.6.1. MANGANESE PORPHYRINS:

(Figure – 2.1)

2.6.1.1. $Mn^{(III)}$[T(2-OMeP)P] OAc:

Mn[T(2-OMeP)P] OAc was prepared as described in the literature[9,10]. The reaction was carried out by taking a mixture of Manganese (II) acetate (335mg, 1.37mmol) in methanol and [T(2-OMeP)P] (358.2mg, 0.42mmol) in chloroform and then refluxed in a 100mL round bottom flask for about 5 hours. The completion of the reaction was monitored by UV – Visible absorption spectroscopy. The crude product was washed with water several times and then purified by silica gel column chromatography using dichloromethane as an eluent. The purity of the product was checked by TLC and UV-visible spectra.

λ_{max} (nm) (in chloroform): 471, 574, 607.

Similarly, Mn[T(4-OMeP)P]OAc, Mn[TNP]OAc, Mn[T(2-MeP)P]OAc, Mn[T(3-MeP)P]OAc and Mn[T(4-MeP)P]OAc were prepared according to the above procedure as described in the literature[9,10].

2.6.1.2. $Mn^{(III)}$[T(4-OMeP)P] OAc

λ_{max} (nm) (in chloroform): 480, 578, 617.

2.6.1.3. $Mn^{(III)}$[TNP]OAc:

λ_{max} (nm) (in chloroform): 479, 580, 614.

2.6.1.4 $Mn^{(III)}$[T(2-MeP)P] OAc:

λ_{max} (nm) (in chloroform): 476, 572, 605.

2.6.1.5. $Mn^{(III)}$[T(3-MeP)P] OAc:

λ_{max} (nm) (in chloroform): 480, 582, 617.

2.6.1.6. $Mn^{(III)}$[T(4-MeP)P] OAc:

λ_{max} (nm) (in chloroform): 480, 581, 619.

2.6.2. COPPER PORPHYRINS: (Figure – 2.2)

2.6.2.1. Cu[T(4-OMeP)P] :

Cu[T(4-OMeP)P] was prepared as described in the literature[9,10].The reaction was carried out by taking a mixture of Cupric (II) acetate (335mg, 1.37mmol) in methanol and [T(4-OMeP)P] (358.2mg, 0.42mmol) in chloroform and then refluxed in a 100mL round bottom flask for about 5 hours. The completion of the reaction was monitored by UV – Vis absorption spectroscopy. The crude product was washed with water several times and then purified by silica gel column chromatography using dichloromethane as an eluent. The purity of the product was checked by TLC and UV-visible spectra.

λ_{max} (nm) (in chloroform): 419, 541.

2.6.2.2. Cu [TNP]:

Cu[TNP] was described according to the above procedure as described in the literature[9,10].

λ_{max} (nm) (in chloroform): 420, 540.

2.6.3. ZINC PORPHYRINS: (Figure – 2.2)

2.6.3.1. Zn[T(4-OMeP)P] :

Zn[T(4-OMeP)P] was prepared as described in the literature[9,10]. The reaction was carried out by taking a mixture of Zinc acetate (335mg, 1.37mmol) in methanol and [T(4-OMeP)P] (358.2mg, 0.42mmol) in chloroform and then refluxed in a 100mL round bottom flask for about 3 hours. The completion of the reaction was monitored by UV –Vis absorption spectroscopy. The crude product was washed with water several times and then purified by silica gel column chromatography using dichloromethane as an eluent. The purity of the product was checked by TLC and UV-visible spectra.

λ_{max} (nm) (in chloroform): 423, 473, 549, 590.

2.6.3.2. Zn [TNP]:

Zn[TNP] was described according to the above procedure as described in the literature[9,10].

λ_{max} (nm) (in chloroform): 424, 548, 601.

2.7 INSTRUMENTATION :

2.7.1. DETERMINATION OF CMC:

Determination of CMC of SDS was done by Conductivity method[11-13] and Cyclic Voltammetry method[14 - 16].

In Conductivity method, conductivity was measured at room temperature by SYSTRONICS CONDUCTIVITY METER 304. 100 mL of methanol was taken in a beaker and to it 0.5mL of 10^{-3}M SDS solution (in methanol) was added. The conductivity of the solution is then measured. The process was continued for each addition of SDS solution till saturation was attained. A graph of Conductivity

against SDS concentration was plotted and the break point in the plot gives the CMC.

In Cyclic Voltammetry method, the electro chemical measurements were measured by CHI 620B ELECTROCHEMICAL ANALYZER. 20mL of 10^{-3}M porphyrin solution (redox active material) in methanol was taken and to it 0.5ml of 10^{-3}M SDS solution (in methanol) was added. TBAP was used as the supporting electrolyte. The redox potential of the solution is then measured. Nitrogen gas was bubbled to the mixture before every measurement. The process was continued for each addition of SDS solution till saturation was attained. A graph of Peak current (i_p) against SDS concentration was plotted and the abrupt change in the values was considered as the CMC point.

Similarly, for CTAB the CMC was determined by conductivity method.

For TX – 100, the CMC was taken as reported in the literature[11].

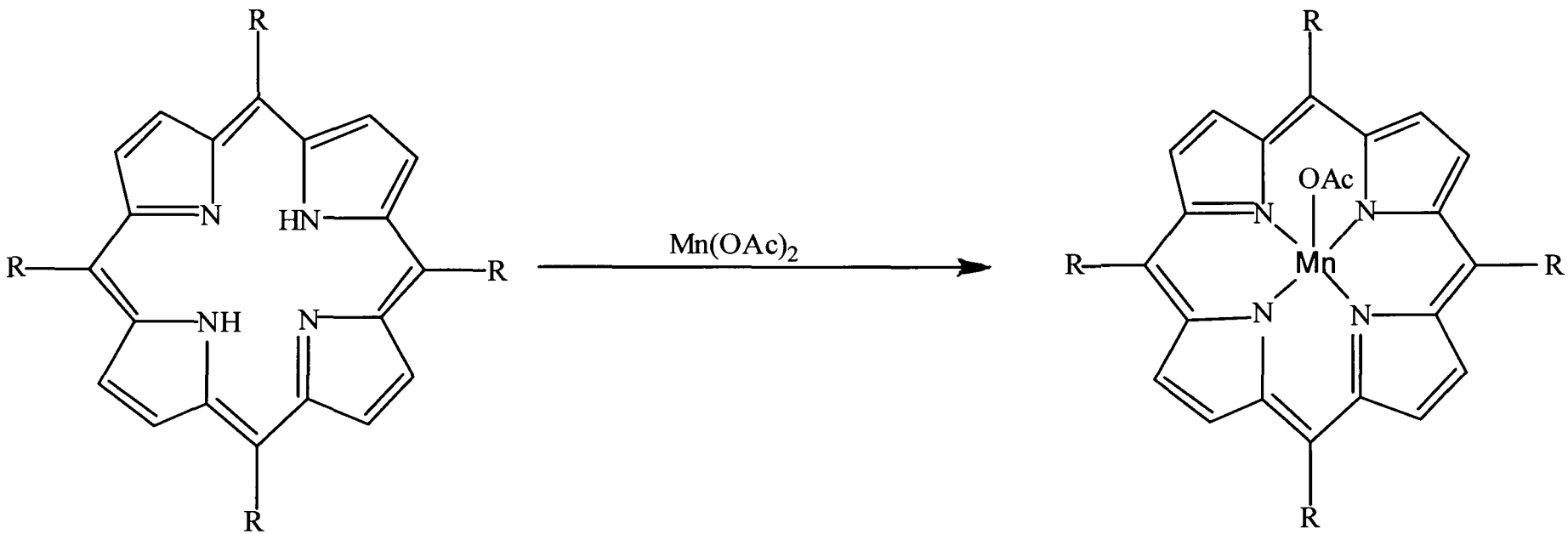
2.7.2. UV-VIS SPECTROPHOTOMETRIC MEASUREMENTS:

UV- Vis absorption spectroscopy was measured at room temperature by PERKIN ELMER LAMBDA 25 UV/VIS SPECTROPHOTOMETER. 2mL of the metalloporphyrin (10^{-5}M) solution in chloroform is taken in the spectrophotometric cuvette and UV - Visible absorption spectra were recorded in between the range 350 – 750 nm. This process was continued for metalloporphyrin – surfactant (10^{-1}M, in methanol) mixture. 0.3 mol. of triethylamine was added to the solution in the cuvette at the end of each measurement, shaken thoroughly and allowed to stand for some time and then the spectra of the mixture are recorded again.

2.7.3. CYCLIC VOLTAMMETRIC MEASUREMENTS:

Redox potentials were measured by using CHI 620B ELECTROCHEMICAL ANALYZER. The electrolytic cell consists of a platinum electrode (working electrode), an Ag/AgCl electrode (reference electrode) and a platinum wire (auxiliary electrode). TBAP was used as the supporting electrolyte. Redox potential of 10^{-3}M metalloporphyrin solution in chloroform was measured. This process was continued for a mixture of 10^{-3}M metalloporphyrin solution (in chloroform) and 10^{-1}M SDS (in methanol). Nitrogen gas was bubbled before every measurement to accomplish deaeration.

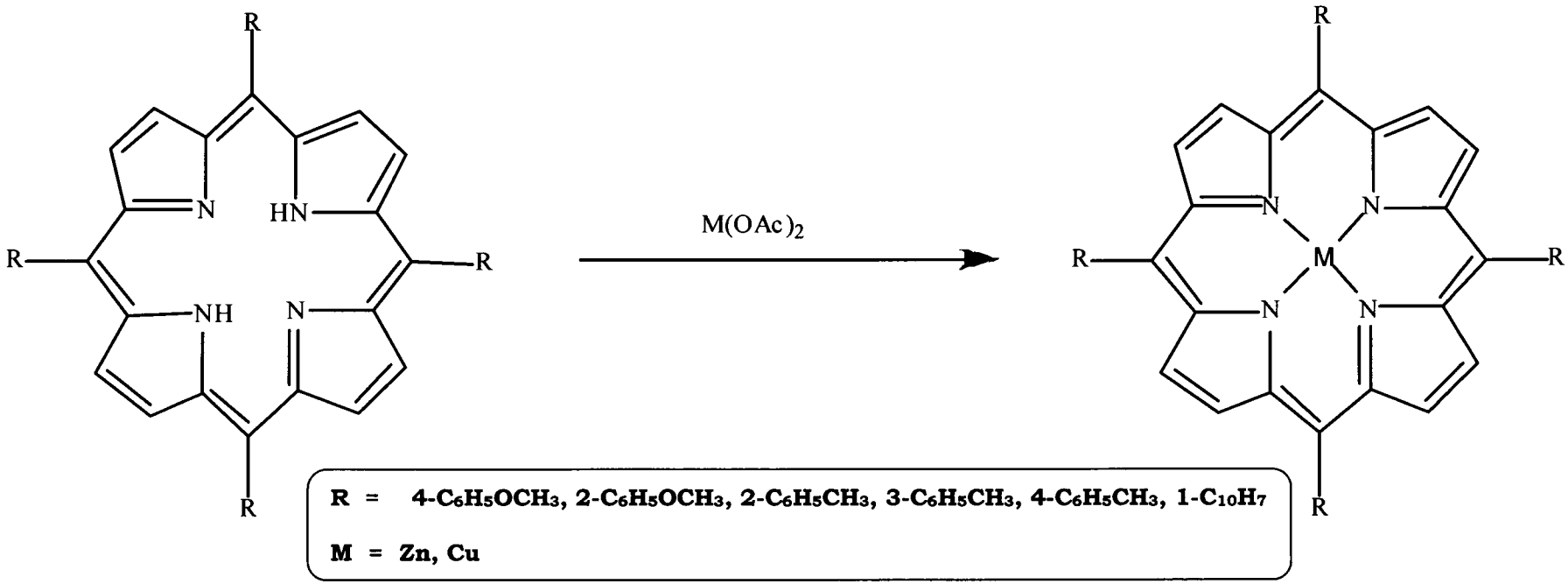
Calibration of $E_{1/2}$ values and diffusion current were done by using a known concentration of pure ZnTPP in dichloromethane /TBAP medium.



R = 4-$C_6H_5OCH_3$, 2-$C_6H_5OCH_3$, 2-$C_6H_5CH_3$, 3-$C_6H_5CH_3$, 4-$C_6H_5CH_3$, 1-$C_{10}H_7$

PORPHYRIN **Mn PORPHYRIN**

Figure: 2.1: ***Scheme Showing The Synthesis Of Manganese Porphyrin.***



PORPHYRIN **METALLO PORPHYRIN**

Figure: 2.2: ***Scheme Showing The Synthesis Of Zinc And Copper Porphyrin.***

REFERENCES:

1. *Hand book of Preparative Inorganic Chemistry*, Edited by G.Brauer (Academic Press, New York, 1965) **Vol. II.** pp 1185.

2. *Inorganic Synthesis*, Editor-in-Chief: Therald Moellur (McGraw Hill, 1975), **Vol.5**, pp154.

3. Richard W. Wagner, David S. Lawrence, and J. S. Lindsey., *Tetrahedron Letters*, **28**, 3069 (1987).

4. J.S. Lindsey, H.C. Hsu, I.C. Schreiman, *Tetrahedron Lett.*, **27**, 4969 (1986).

5. J.S. Lindsey and R.W. Wagner, *J. Org .Chem..*, **54**, 828 – 836 (1989).

6. D.W. Thomas and A.E. Martell, *J. Am. Chem. Soc.*, **78**, 1335 – 1338 (1956).

7. D.W. Thomas and A.E. Martell, *J. Am. Chem. Soc.*, **78**, 1338 – 1343 (1956).

8. K. Uneo and A.E. Martell, *J. Phys. Chem.*, **60**, 934 – 938 (1956).

9. J.S. Erdman, V.G. Ramsey, N.W. Kalenda and W.E. Hanson, *J. Am. Chem. Soc.*, **78**, 5844 – 5847 (1956).

10. A.D. Adler, F.R. Longo, F. Kampus, and J.Kim, *J. Inorg. Nucl. Chem.* **32**, 2443 (1970).

11. J.H. Fendler, E.J. Fendler, *Catalysis in Micellar and Macromolecular Systems*; Academic Press: New York, 1975.

12. A. Dominguez, A. Fernandez, N. Gonzalez, E. Iglesias and L. Montenegro, *J. Chemical Education*, **74**, 1227 (1997)

13. E. Fuguet, C. Rafols, M. Roses and E. Bosch, *Analytica Chimica Acta,* **548**, 95 – 100 (2005).

14. A.B. Mandal and B.U. Nair, *J. Phys. Chem.*, **95**, 9008 – 9013 (1991).

15. A.B. Mandal, B.U. Nair and D. Ramaswamy, *Langmuir*, **4**, 736 – 739 (1988).

16. A.B. Mandal, B.U. Nair and D. Ramaswamy, *Bull. Electrochem.*, **4**, 565 – 569 (1988).

CHAPTER - 3

DETERMINATION

OF CMC

OF

SDS AND CTAB

CHAPTER - 3

3.1. INTRODUCTION:

Determination of CMC of SDS and CTAB in organic solvents such as methanol, chloroform and in their mixtures of different proportions are done by the conductivity method. This method may not give accurate CMC values, yet we have used this method simply to obtain approximate values because all UV – Visible and Cyclic Votammetric measurements are carried out well above the CMC.

Cyclic Voltammetric technique is also used to monitor the CMC. A solution of 10^{-3}M metalloporphyrin in methanol is used. Voltammograms at various concentration of SDS are recorded. A plot of i_p Vs. concentration of SDS gives a break point at CMC.

3.2. RESULTS:

The plot of conductivity Vs. concentration of SDS is presented in the Figure: 3.2.a. and from the plot the CMC of SDS in methanol is found to be 6.4 x 10^{-3}M. All measurements were done at room temperature.

The CMC of SDS in 1:1 solution of methanol : chloroform is also determined and the plot is represented in the Figure: 3.2.b. From the plot the CMC is found to be 3.6 x 10^{-3}M.

The CMC of CTAB in chloroform is determined. The plot of conductivity Vs. concentration of CTAB is presented in the Figure: 3.2.c. From the plot the value of CMC is found to be 4.6 x 10^{-3}M.

The Cyclic Voltammogram of 10^{-3}M solution of Mn[T(4-OMeP)P]OAc in methanol in various concentrations of SDS (in methanol) is presented in the Figure: 3.2.d. The plot of i_p Vs. concentration of SDS is presented in the Figure: 3.2.e. From the plot the CMC is found to be 6.0 x 10^{-3}M.

3.3. DISCUSSION:

From our experimental data the CMC of SDS in methanol is found to be 6.4 x 10^{-3}M which is lower than that in aqueous medium. Again the CMC of SDS in 1:1 methanol : chloroform is found to be lower than that in pure methanol.

The CMC of CTAB in chloroform is found to be 4.6 x 10^{-3}M.

The CMC of SDS from the Cyclic Voltammetric measurements is found to be 6.0 x 10^{-3}M which is close to the value obtained by the conductivity method.

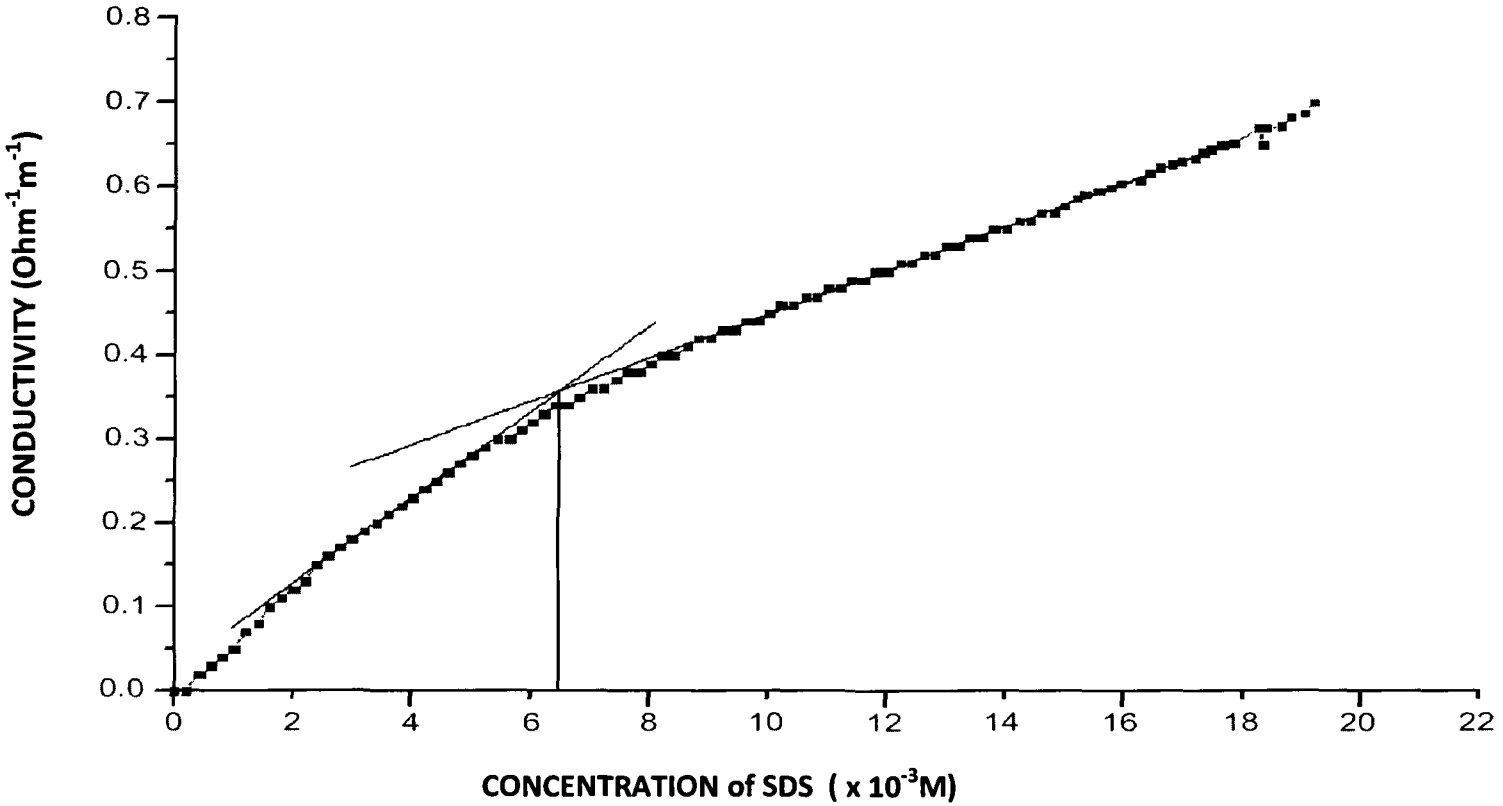


Figure : 3.2.a. Plot of Conductivity Vs. Concentration of SDS in pure methanol at Room Temperature.

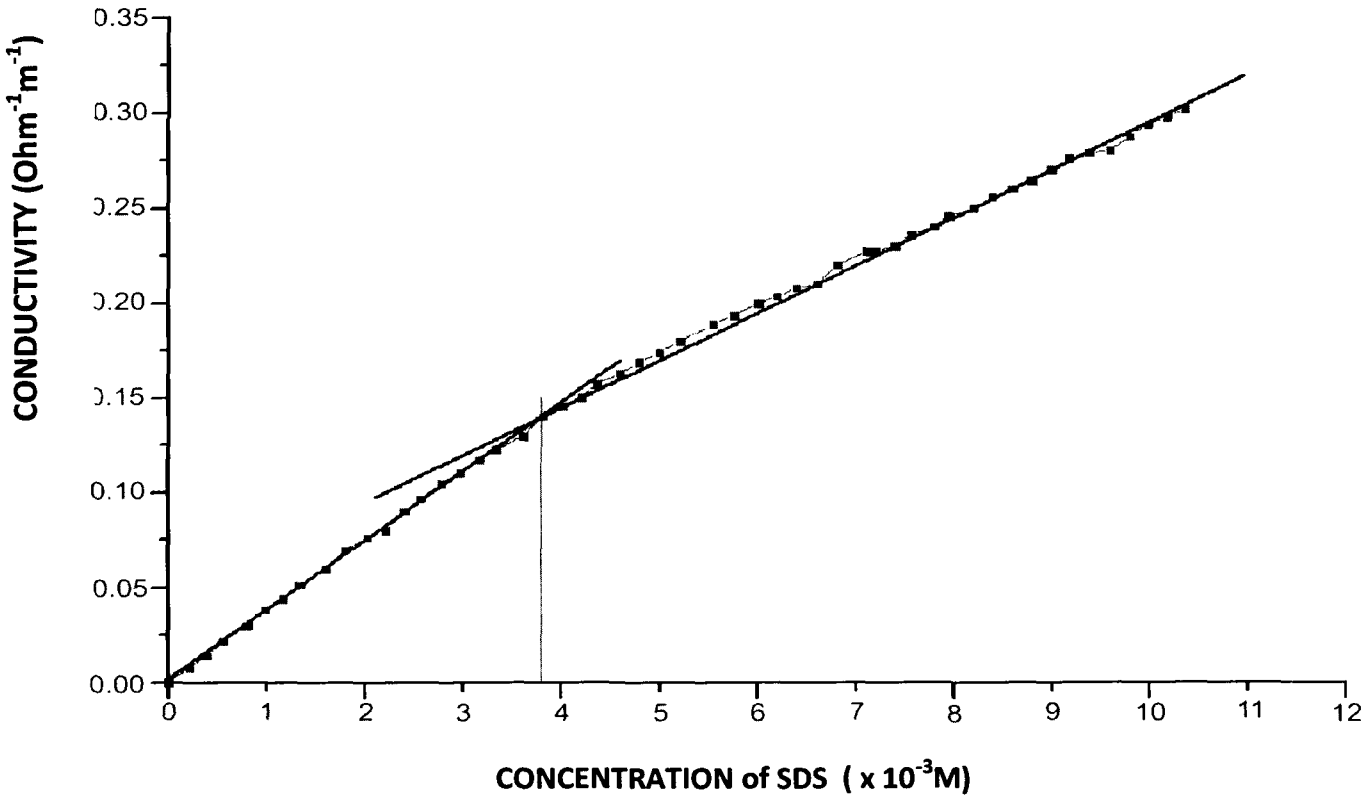


Figure : 3.2.b. Plot of Conductivity Vs. Concentration of SDS in 1:1 solution of CH_3OH : $CHCl_3$ at Room Temperature.

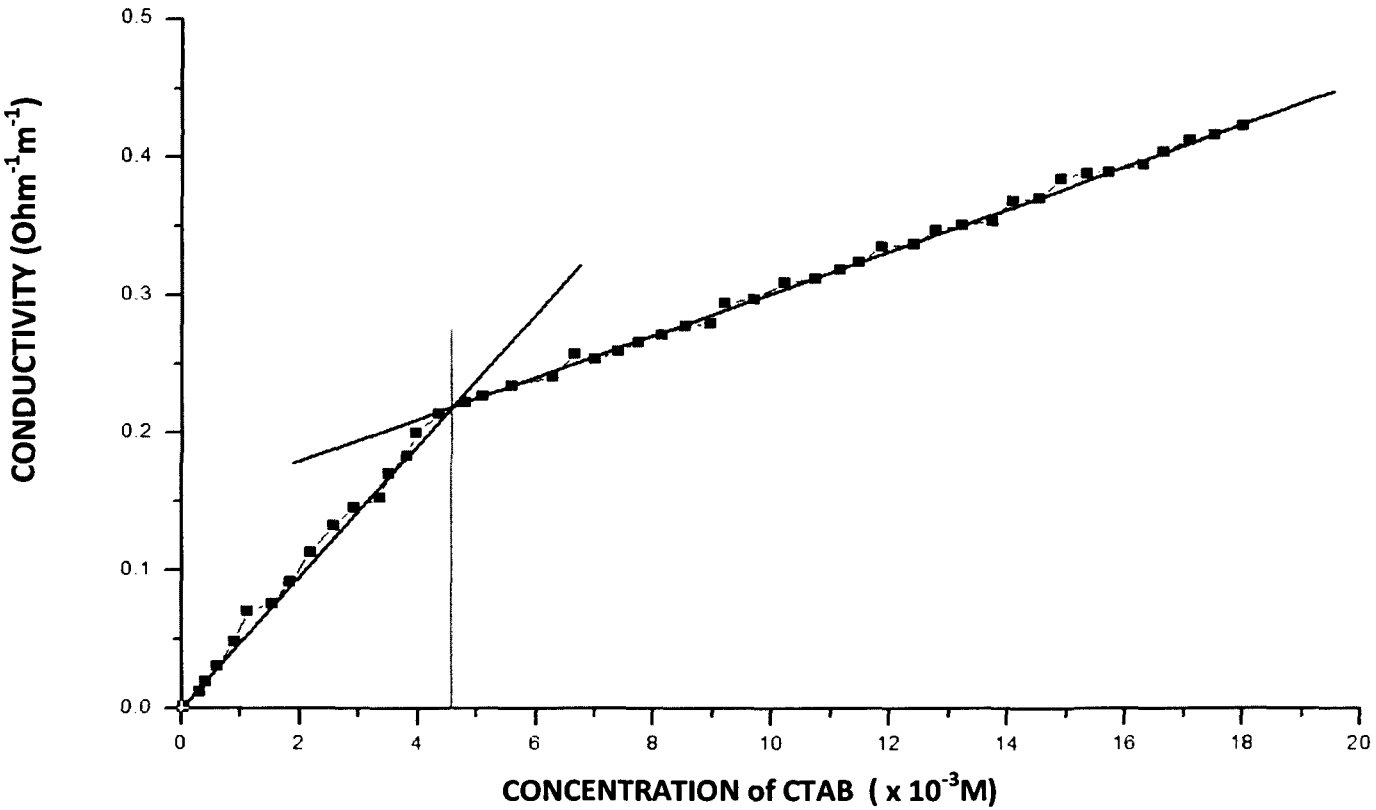


Figure : 3.2.c. Plot of Conductivity Vs. Concentration of CTAB in pure chloroform at Room Temperature.

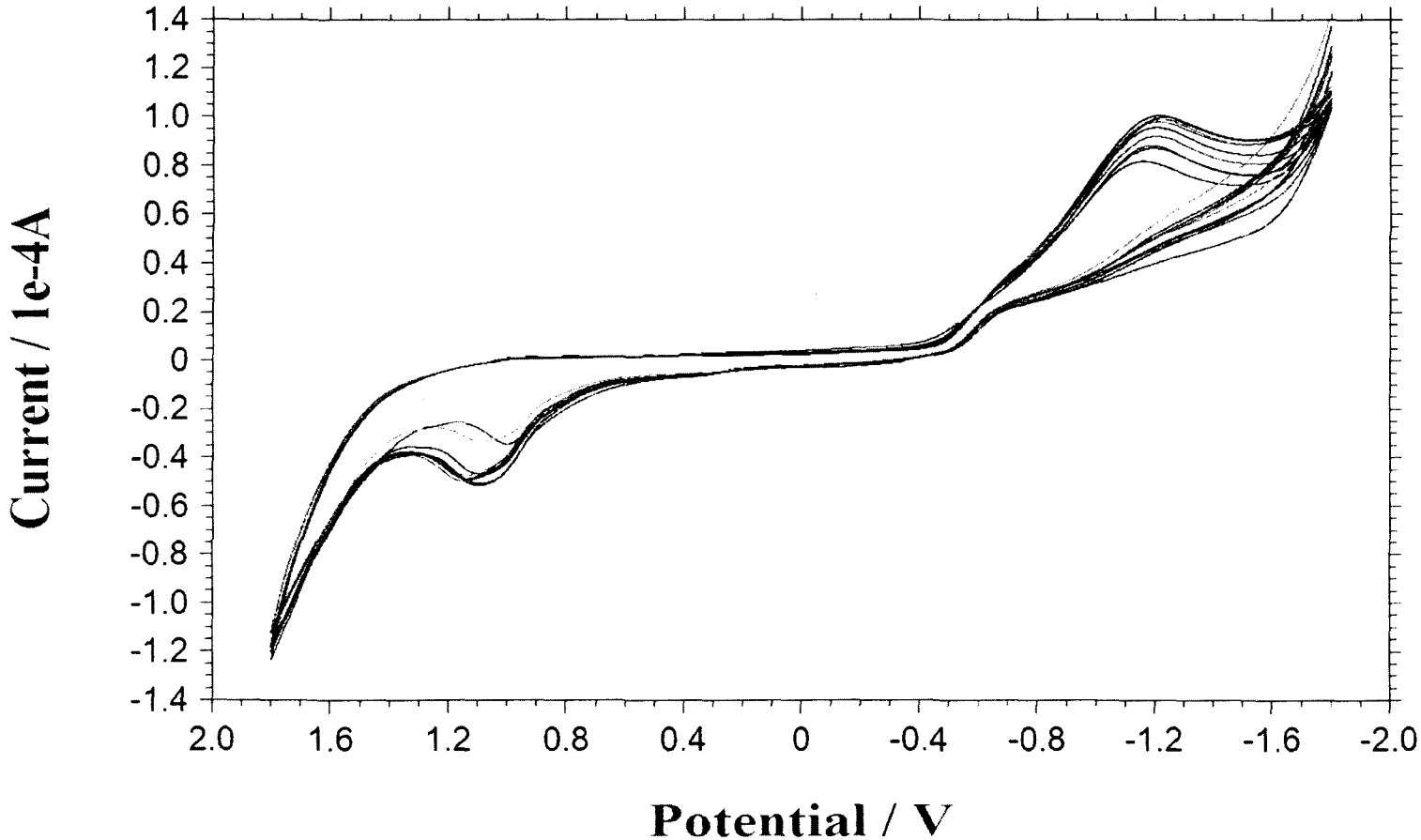


Figure 3.2.d.: **Cyclic Voltammograms of Mn[T(4-OMeP)P]OAc solution (10^{-3}M, fixed) in CH_3OH in the presence of various concentration of SDS (in CH_3OH) at Room Temperature**

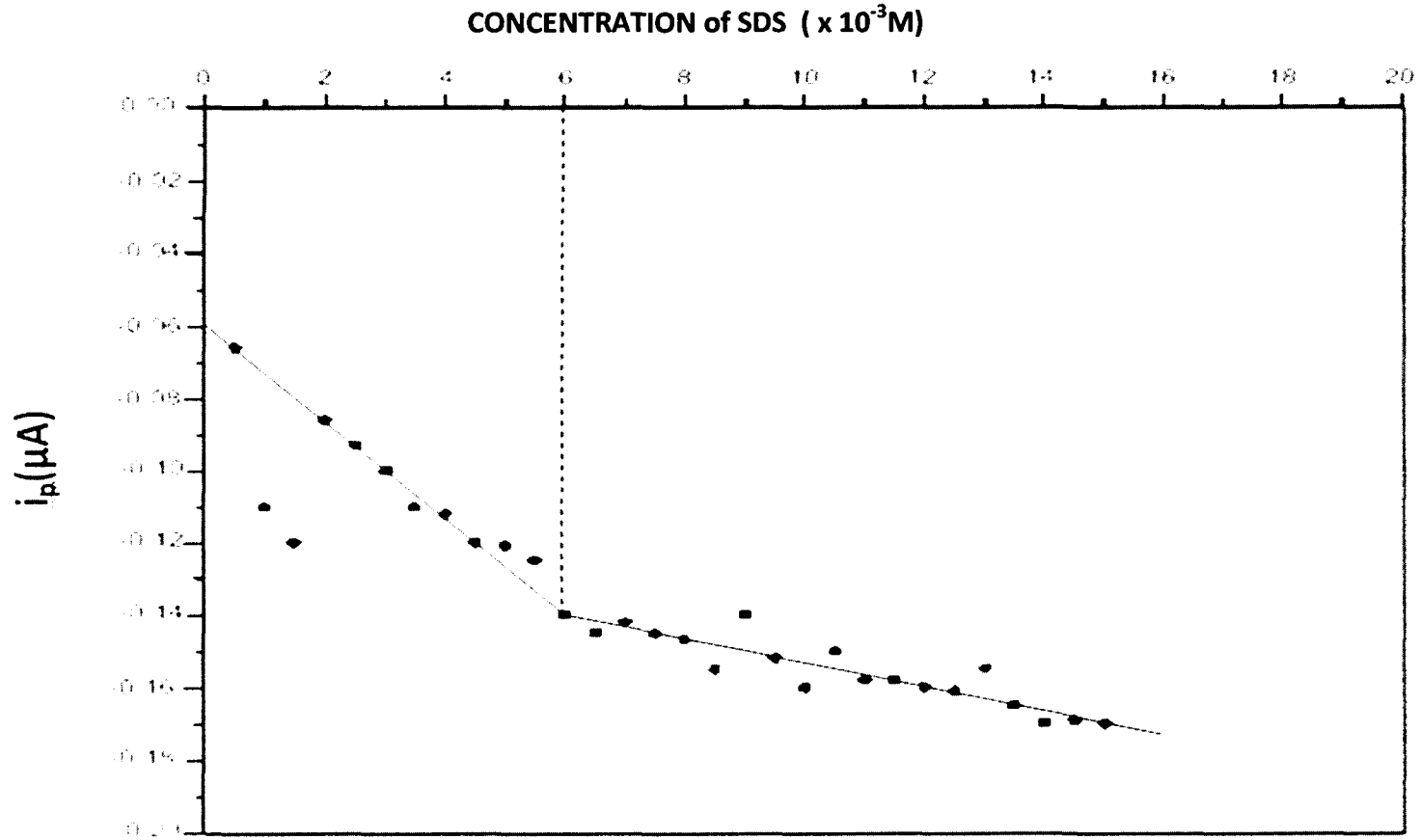


Figure : 3.2.e. Plot of Peak Current, i_p Vs. Concentration of SDS in pure Methanol at Room Temperature.

REFERENCES:

1. G.K. Vemulapalli, *Physical Chemistry*, Prentice Hall, Engle wood Cliffs, N.J., 1993.

2. A. A. Dominguez, A. Fernandes, N. Gonzales, E. Iglesias and L. Montenegro, *J. Chem. Edn.*, **74 (10)**, 1227 – 1231 (1997).

3. A.B. Mandal, B.U. Nair and D. Ramaswamy, *Langmuir*, **4**, 736-739 (1988).

4. A.B. Mandal and B.U. Nair, *J. Phys. Chem.*, **95**, 9008-9013 (1991).

5. Y.C. Ko, *Bull. Korean Chem. Soc.*, **28(10)** 1857 (2007).

CHAPTER -4

UV - VISIBLE STUDIES OF MANGANESE PORPHYRINS IN SURFACTANT MEDIUM

CHAPTER – 4

4.1. INTRODUCTION:

Interaction of porphyrins with micelles (aqueous micelles) and encapsulation of the porphyrin molecules inside micelles are studied as biological model systems[1, 2]. The physico - chemical properties of porphyrins become more specific in micellar environment[3–5]. In such environment aggregation of porphyrins forming dimers is also possible and is reflected in the UV – Visible spectra. Generally, H – type of aggregation exhibits blue shift while J – type aggregates show red shifts[6–14].

All measurements are carried out well above the CMC. Concentration of 10^{-5} M solutions of manganese porphyrins in chloroform are used. This chapter presents the UV–Visible studies of Mn[T(2-OMeP)P]OAc, Mn[T(4-OMeP)P]OAc, Mn[T(2-MeP)P]OAc, Mn[T(3-MeP)P]OAc, Mn[T(4-MeP)P]OAc and Mn[T(naphthyl)P]OAc in SDS, TX – 100 and CTAB

media. Triethylamine which coordinates with manganese porphyrins as axial ligand is used as a probe.

4.2. RESULTS:

4.2.1. Mn[T(2-OMeP)P]OAc:

Results are summarized in the Table 4.A. Without surfactant the Soret band occurs at 471nm and the Q bands occur at 574nm and 607nm.

IN SDS MEDIUM:

In SDS medium (in methanol) the soret band slightly shifts to 469nm (blue shift) while the two Q bands also show blue shift. The Q band at 574nm shifts to 563nm while the band at 607nm shifts to 595nm. The shift of the soret band is very less and is about 2nm. The shift of the Q bands is about 11–12nm which is quite significant. Addition of 0.3mol of triethylamine does not show any changes and the spectrum remains the same. (Figure : 4.2.1.a.(i) & (Figure : 4.2.1.a. (ii).

IN TX – 100 MEDIUM:

The soret band does not show any shift and also the Q bands remain more or less the same. Addition of 0.3mol of triethylamine does not make any difference except slight decrease in the intensity [Figure: 4.2.1.b.(i) & Figure: 4.2.1.b.(ii)].

IN CTAB MEDIUM:

The soret band remains more or less the same while the Q band at 574nm shows a blue shift by about 8nm i.e. λ_{max} at 566nm. Addition of 0.3mol of triethylamine shows slight blue shift in the soret band which is not very significant. On the other hand, the Q band at 607nm does not show any shift [Figure: 4.2.1.c.(i) & Figure: 4.2.1.c.(ii)].

4.2.2. Mn[T(4-OMeP)P]OAc:

Results are summarized in the Table 4.B. Without surfactant, the visible absorption spectrum exhibits a Soret band at 480nm while the two Q bands at 578nm and at 617nm respectively.

IN SDS MEDIUM:

The soret band shifts from 480nm to 471nm (blue shift) while the two Q bands also show blue shift. The Q band at 578nm shifts to 569nm (9nm shift) while the other Q band at 617nm shifts to 606nm (11nm shift). Addition of 0.3mol of triethylamine does not show any changes in the spectrum [(Figure: 4.2.2.a.(i) & Figure: 4.2.2.a.(ii)].

IN TX – 100 MEDIUM:

The soret band exhibits a blue shift from 480nm to 473nm (7nm shift) while the two Q bands remain more or less the same. Addition of 0.3mol of triethylamine has no effect on the spectrum except slight dilution effect [Figure: 4.2.2.b.(i) & Figure: 4.2.2.b.(ii)].

IN CTAB MEDIUM:

All three bands show blue shift. The soret band shifts from 480nm to 473nm (7nm shift) while the Q band at 578nm shifts to 573nm (5nm shift) and the

band at 617nm shifts to 608nm (9nm shift). Addition of 0.3mol of triethylamine shows no effect [Figure:4.2.2.c.(i) & Figure:4.2.2.c.(ii)].

4.2.3. Mn[T(2-MeP)P]OAc:

Results are summarized in the Table 4.C. The solution 10^{-5}M in chloroform exhibits a Soret band at 476nm and the two Q bands at 572nm and 605 nm.

IN SDS MEDIUM:

All three bands exhibit blue shifts. The soret band at 476nm shifts to 468nm (8nm shift) while the Q band at 572nm shifts to 564nm (8nm shift) and the Q band at 605nm shifts to 595nm (10nm shift). Addition of 0.3 mol of triethylamine does not change the spectrum except dilution effect [Figure: 4.2.3.a.(i) & Figure: 4.2.3.a.(ii)].

IN TX – 100 MEDIUM:

The soret band exhibits a blue shift while the two Q bands show slight red shift. The soret band

shifts from 476nm to 471nm (5nm shift) while the Q band at 572nm shifts to 575nm (3nm shift). The other Q band at 605nm shifts to 609nm (4nm shift). Addition of 0.3mol of triethyamine does not change the UV-Visible spectrum [Figure: 4.2.3.b(i) & Figure: 4.2.3.b(ii)].

IN CTAB MEDIUM:

All three bands show red shift. The soret band shifts from 476nm to 486nm (10nm shift) while the other two Q bands shift from 572nm to 586nm (14nm shift) and from 605nm to 621nm (16nm shift) respectively. Addition of 0.3mol of triethylamine has no significant effect on the spectrum. [Figure:4.2.3.c.(i) & Figure:4.2.3.c.(ii)]

4.2.4. Mn[T(3-MeP)P]OAc:

Results are summarized in the Table: 4.D. A concentration of 10^{-5}M solution of the compound in $CHCl_3$ shows the soret band at 480nm and the two Q bands at 582nm and 617nm respectively.

IN SDS MEDIUM:

All three bands exhibit blue shift. The soret band shifts from 480nm to 470nm (10nm shift), the Q band at 582nm shifts to 566nm (16nm shift) and the other Q band shifts from 617nm to 600nm (17nm shift). Addition of 0.3 mol of triethylamine has no effect on the spectrum except the dilution effect [Figure:4.2.4.a.(i) & Figure:4.2.4.a.(ii)].

IN TX – 100 MEDIUM:

All three bands show blue shift. The soret band shifts from 480nm to 471nm (9nm shift) while the Q band at 582nm shifts to 575nm (7nm shift) and the other Q band shifts from 617nm to 611nm (6nm shift). Addition of 0.3mol of triethylamine has no effect on the spectrum [Figure: 4.2.4.b.(i) & Figure: 4.2.4.b.(ii)].

IN CTAB MEDIUM:

All three bands exhibit red shift. The soret band shifts from 480nm to 486nm (6nm shift), the Q band

at 582nm shifts to 586nm (4nm shift) and the other Q band shifts from 617nm to 622nm (5nm shift). Interestingly, addition of 0.3mol of triethylamine exhibits blue shift. The soret band shifts to 469nm, the Q band at 582nm shifts to 576nm while the other Q band at 617nm remains the same [Figure: 4.2.4.c.(i) & Figure: 4.2.4.c.(ii)].

4.2.5. Mn[T(4-MeP)P]OAc:

Results are summarized in the Table: 4.E. In chloroform its 10^{-5}M solution shows three bands. The soret band is at 480nm and the Q bands are at 581nm and 619nm respectively.

IN SDS MEDIUM:

The soret band shifts from 480nm shifts to 470nm (10nm shift, a blue shift), while the Q band at 582nm shifts to 577nm (5nm shift) and the other Q band shifts from 619nm to 615nm (4nm shift). Addition of 0.3mol of triethylamine shifts the soret

band to 468nm while the Q bands suffer no shift [Figure:4.2.5.a.(i) & Figure:4.2.5.a.(ii)].

IN TX – 100 MEDIUM:

The soret band shows blue shift and the Q bands also show blue shift. The soret band shifts from 480nm to 470nm (10nm shift) while the two Q bands shift from 581nm to 577nm (4 nm) and from 619nm to 613nm (6nm shift). Addition of 0.3mol of triethylamine has no effect on the spectrum [Figure: 4.2.5.b.(i) & Figure: 4.2.5.b.(ii)].

IN CTAB MEDIUM:

All three bands are red shifted. The soret band shifts from 480nm to 486nm (6nm shift), the Q band at 581nm shifts to 588nm (7nm shift) and the other Q band shifts from 619nm to 625nm (6nm shift). Practically, addition of 0.3mol of triethylamine has no effect on the UV – Visible spectrum (Figure: 4.2.5.c.(i) & Figure: 4.2.5.c.(ii)].

4.2.6. Mn[T(naphthyl)P]OAc:

Results are summarized in the Table: 4.F. A 10^{-5}M solution of the compound in $CHCl_3$ shows the soret band at 479nm and the two Q bands at 580nm and 614nm respectively.

IN SDS MEDIUM:

The soret band shifts from 479nm to 473nm (6nm shift) and the Q band at 580nm shifts to 565nm (15nm shift). The other Q band at 614nm disappears in the presence of SDS. Addition of 0.3mol of triethylamine has no effect on the spectrum [Figure 4.2.6.a.(i) & Figure 4.2.6.a.(ii).

IN TX – 100 MEDIUM:

All three bands are blue shifted. The soret band shifts from 479nm to 474nm (5nm shift) while the other two Q bands shifts from 580nm to 577nm (3nm shift) and from 614nm to 609nm (5nm shift). Addition

of 0.3mol of triethylamine has no effect on the spectrum [Figure: 4.2.6.b.(i). & Figure: 4.2.6.b.(ii)].

IN CTAB MEDIUM:

All three bands are red shifted. The soret band shifts from 479nm to 490nm (11nm shift), while the two Q bands shift from 580nm to 586nm (6nm shift) and from 614nm to 620nm (6nm shift). Addition of 0.3mol of triethylamine has no effect on the UV – Visible spectrum (Figure: 4.2.6.c).

4.3. DISCUSSION:

All manganese porphyrins exhibit similar pattern of spectra in a particular surfactant medium. In SDS medium almost all soret bands show blue shift (2nm–9nm). This is most likely due to the replacement of the axial ligand (OAc^-) by the negatively charged head group of SDS. It is known that the axial ligand of the manganese porphyrins are weakly bound. Q bands are also observed to be blue shifted (8nm–9nm).

Another possibility is that the porphyrin molecules aggregate in the space between micelles and form dimers.

In TX – 100 medium the soret bands are blue shifted (4nm–9nm). Although TX – 100 is non ionic there is likely an interaction between the manganese ion of the porphyrin and the –OH group of the TX – 100. Thus –OH group of the TX – 100 may have an affinity towards the manganese. As a result blue shift is observed. There is not much change in the Q bands of Mn[T(2-OMeP)P]OAc and Mn[T(4-OMeP)P]OAc.

In the CTAB medium the spectral pattern is reversed. Both soret band as well as Q bands are red shifted. Soret bands are red shifted by about 6nm – 10nm while the Q bands are red shifted by about 4nm – 15nm. This could be due to the replacement of OAc^- by Br^- ion of the CTAB as axial ligand. As a result there is a charge flow from Br^- to the porphyrin ligand

through the manganese ion. This raises the energy level of the porphyrin ligand (a_{1u}/a_{2u}) making the energy difference between the e_g level and the a_{1u}/a_{2u} level smaller. Thus we observed red shift. Another possibility is the formation of dimers in the surfactant medium. Ironically, no appreciable changes in the spectra of Mn[T(2-OMeP)P]OAc and Mn[T(4-OMeP)P]OAc are observed.

Another alternative explanation can be made to explain the blue shift as well as the red shift observed in the UV – Visible spectra. In restricted environment of the surfactant medium, porphyrin molecules can aggregate forming dimers. Those species which exhibit blue shifts may be of H – type dimers while the species which exhibit red shifts may be of J – type dimers.

It is also possible that manganese porphyrins are mono dispersed in between the surfactant

molecules and the metal ion binds peripherally to surfactant surfaces.

Another interesting observation is that addition of 0.3mol of triethylamine does not exhibit any changes in the spectra except in one case i.e., in Mn[T(3-MeP)P]OAc in CTAB medium. This indicates that the central metal ion of the metalloporphyrin is not available for ligation with the amine. This raises a question whether the porphyrin is embedded inside the micelle or not. The diameter of the porphyrin ring is ~13A which could be smaller than the dimension of the micelles[5,15].

In any case, in the surfactant medium the manganese ion of the porphyrin is not accessible by the amine which is evident from the UV-Visible spectra.

4.4. CONCLUSION:

From the UV – Visible studies the following observations are put forward :

(i) In the SDS medium there is a possibility of replacement of the axial ligand (OAc^-) by the negatively charged head group of the surfactant.

(ii) In TX – 100 medium there is likely an interaction between the manganese ion and the -OH group of the TX – 100.

(iii) In the CTAB medium there is a possibility of replacement of the axial ligand (OAc^-) by the Br^- ion.

(iv) Encapsulation of the porphyrin molecule within the micelle is not ruled out.

(v) There is a strong possibility of aggregation of porphyrin molecules forming dimers within the inter layer spaces of the micelles.

TABLE 4.A. : UV- VIS ABSORPTION SPECTRAL DATA OF Mn[T(2-OMeP)P]OAc AT ROOM TEMPERATURE
SOLVENT : CHLOROFORM
CONCENTRATION : 10^{-5}M

COMPOUND		B- BAND	Q – BANDS	
Mn[T(2-OMeP)P]OAc	In Chloroform	471 (2.467)	574(0.314)	607(0.222)
	With SDS (10^{-1}M, in CH_3OH)	469(1.839)	563(0.258)	595(0.162)
	With SDS and Triethylamine	469(1.798)	563(0.25)	595(0.158)
	With TX - 100	471(2.163)	574(0.277)	609(0.22)
	With TX - 100 and Triethylamine	471(2.006)	574(0.262)	607(0.198)
	With CTAB (10^{-1}M, in $CHCl_3$)	470(1.294)	566(0.259)	607(0.11)
	With CTAB and Triethylamine	469(1.48)	567(0.231)	607(0.082)

TABLE 4.B. : UV- VIS ABSORPTION SPECTRAL DATA OF Mn[T(4-OMeP)P]OAc AT ROOM TEMPERATURE
SOLVENT : CHLOROFORM
CONCENTRATION : 10^{-5}M

COMPOUND		B- BAND	Q – BANDS	
Mn[T(4-OMeP)P]OAc	In Chloroform	480(1.867)	578(0.202)	617(0.216)
	With SDS (10^{-1}M, in CH_3OH)	471(1.84)	569(0.36)	606(0.34)
	With SDS and Triethylamine	471(1.81)	569(0.357)	606(0.33)
	With TX - 100	473(2.329)	579(0.289)	617(0.339)
	With TX - 100 and Triethylamine	472(1.469)	578(0.244)	617(0.28)
	With CTAB (10^{-1}M, in $CHCl_3$)	473(1.128)	573(0.218)	608(0.211)
	With CTAB and Triethylamine	471(1.279)	573(0.213)	609(0.215)

TABLE 4.C. : UV- VIS ABSORPTION SPECTRAL DATA OF Mn[T(2-MeP)P]OAc AT ROOM TEMPERATURE
SOLVENT : CHLOROFORM
CONCENTRATION : 10^{-5}M

COMPOUND		B- BAND	Q – BANDS	
Mn[T(2-MeP)P]OAc	In Chloroform	476(1.967)	572(0.352)	605(0.269)
	With SDS (10^{-1}M, in CH_3OH)	468(2.337)	564(0.341)	596(0.239)
	With SDS and Triethylamine	468(2.115)	566(0.296)	596(0.20)
	With TX - 100	471(2.709)	575(0.322)	609(0.264)
	With TX - 100 and Triethylamine	470(2.832)	575(0.321)	609(0.264)
	With CTAB (10^{-1}M, in $CHCl_3$)	486(1.635)	586(0.196)	621(0.203)
	With CTAB and Triethylamine	486(1.408)	585(0.192)	620(0.192)

TABLE 4.D. : UV- VIS ABSORPTION SPECTRAL DATA OF Mn[T(3-MeP)P]OAc AT ROOM TEMPERATURE
SOLVENT : CHLOROFORM
CONCENTRATION : 10^{-5}M

COMPOUND		B- BAND	Q – BANDS	
Mn[T(3-MeP)P]OAc	In Chloroform	480 (2.209)	582(0.244)	617(0.266)
	With SDS (10^{-1}M, in CH_3OH)	470(1.804)	566(0.249)	600(0.2004)
	With SDS and Triethylamine	470(1.699)	567(0.216)	601(0.182)
	With TX - 100	471(2.120)	575(0.26)	611(0.24)
	With TX - 100 and Triethylamine	470(1.838)	575(0.230	611(0.221)
	With CTAB (10^{-1}M, in $CHCl_3$)	486(1.665)	586(0.226)	622(0.262)
	With CTAB and Triethylamine	469(1.029)	576(0.212)	617(0.215)

TABLE : 4.E. : UV- VIS ABSORPTION SPECTRAL DATA OF Mn[T(4-MeP)P]OAc AT ROOM TEMPERATURE
SOLVENT : CHLOROFORM
CONCENTRATION : 10^{-5}M

COMPOUND		B- BAND	Q – BANDS	
Mn[T(4-MeP)P]OAc	In Chloroform	480(1.597)	581(0.123)	619(0.112)
	With SDS (10^{-1}M, in CH_3OH)	470(1.583)	577(0.1406)	615(0.1477)
	With SDS and Triethylamine	468(1.3306)	577(0.119)	615(0.116)
	With TX - 100	470(1.961)	577(0.281)	613(0.293)
	With TX - 100 and Triethylamine	470(1.859)	577(0.28)	613(0.291)
	With CTAB (10^{-1}M, in $CHCl_3$)	486(1.962)	588(0.255)	625(0.331)
	With CTAB and Triethylamine	486(1.582)	586(0.247)	623(0.308)

TABLE: 4.F. : UV- VIS ABSORPTION SPECTRAL DATA OF Mn[T(Naphthyl)P]OAc AT ROOM TEMPERATURE
SOLVENT : CHLOROFORM
CONCENTRATION : 10^{-5}M

COMPOUND		B- BAND	Q - BANDS	
Mn[T(Naphthyl)P]OAc	In Chloroform	479(1.964)	580(0.299)	614(0.205)
	With SDS (10^{-1}M, in CH_3OH)	473(2.927)	565(0.388)	-
	With SDS and Triethylamine	473(2.493)	565(0.33)	-
	With TX - 100	474(2.227)	577(0.32)	609(0.232)
	With TX - 100 and Triethylamine	475(2.069)	577(0.315)	609(0.232)
	With CTAB (10^{-1}M, in $CHCl_3$)	490(2.891)	586(0.359)	620(0.295)
	With CTAB and Triethylamine	489(2.655)	585(0.356)	620(0.285)

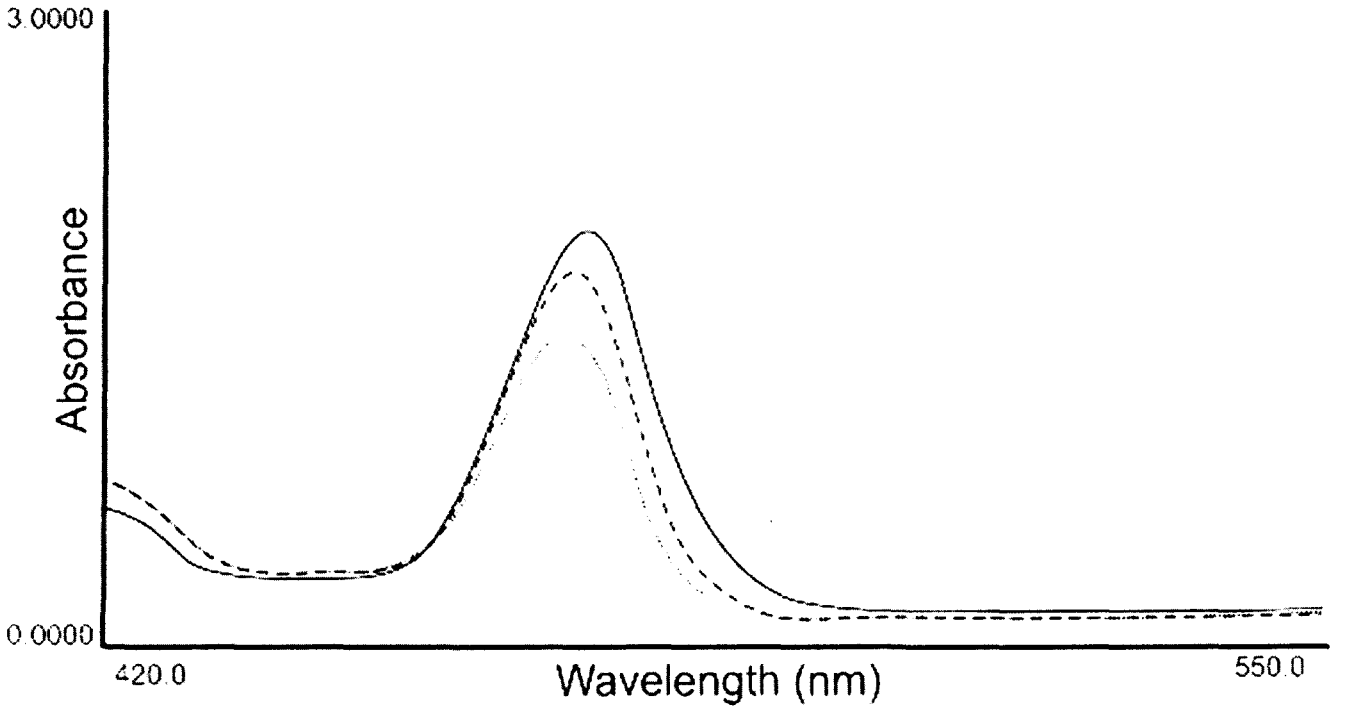


Figure: 4.2.1.a.(i). UV-Vis Overlay Spectra (B- Band) of Mn[T(2-OMeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of SDS (10^{-1}M in CH_3OH)(– – –) and 0.3mol of triethylamine (·····) at Room Temperature.

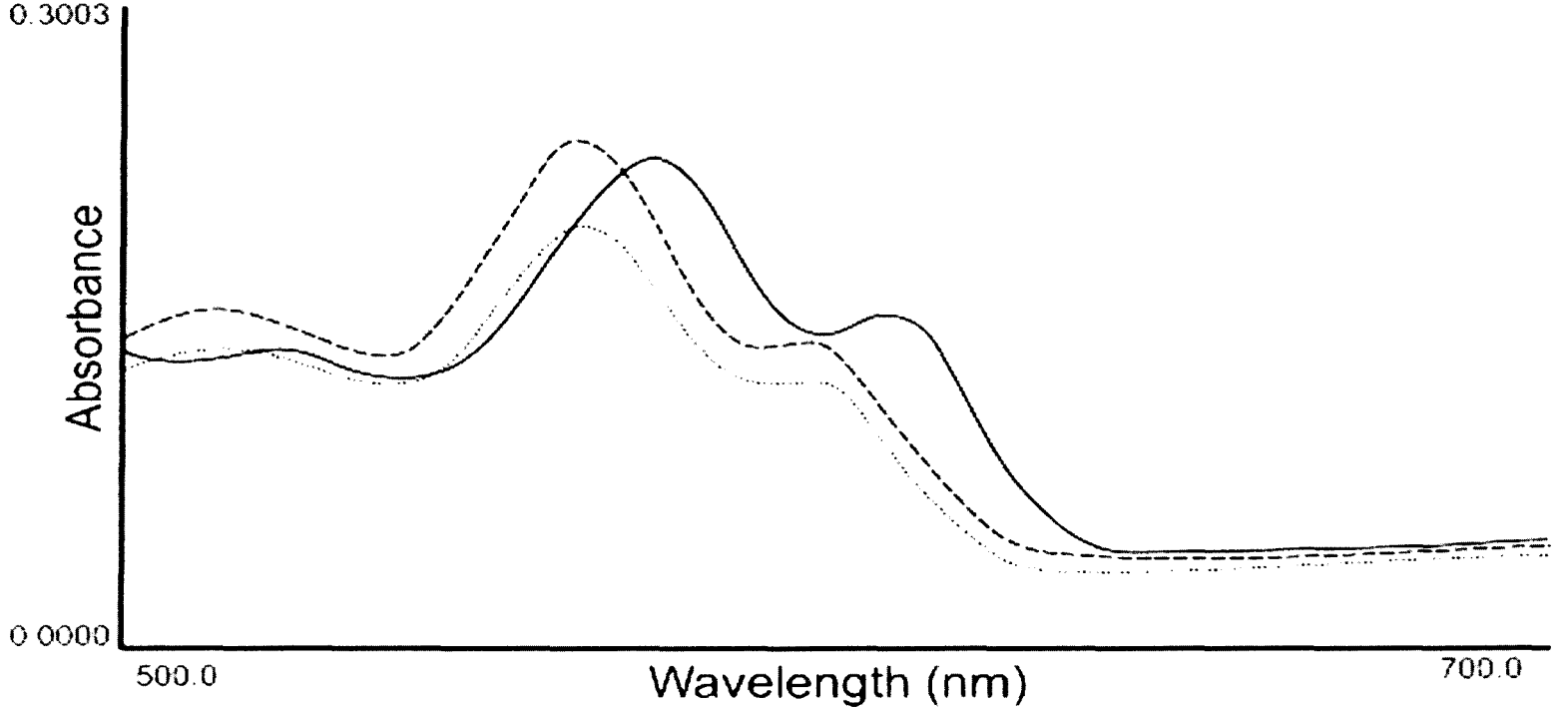


Figure: 4.2.1.a.(ii). UV-Vis Overlay Spectra (Q- Band) of Mn[T(2-OMeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of SDS (10^{-1}M in CH_3OH)(– – –) and 0.3mol of triethylamine (·····) at Room Temperature.

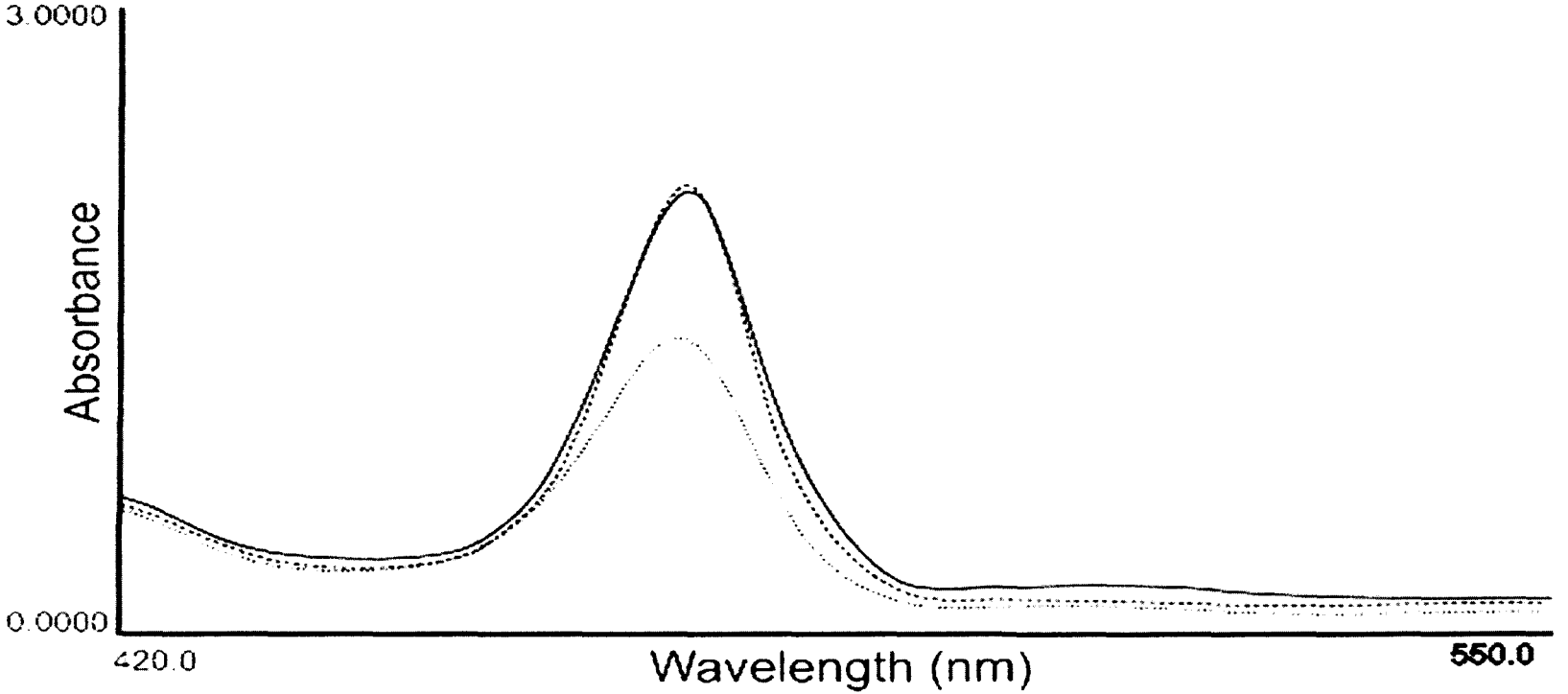


Figure: 4.2.1.b.(i). UV-Vis Overlay Spectra (B- Band) of Mn[T(2-OMeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of TX-100 (·····) and 0.3mol of triethylamine (·····) at Room Temperature.

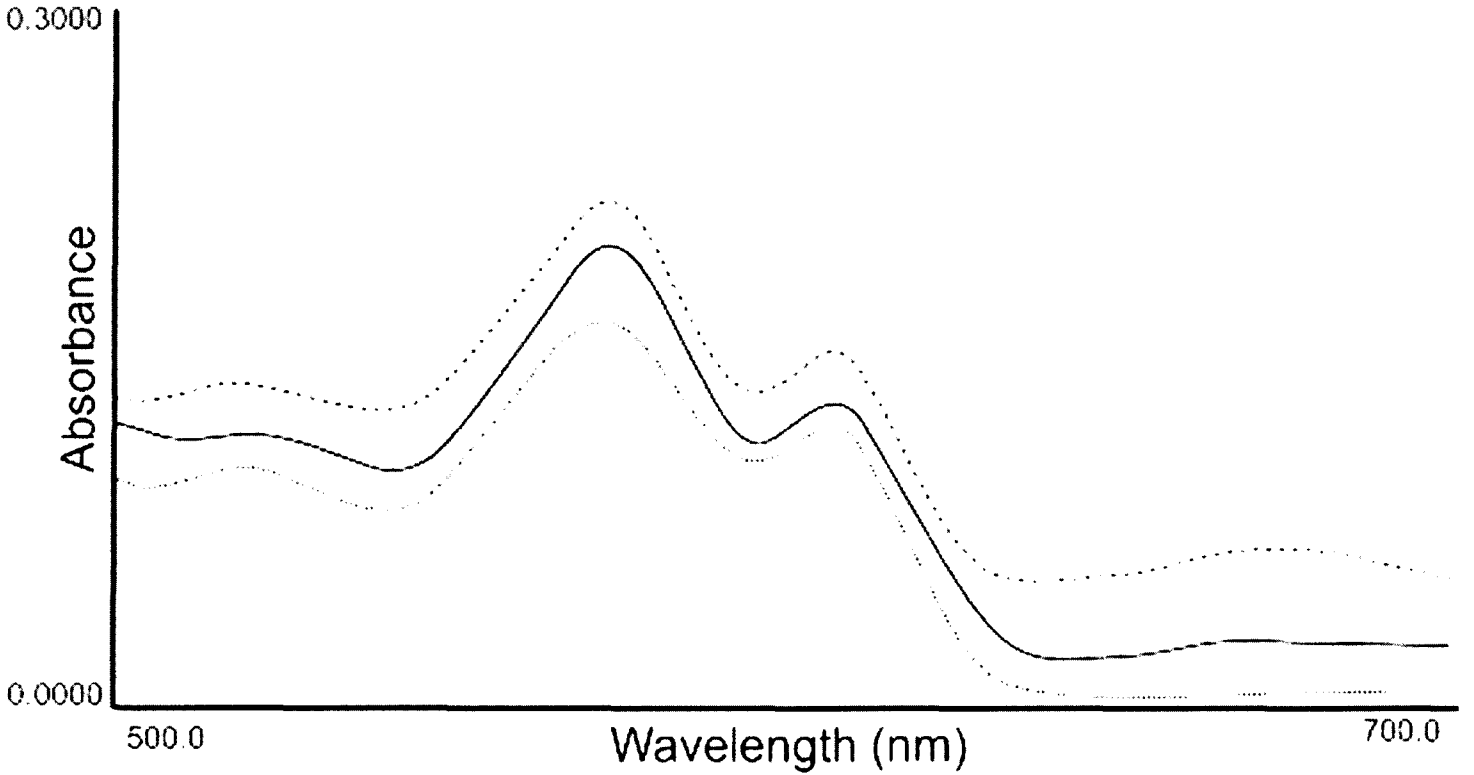


Figure: 4.2.1.b.(ii). UV-Vis Overlay Spectra (Q- Band) of Mn[T(2-OMeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of TX-100 (·····) and 0.3mol of triethylamine (·····) at Room Temperature.

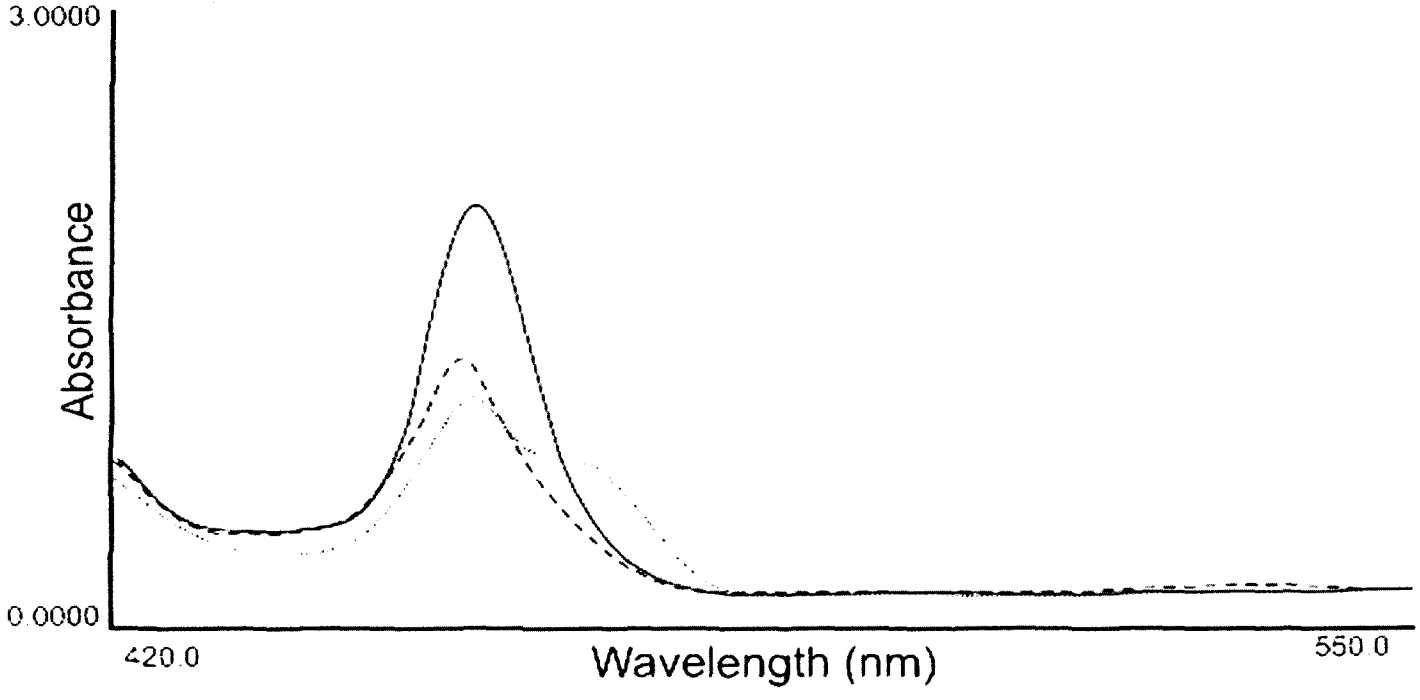


Figure: 4.2.1.c.(i). UV-Vis Overlay Spectra (B- Band) of Mn[T(2-OMeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of CTAB (10^{-1}M in $CHCl_3$) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.

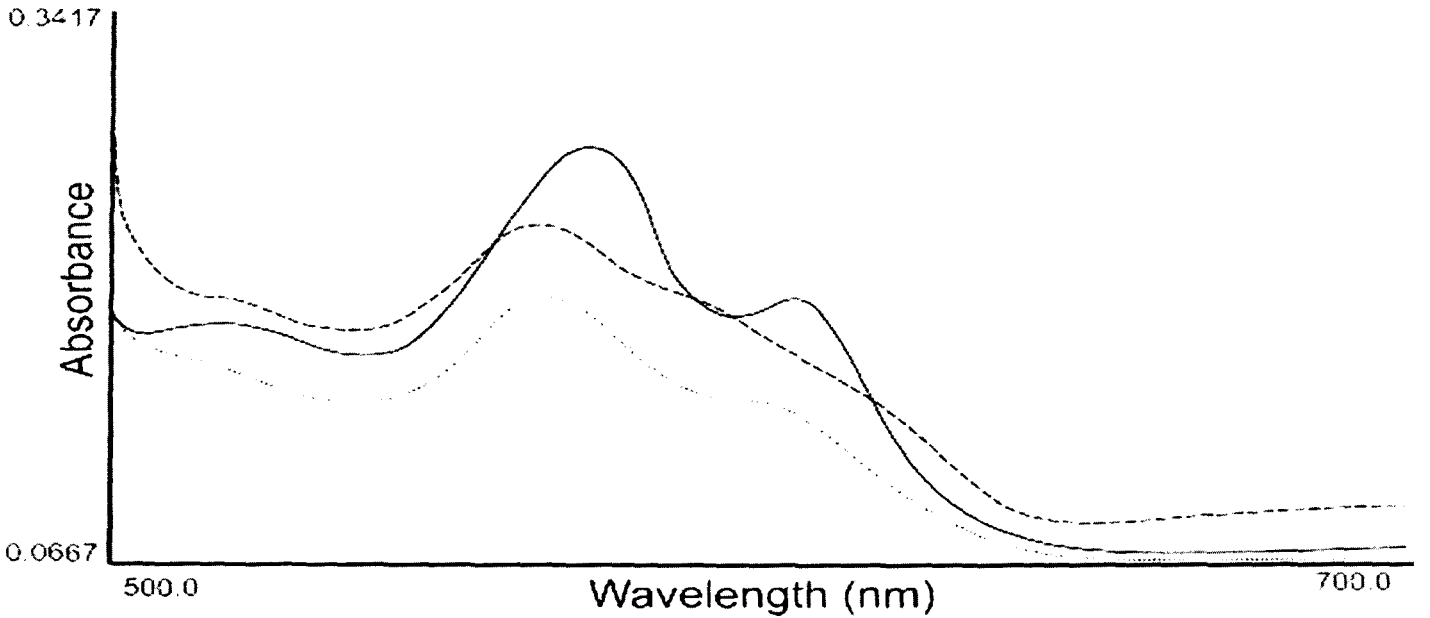


Figure: 4.2.1.c.(ii). UV-Vis Overlay Spectra (Q- Band) of Mn[T(2-OMeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of CTAB (10^{-1}M in $CHCl_3$) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.

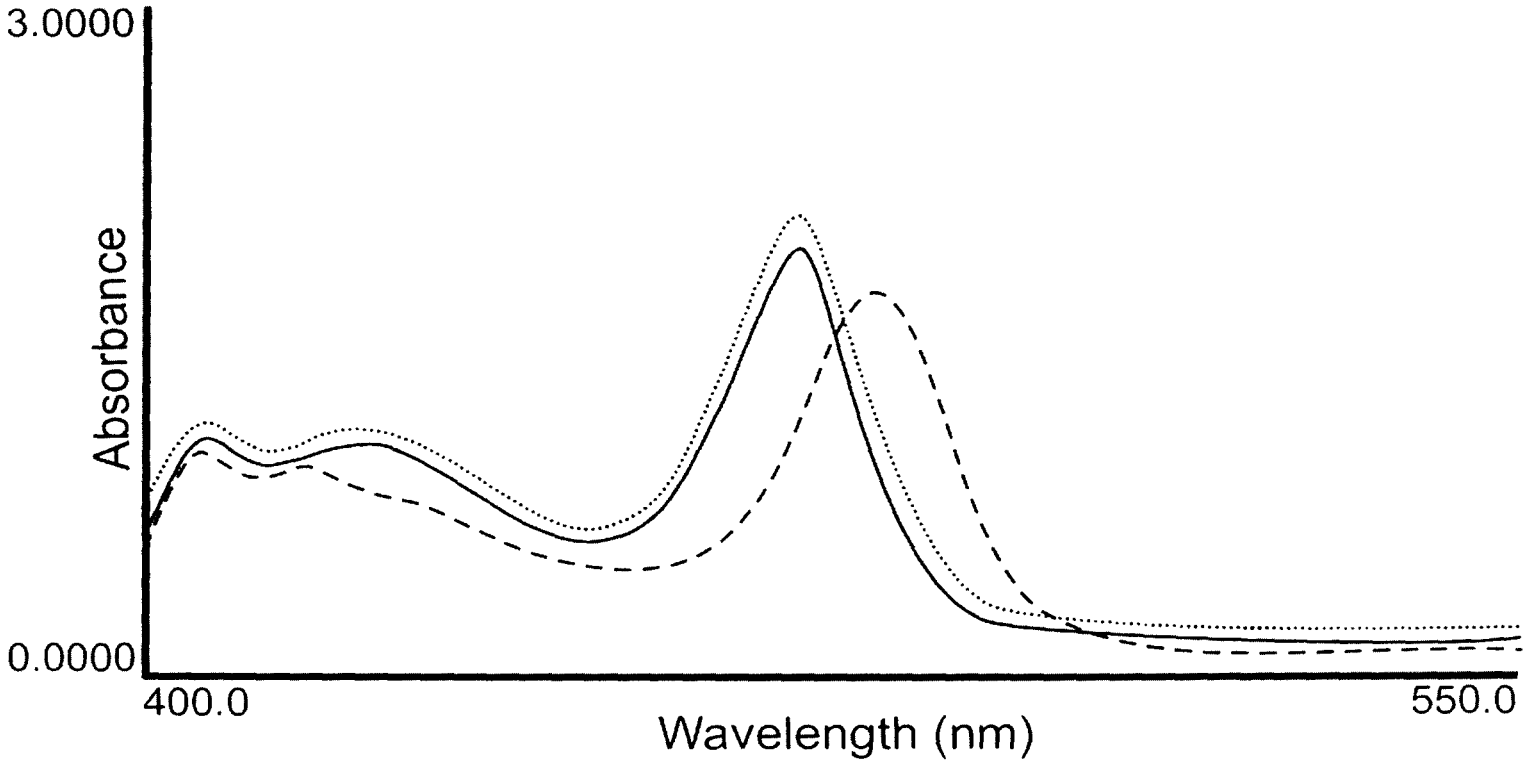


Figure: 4.2.2.a.(i). UV-Vis Overlay Spectra (B- Band) of Mn[T(4-OMeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of SDS (10^{-1}M in CH_3OH) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.

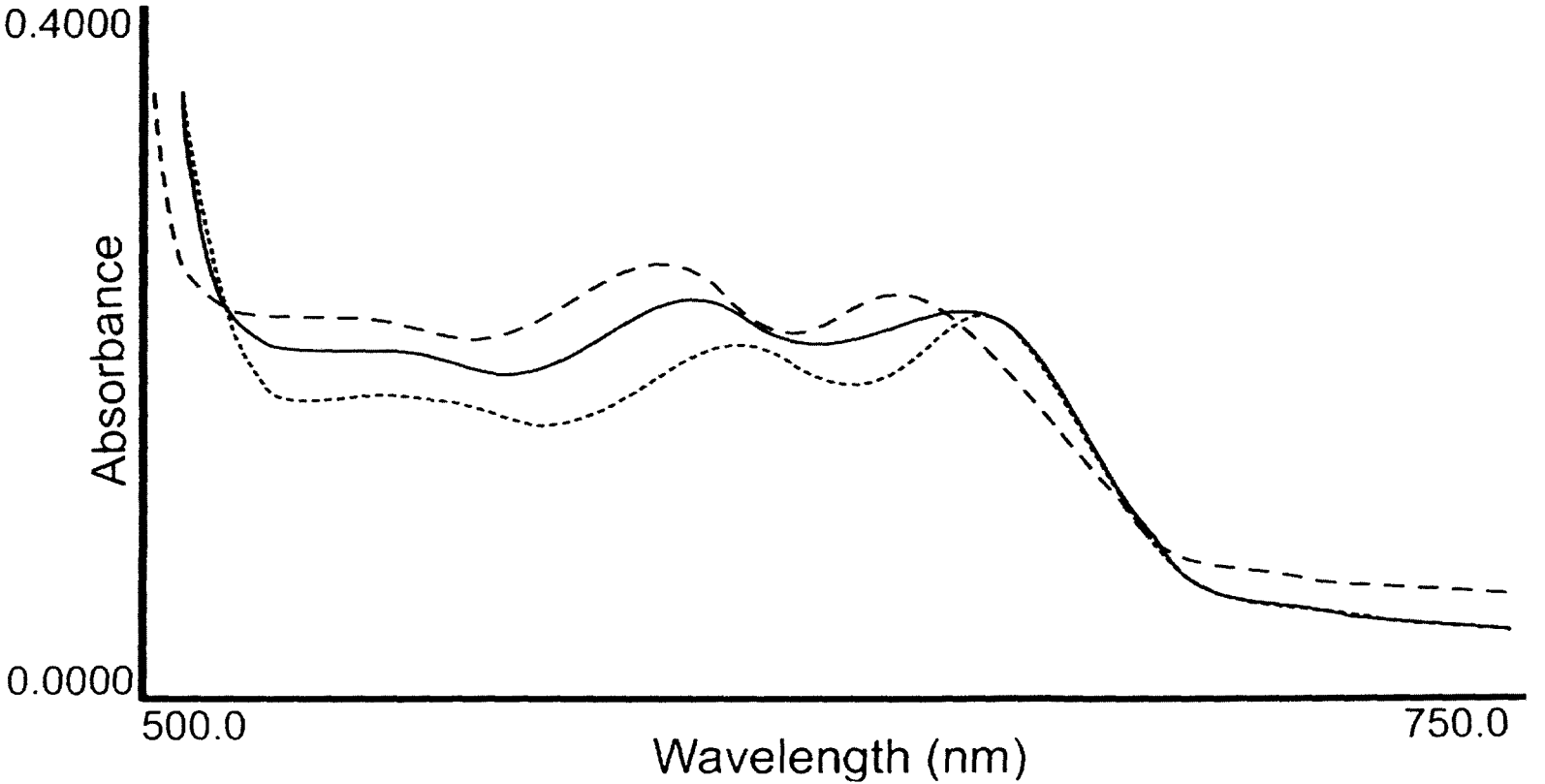


Figure: 4.2.2.a.(*ii*). **UV-Vis Overlay Spectra (Q- Band) of Mn[T(4-OMeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of SDS (10^{-1}M in CH_3OH) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

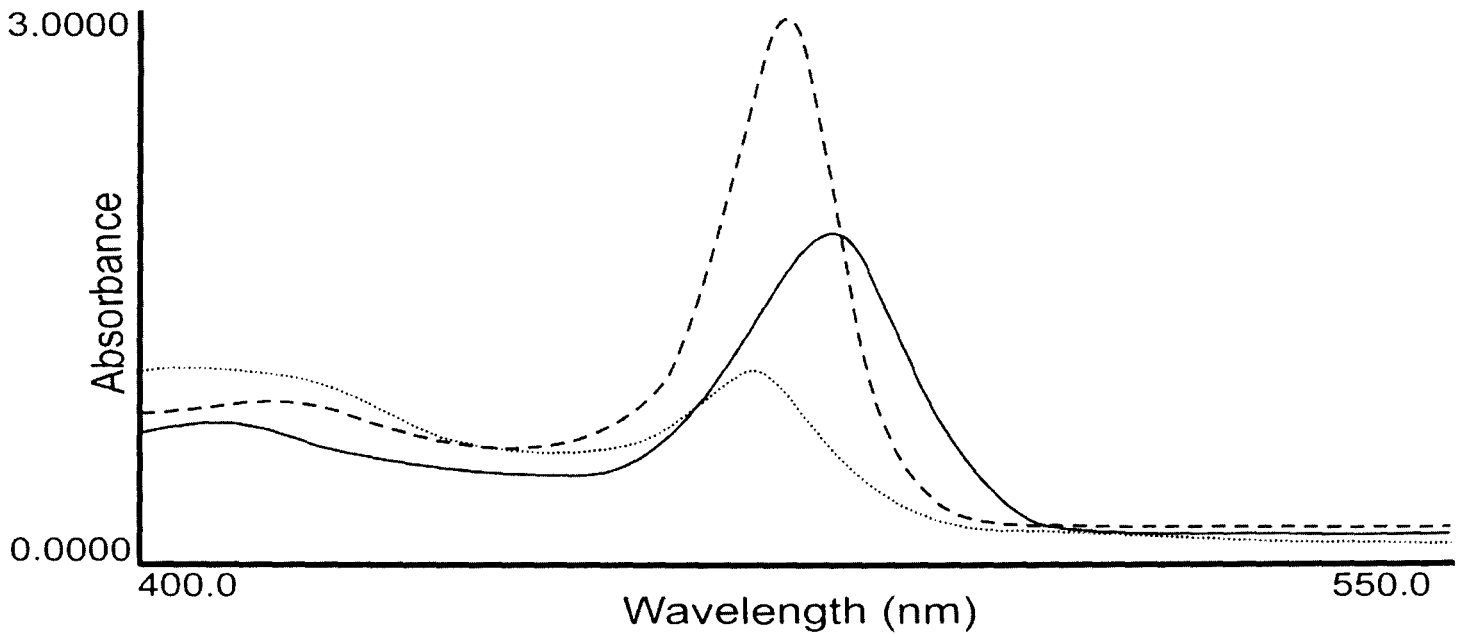


Figure: 4.2.2.b.(i). **UV-Vis Overlay Spectra (B- Band) of Mn[T(4-OMeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of TX - 100 (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

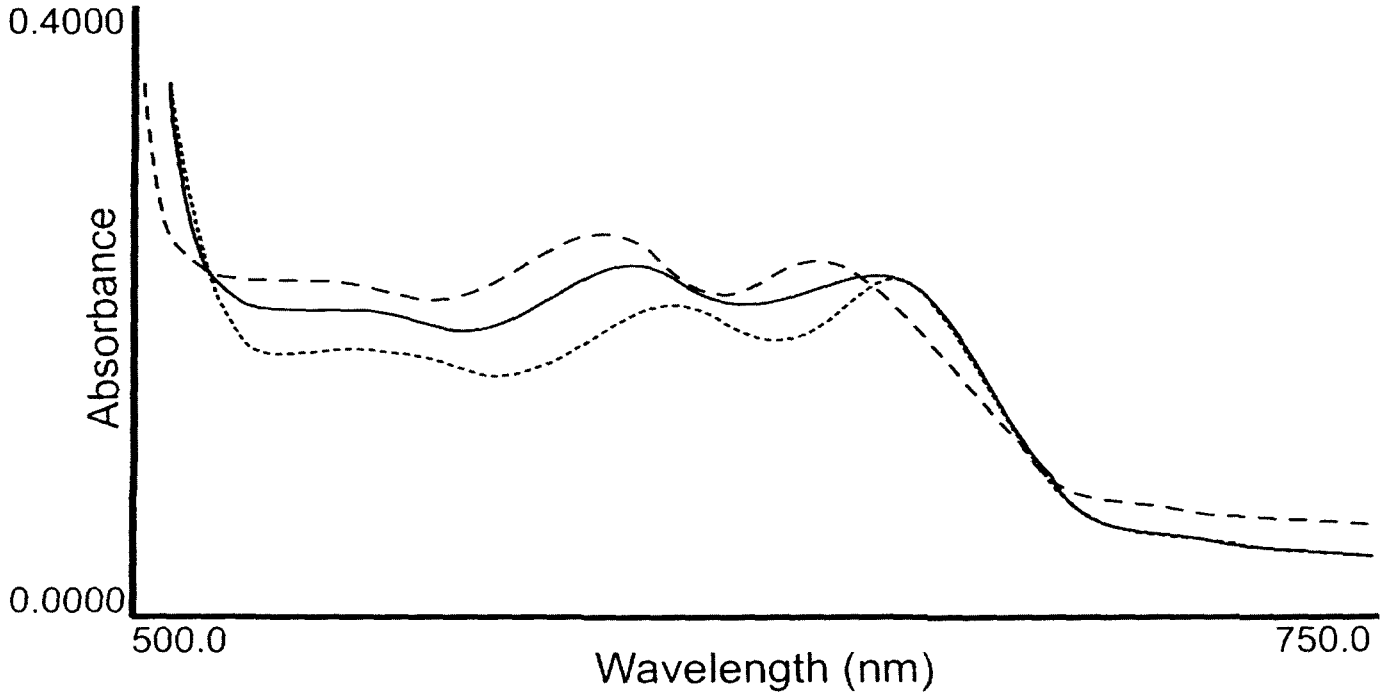


Figure: 4.2.2.b.(ii). **UV-Vis Overlay Spectra (Q- Band) of Mn[T(4-OMeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of TX - 100 (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

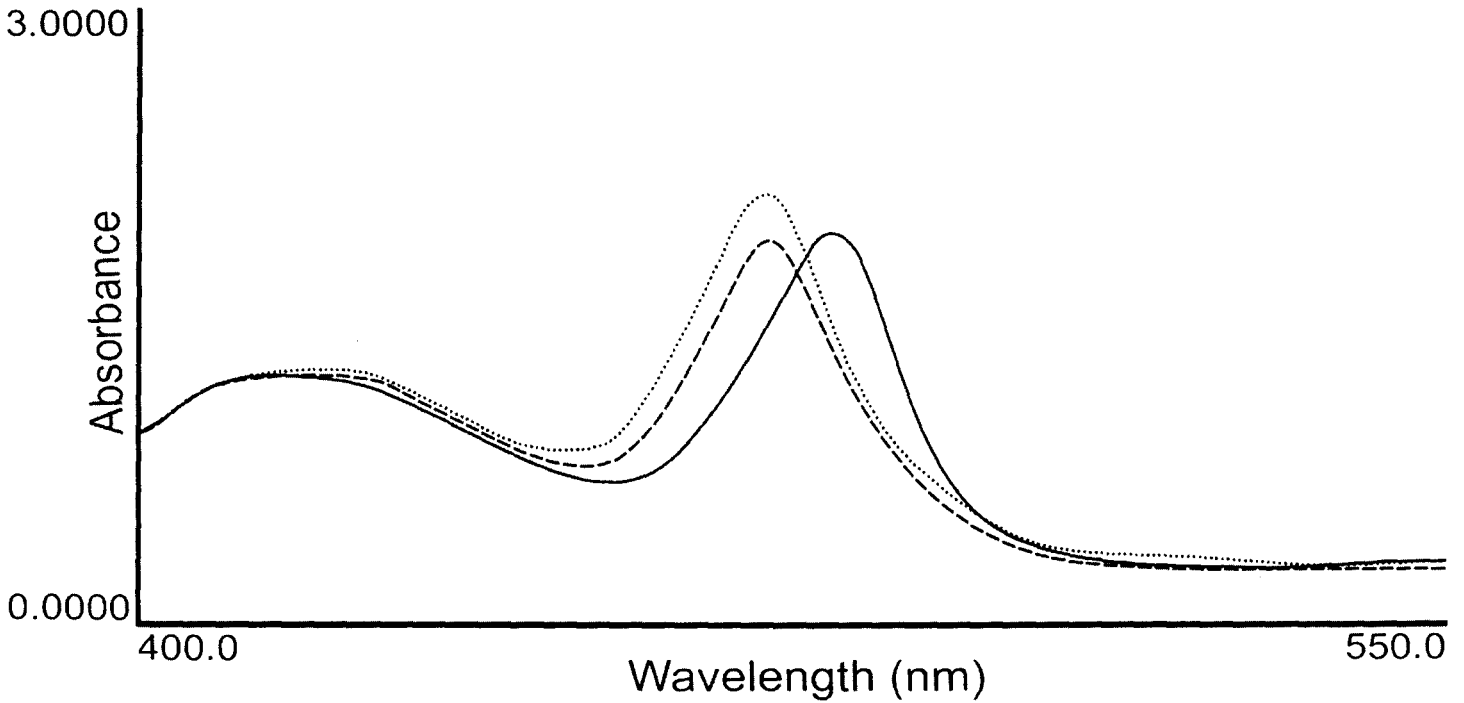


Figure: 4.2.2.c.(i). UV-Vis Overlay Spectra (B- Band) of Mn[T(4-OMeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of CTAB (10^{-1}M in $CHCl_3$) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.

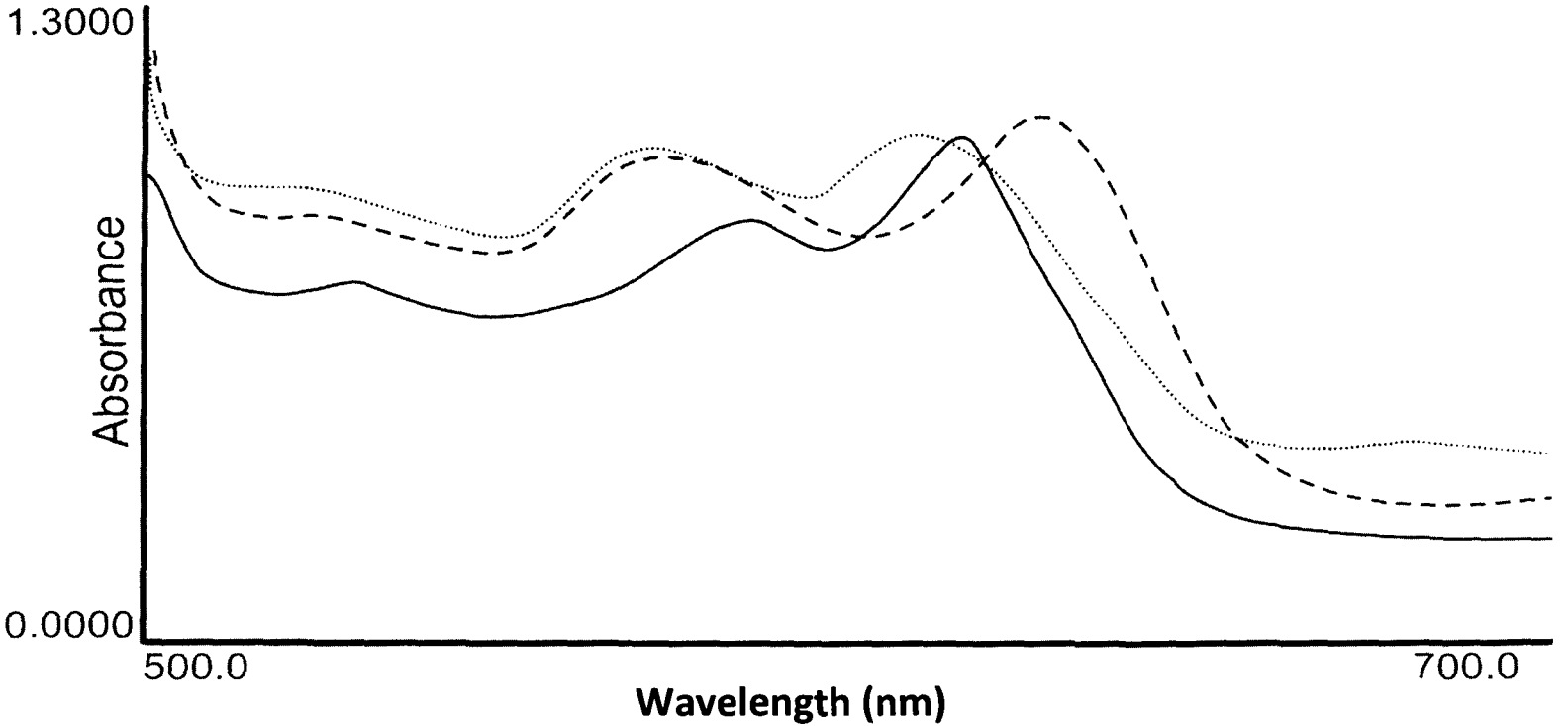


Figure: 4.2.2.c.(ii). UV-Vis Overlay Spectra (Q- Band) of Mn[T(4-OMeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of CTAB (10^{-1}M in $CHCl_3$) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.

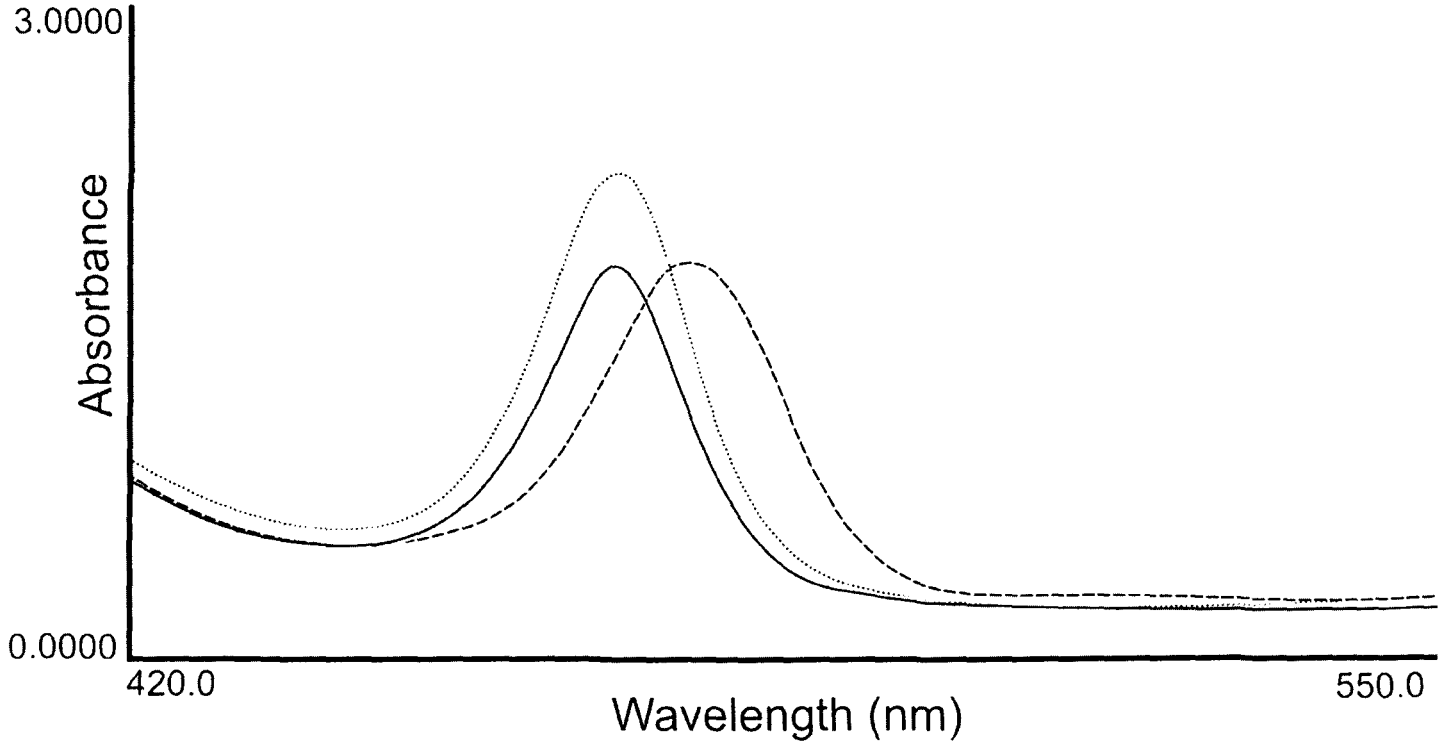


Figure:4.2.3.a.(i). UV-Vis Overlay Spectra (B- Band) of Mn[T(2-MeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of SDS (10^{-1}M in CH_3OH) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.

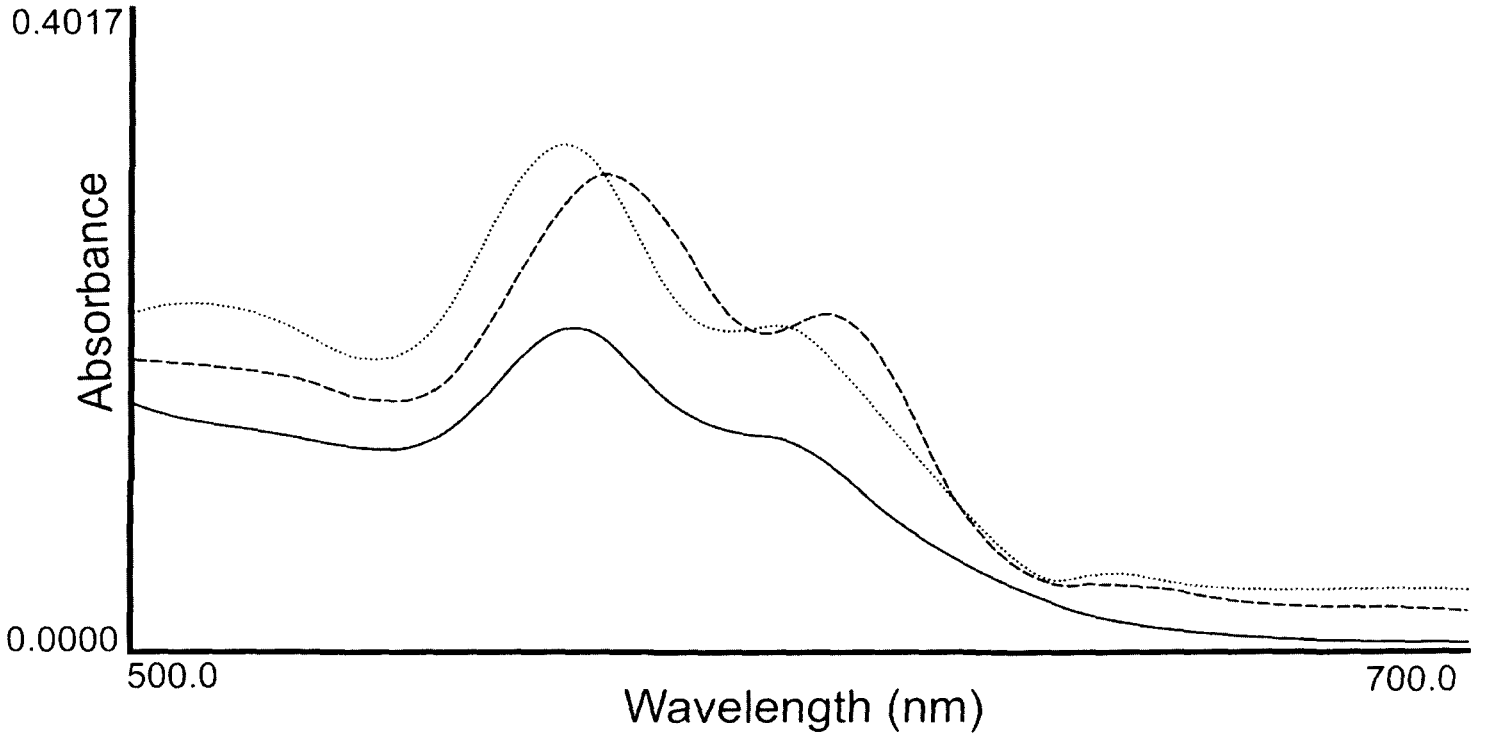


Figure:4.2.3.a.(ii). UV-Vis Overlay Spectra (Q- Band) of Mn[T(2-MeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of SDS (10^{-1}M in CH_3OH) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.

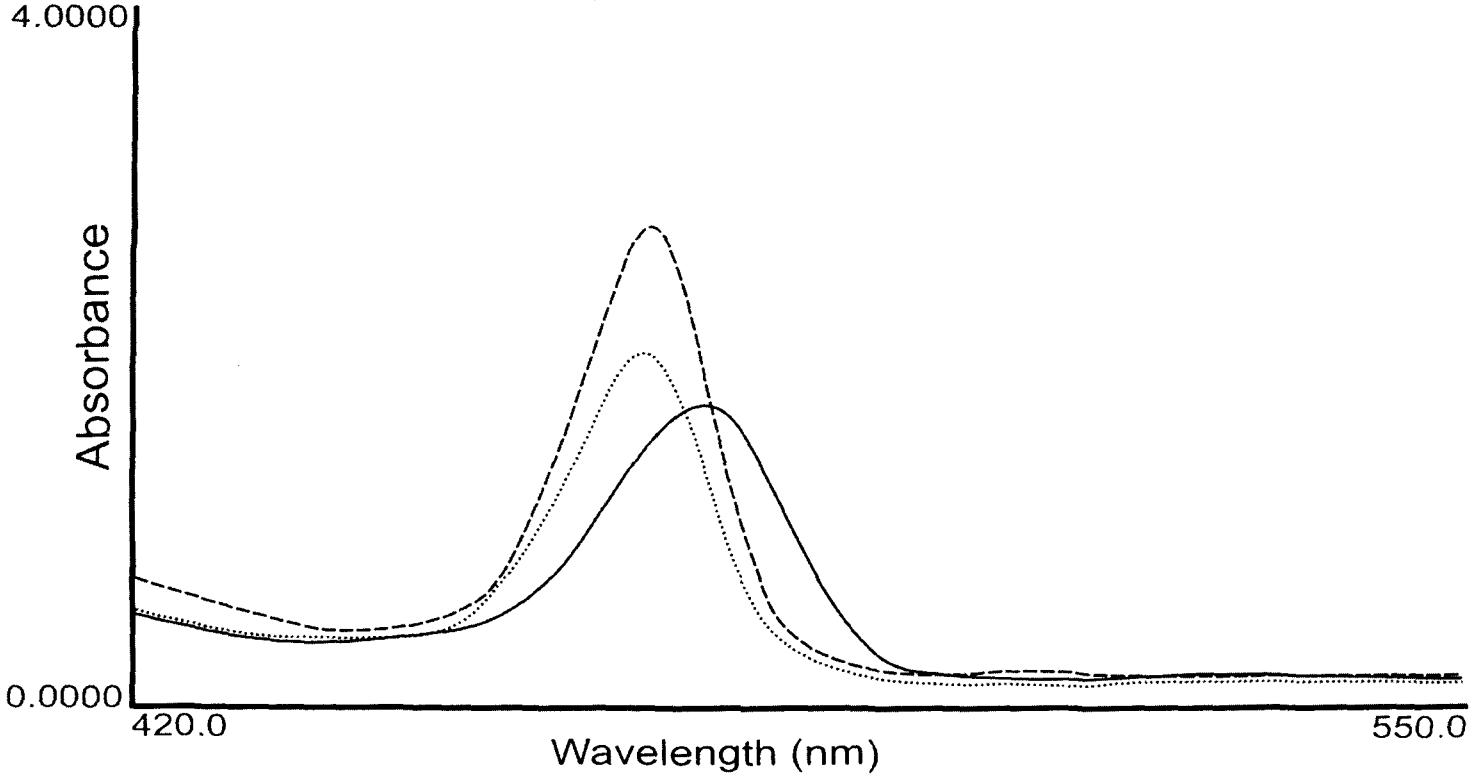


Figure: 4.2.3.b.(i). **UV-Vis Overlay Spectra (B- Band) of Mn[T(2-MeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of TX - 100 (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

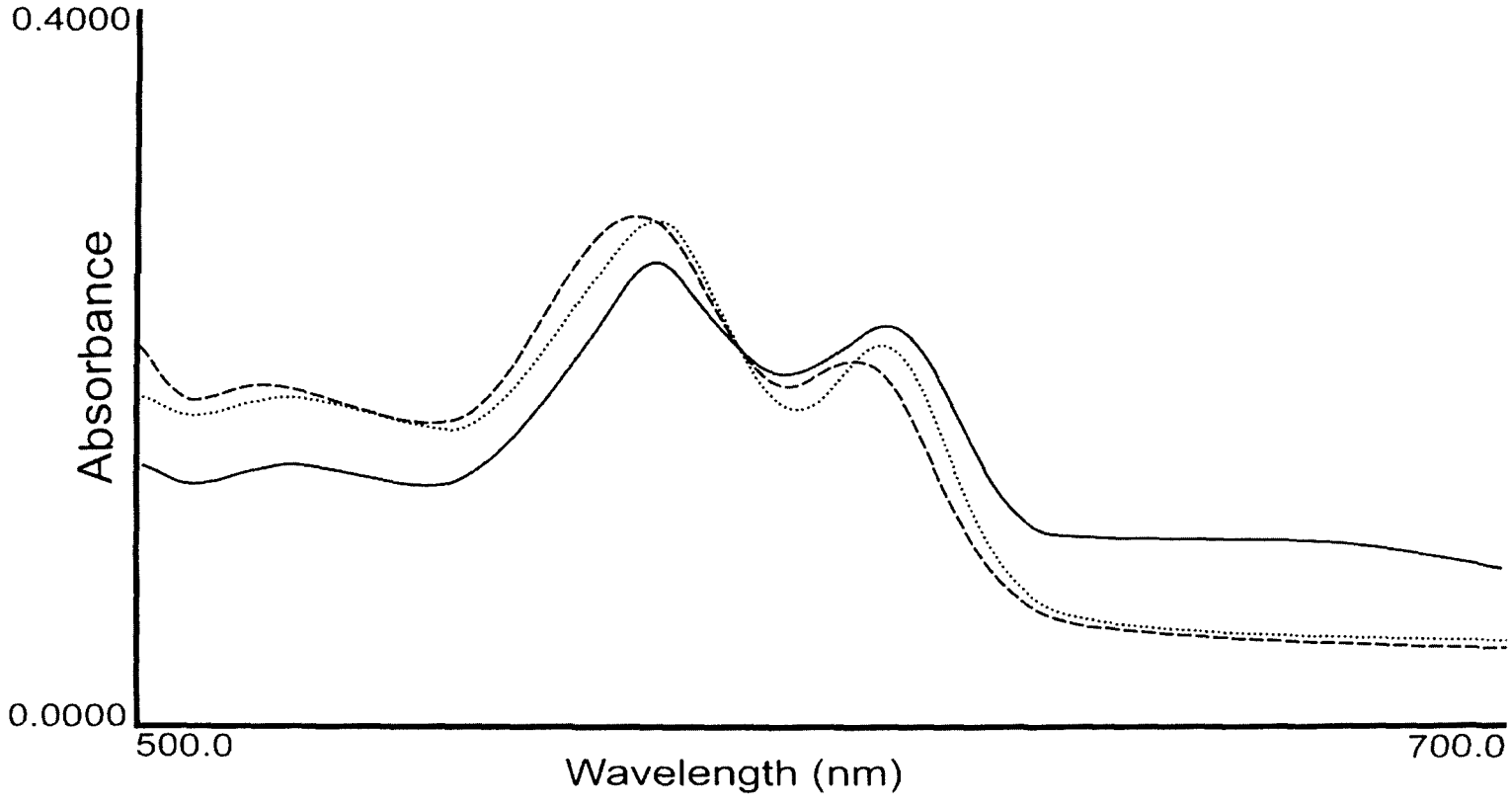


Figure: 4.2.3.b.(ii). **UV-Vis Overlay Spectra (Q- Band) of Mn[T(2-MeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of TX - 100 (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

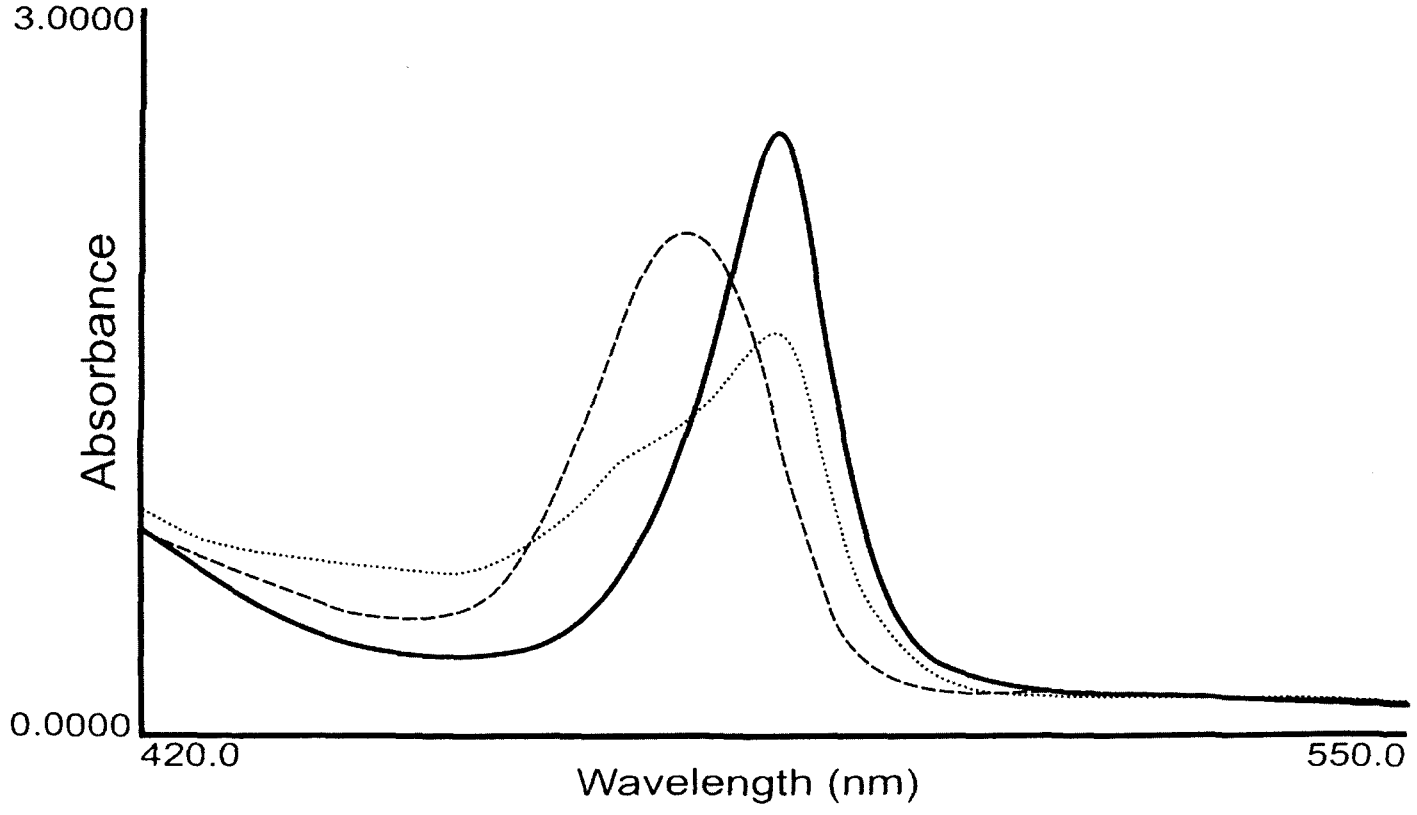


Figure:4.2.3.c.(i). **UV-Vis Overlay Spectra (B- Band) of Mn[T(2-MeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of CTAB (10^{-1}M in $CHCl_3$) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

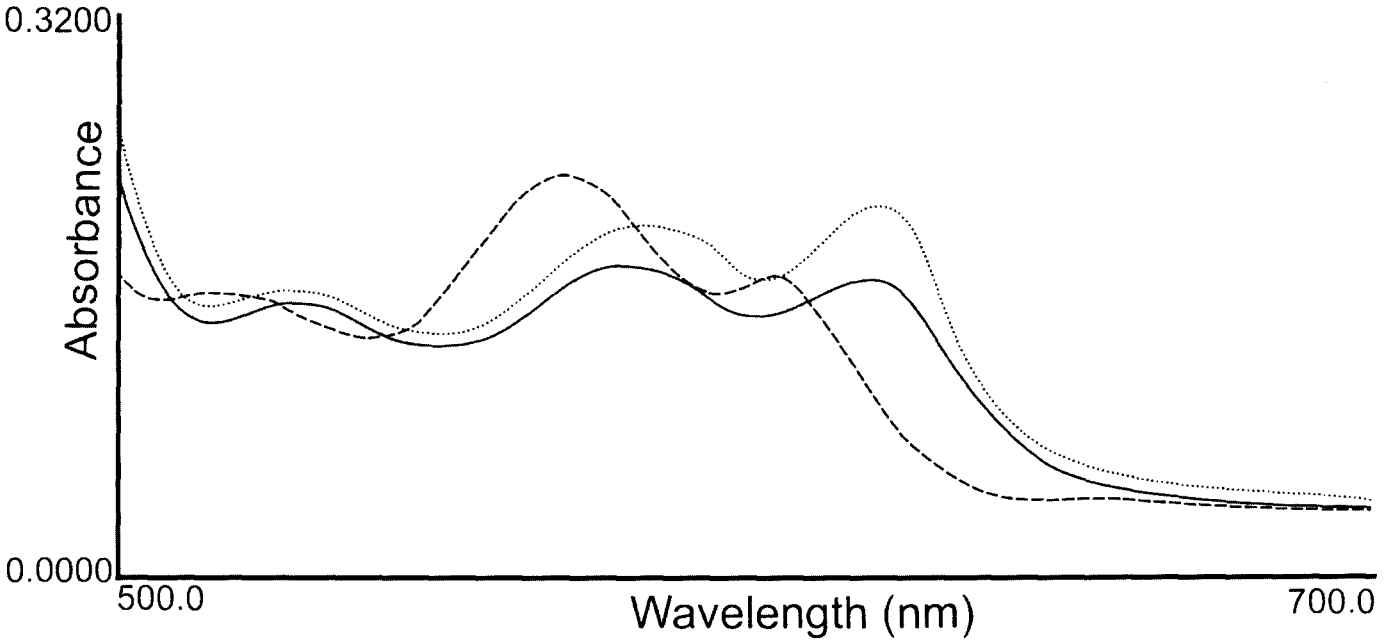


Figure:4.2.3.c.(ii). UV-Vis Overlay Spectra (Q- Band) of Mn[T(2-MeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of CTAB (10^{-1}M in $CHCl_3$) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.

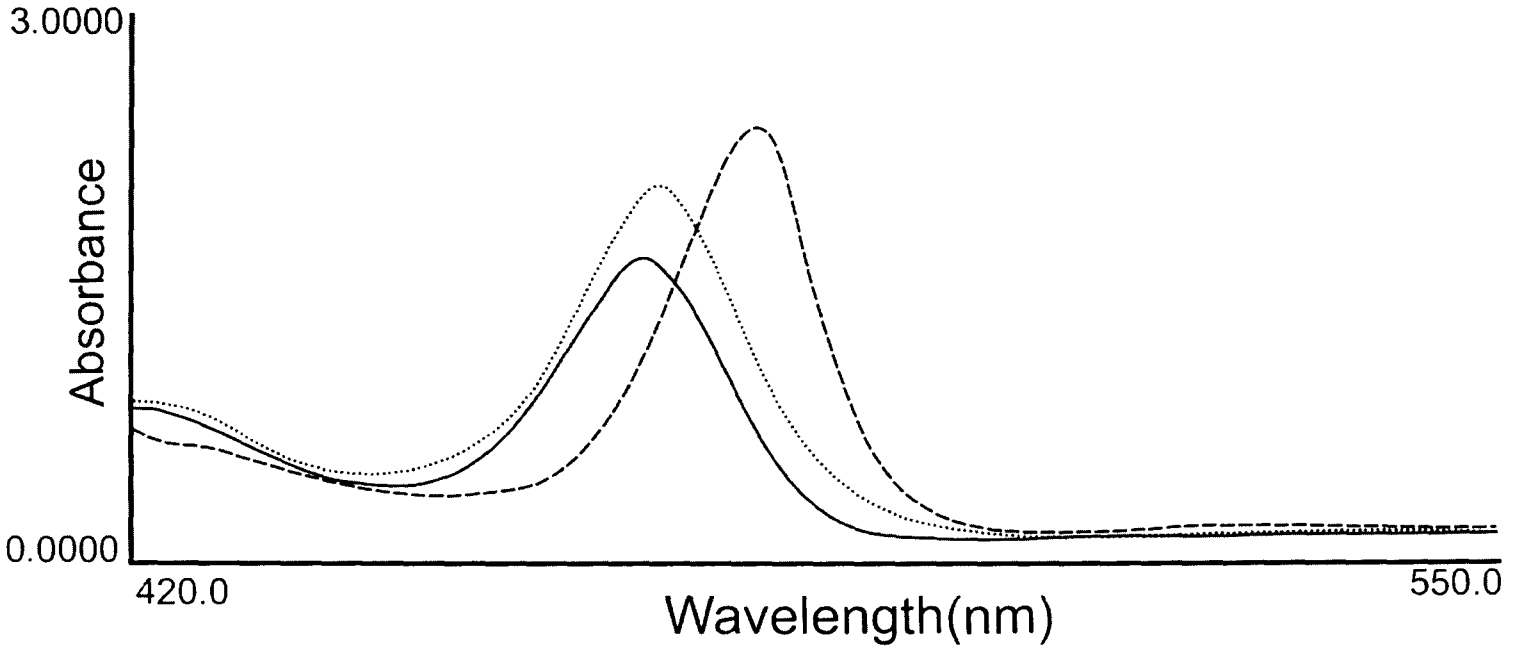


Figure:4.2.4.a.(i). **UV-Vis Overlay Spectra (B- Band) of Mn[T(3-MeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of SDS (10^{-1}M in CH_3OH) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

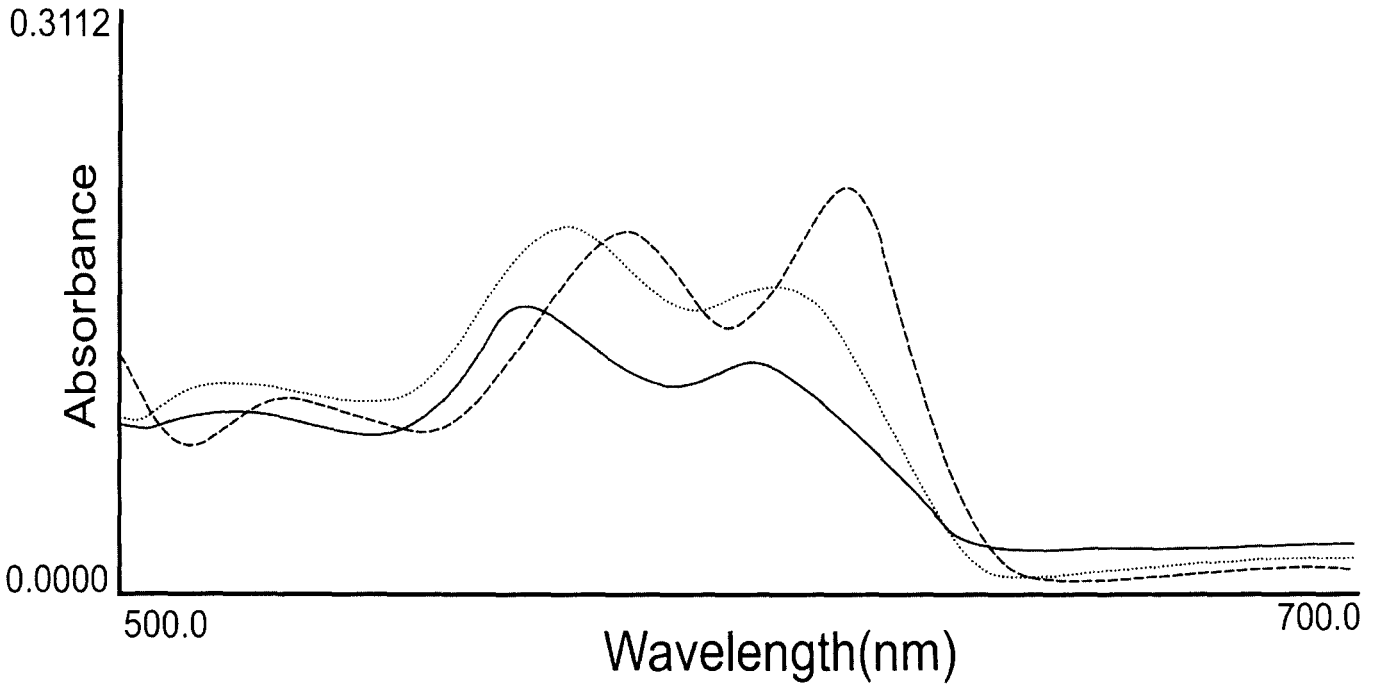


Figure:4.2.4.a.(ii). UV-Vis Overlay Spectra (Q- Band) of Mn[T(3-MeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of SDS (10^{-1}M in CH_3OH) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.

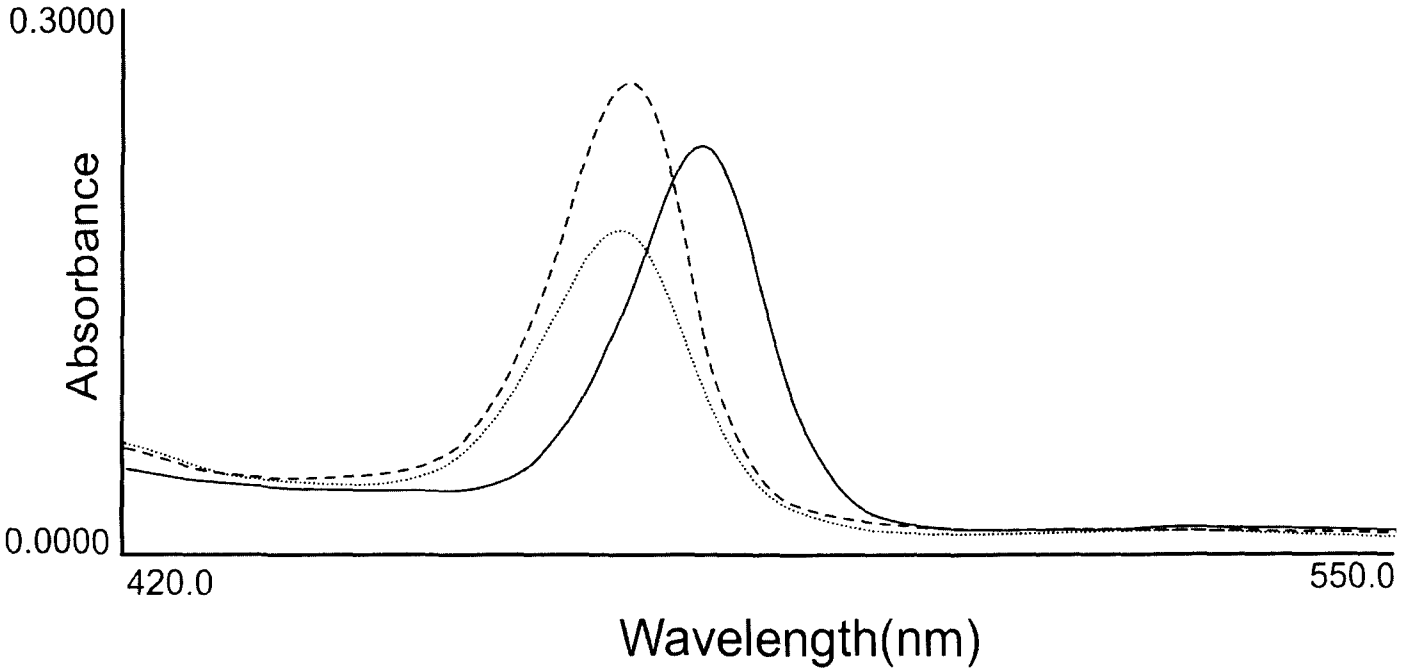


Figure: 4.2.4.b.(i). **UV-Vis Overlay Spectra (B- Band) of Mn[T(3-MeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of TX - 100 (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

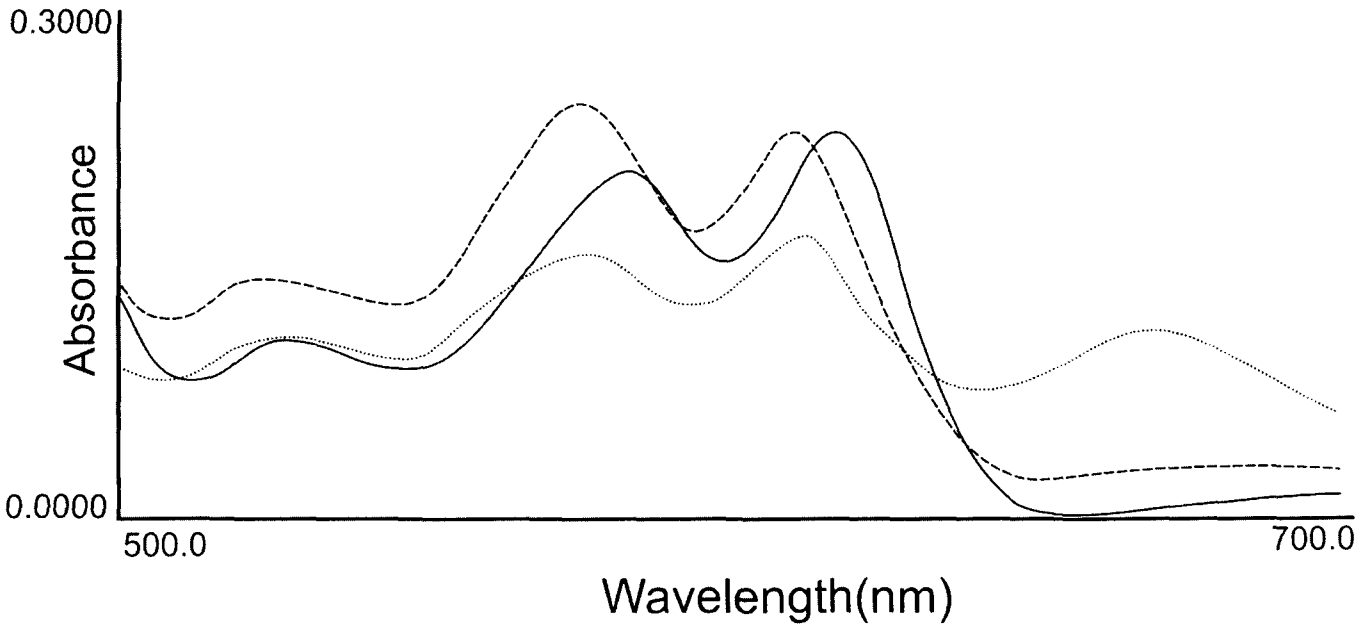


Figure: 4.2.4.b.(ii). **UV-Vis Overlay Spectra (Q- Band) of Mn[T(3-MeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of TX - 100 (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

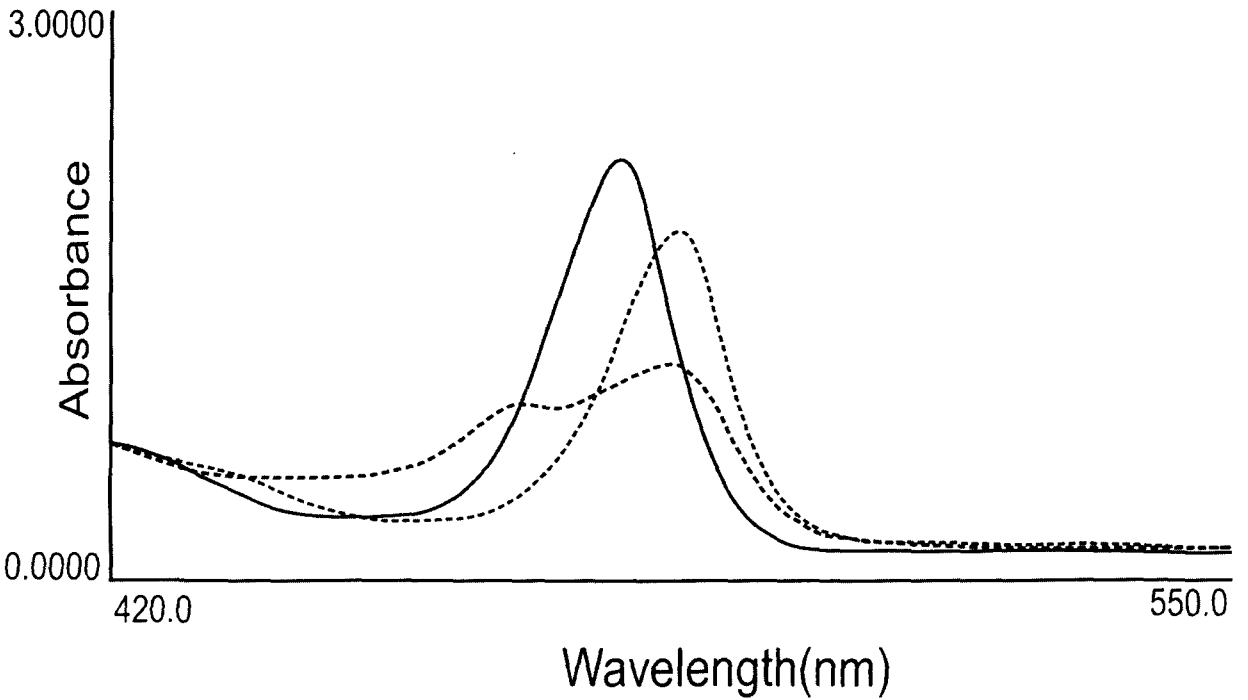


Figure:4.2.4.c.(i). **UV-Vis Overlay Spectra (B- Band) of Mn[T(3-MeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of CTAB (10^{-1}M in $CHCl_3$) (- - -) and 0.3mol of triethylamine (·····) at Room Temperature.**

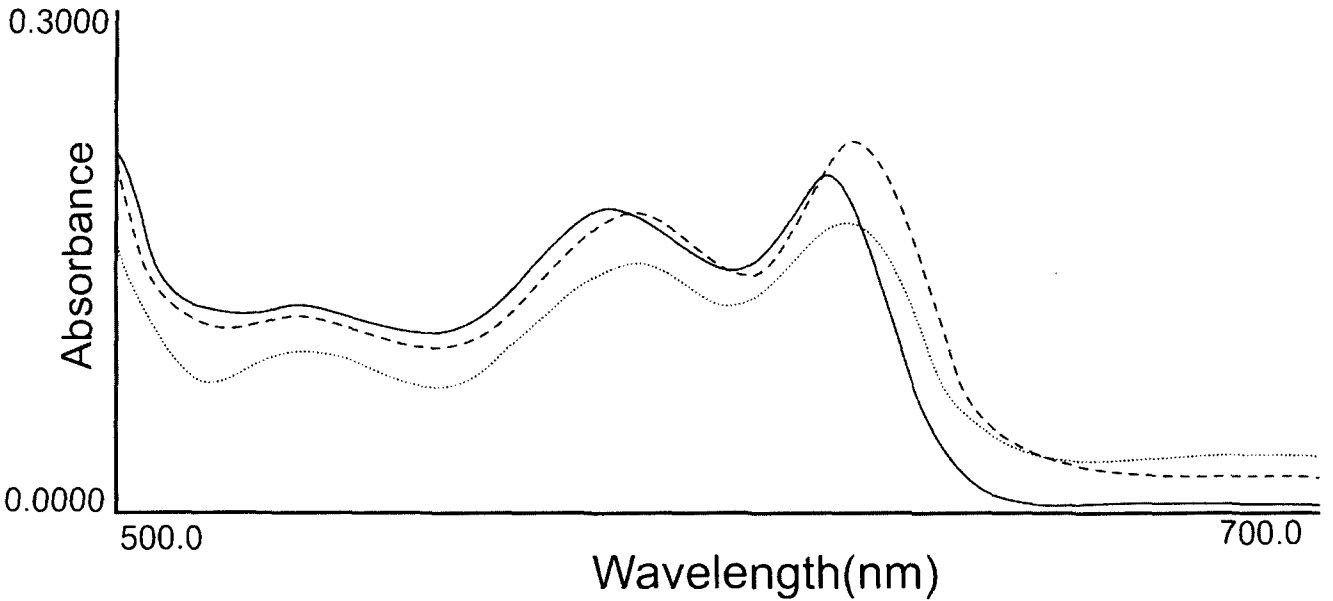


Figure:4.2.4.c.(ii). UV-Vis Overlay Spectra (Q- Band) of Mn[T(3-MeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of CTAB (10^{-1}M in $CHCl_3$) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.

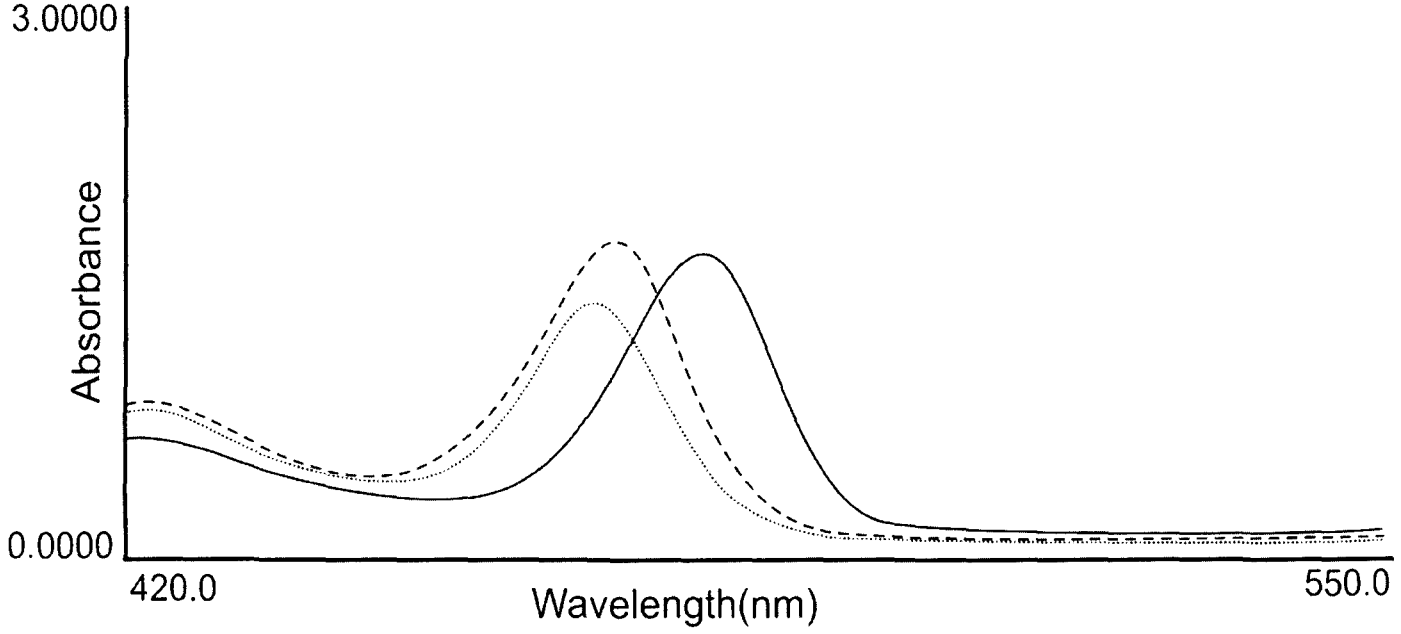


Figure:4.2.5.a.(i). **UV-Vis Overlay Spectra (B- Band) of Mn[T(4-MeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of SDS (10^{-1}M in CH_3OH) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

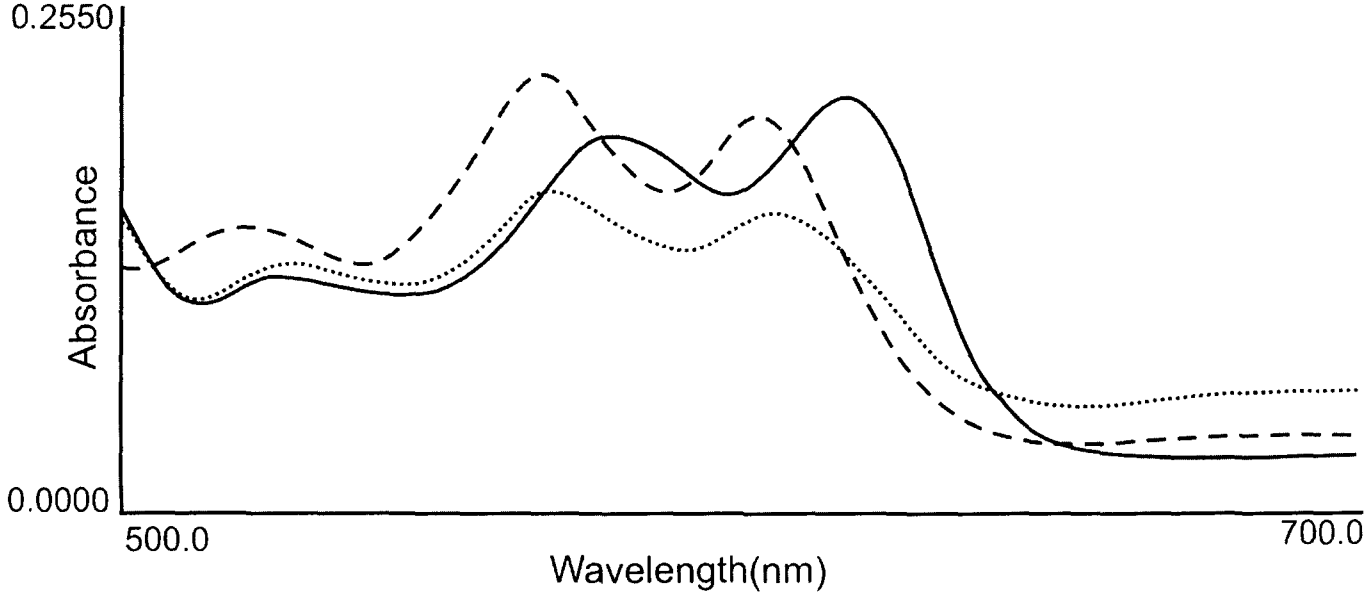


Figure:4.2.5.a.(ii). UV-Vis Overlay Spectra (Q- Band) of Mn[T(4-MeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of SDS (10^{-1}M in CH_3OH) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.

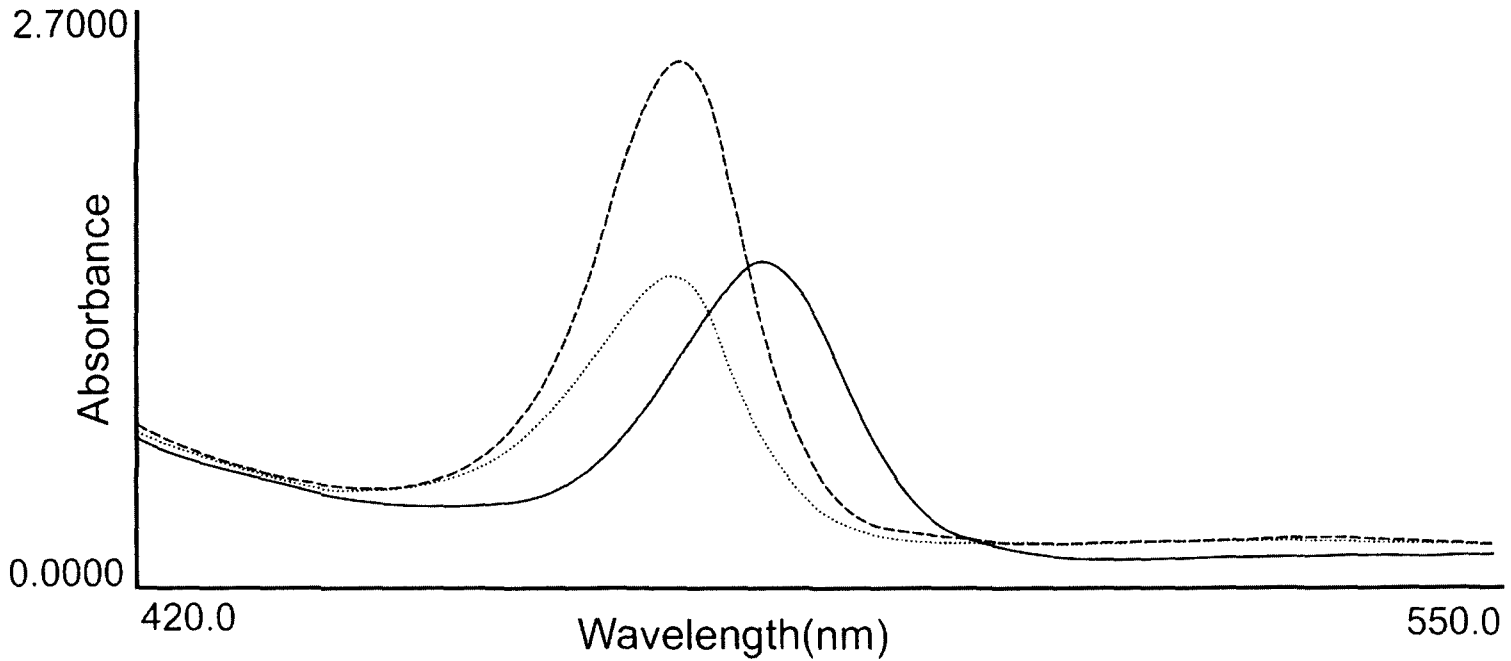


Figure: 4.2.5.b.(i). **UV-Vis Overlay Spectra (B- Band) of Mn[T(4-MeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of TX - 100 (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

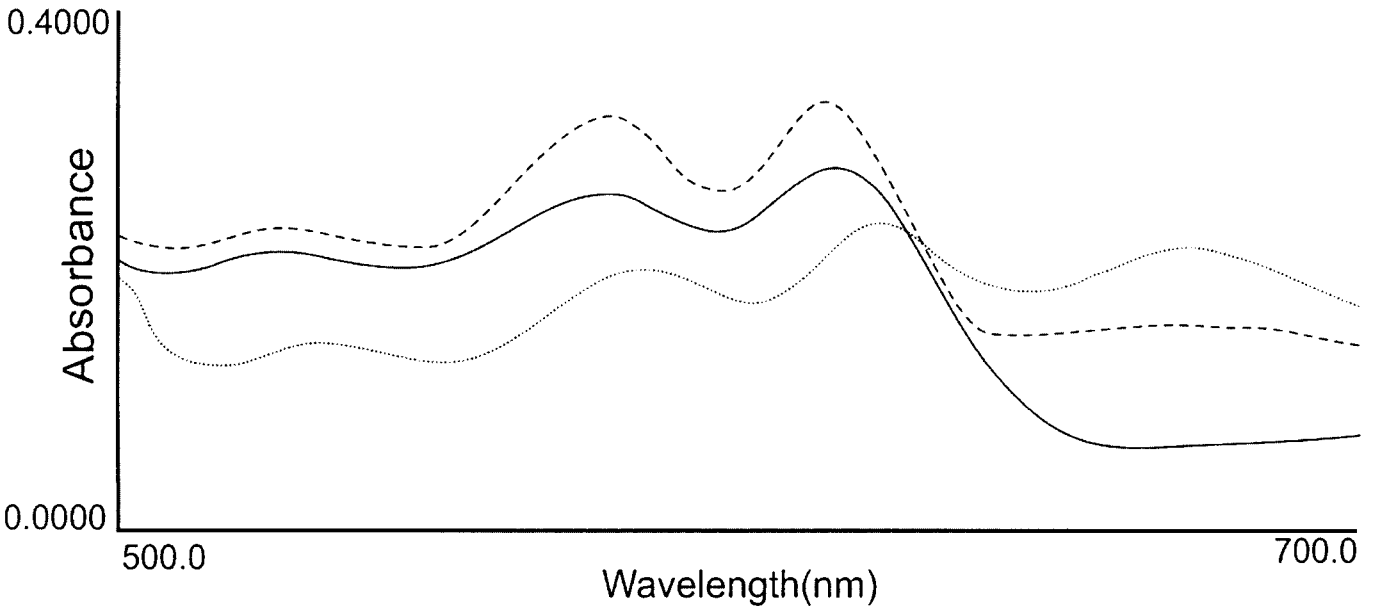


Figure: 4.2.5.b.(ii). **UV-Vis Overlay Spectra (Q- Band) of Mn[T(4-MeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of TX - 100 (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

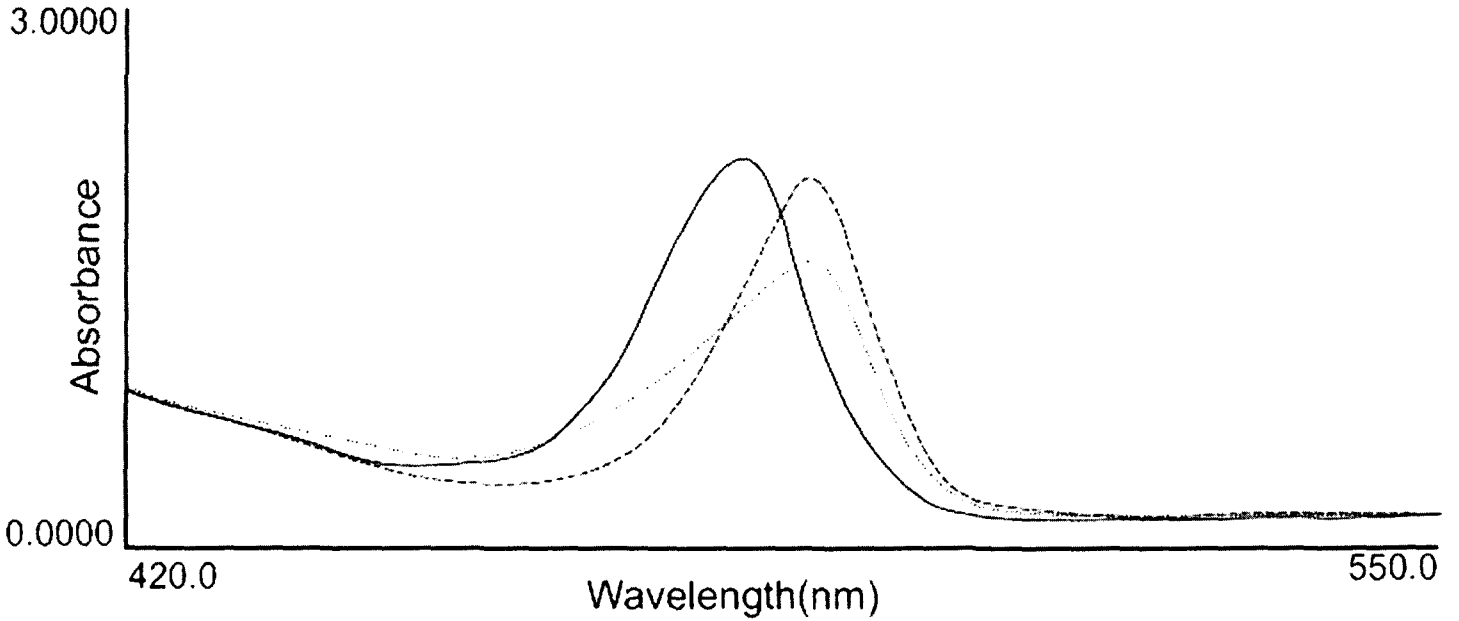


Figure:4.2.5.c.(i). **UV-Vis Overlay Spectra (B- Band) of Mn[T(4-MeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of CTAB (10^{-1}M in $CHCl_3$) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

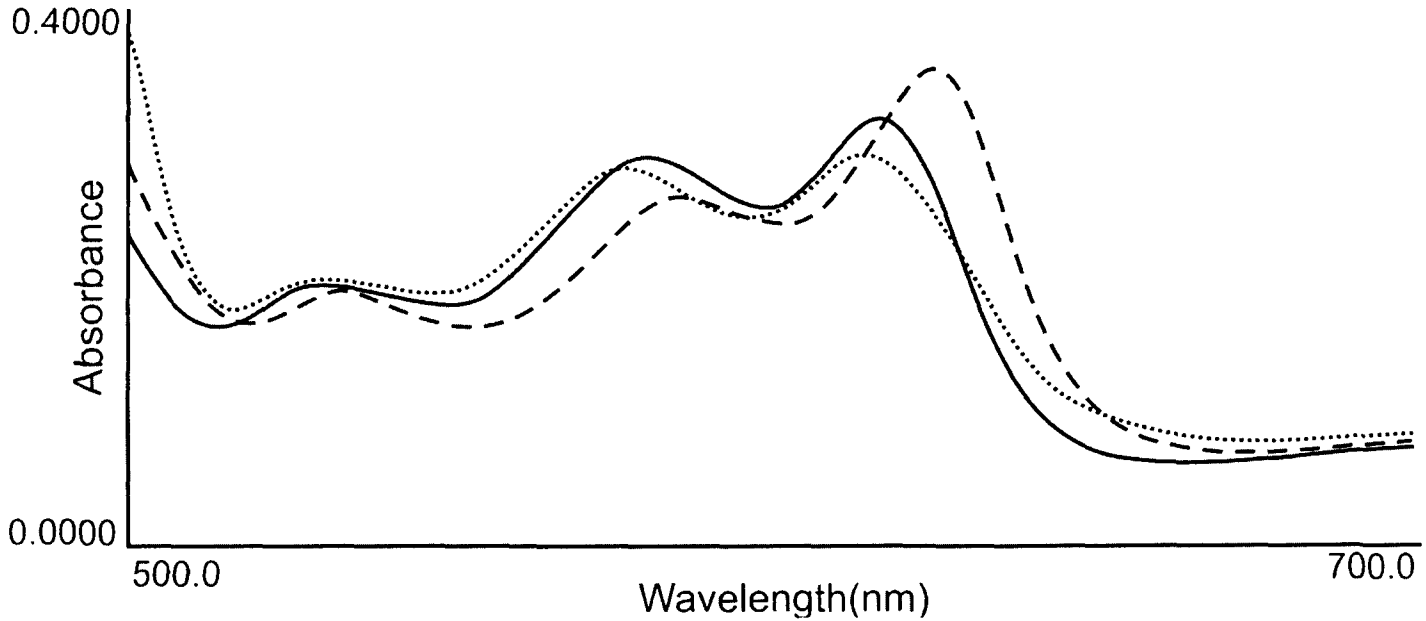


Figure:4.2.5.c.(ii). UV-Vis Overlay Spectra (Q- Band) of Mn[T(4-MeP)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of CTAB (10^{-1}M in $CHCl_3$) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.

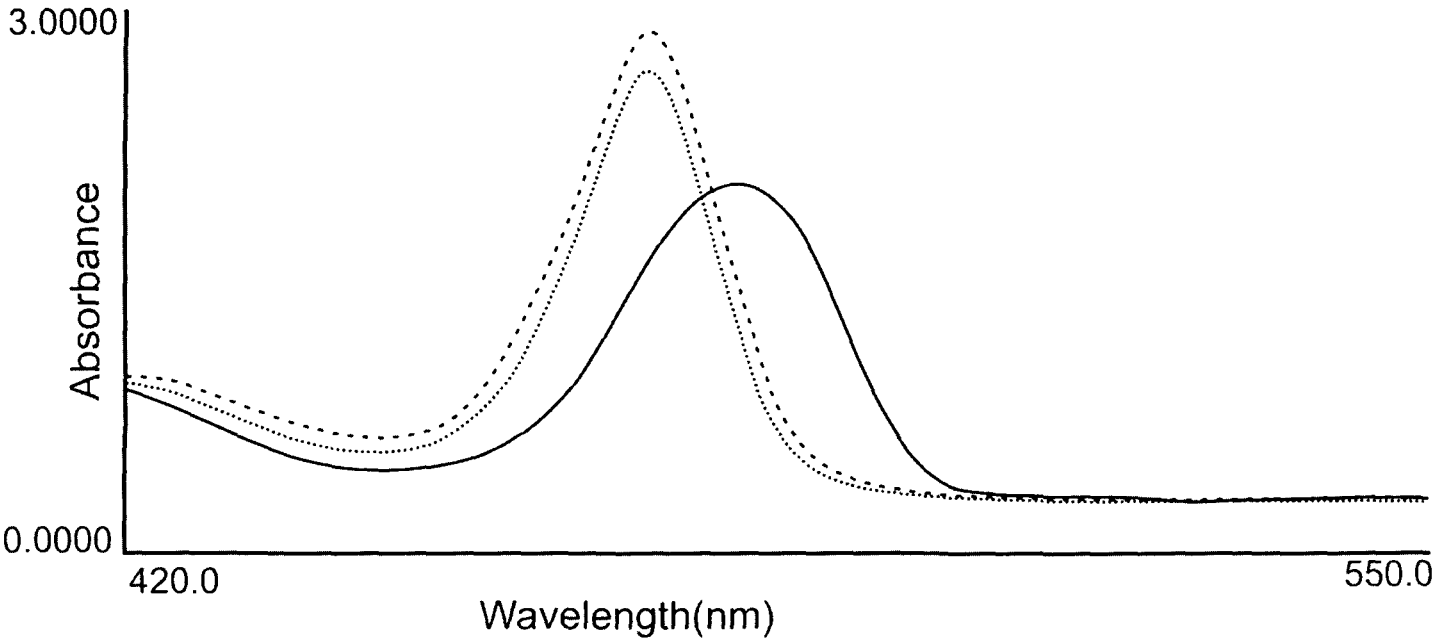


Figure:4.2.6.a.(i). UV-Vis Overlay Spectra (B- Band) of Mn[T(naphthyl)]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of SDS (10^{-1}M in CH_3OH) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.

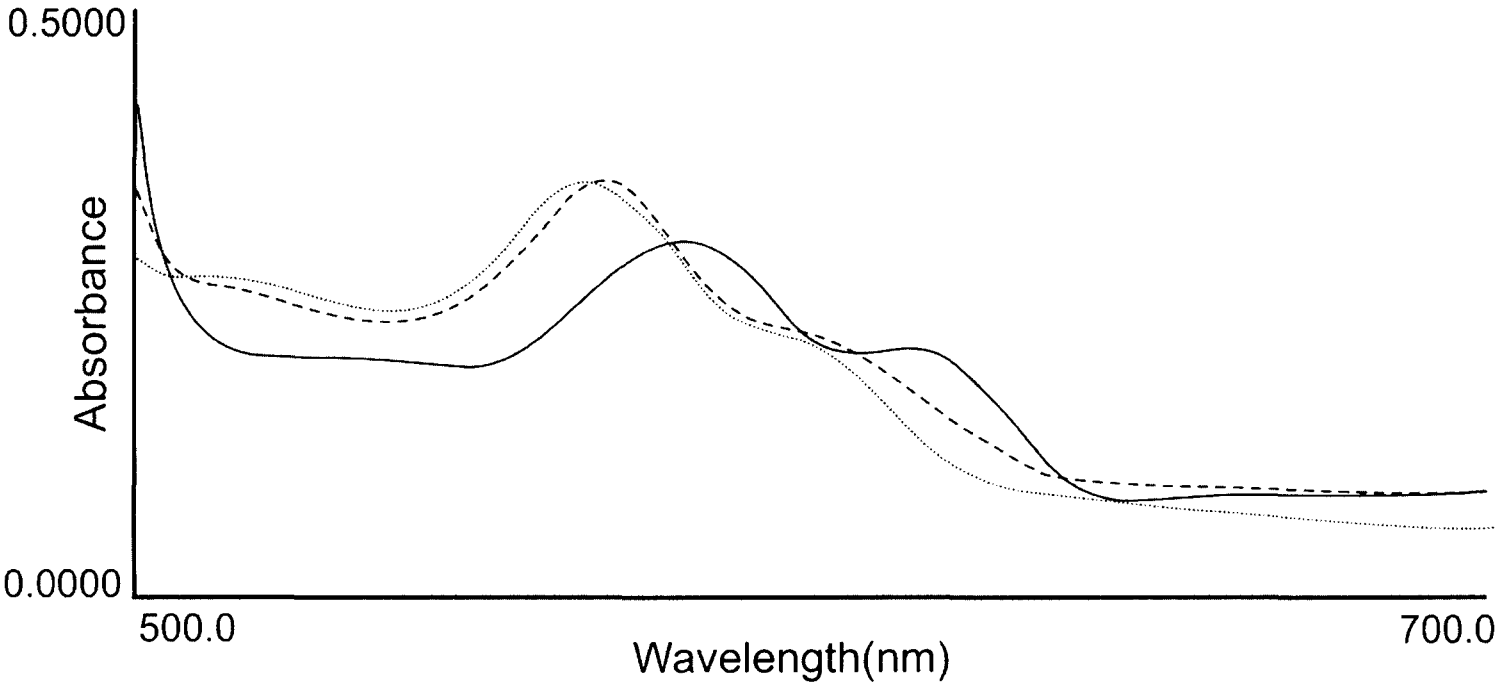


Figure:4.2.6.a.(ii). UV-Vis Overlay Spectra (Q- Band) of Mn[T(naphthyl)]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of SDS (10^{-1}M in CH_3OH) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.

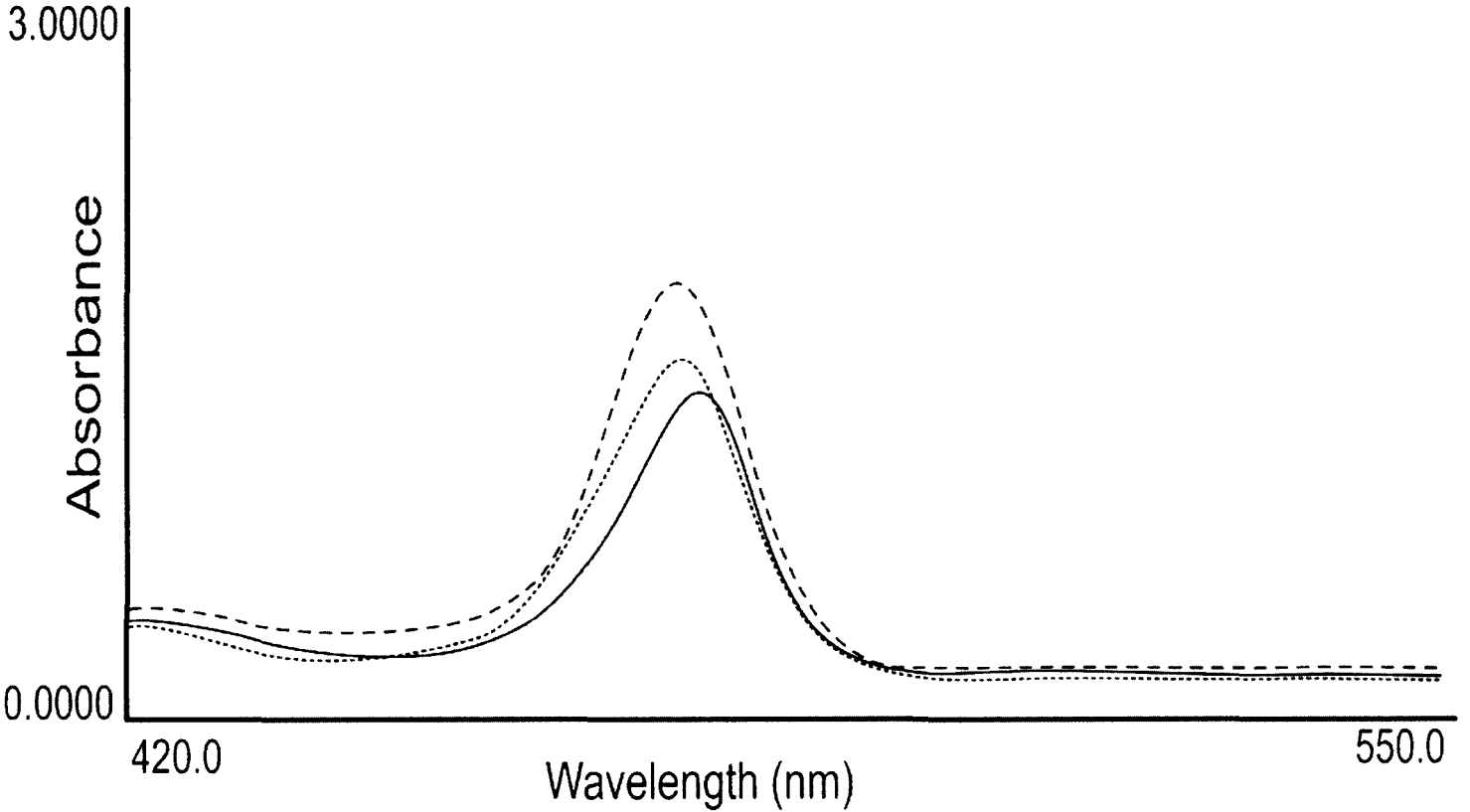


Figure: 4.2.6.b.(i). **UV-Vis Overlay Spectra (B- Band) of Mn[T(naphthyl)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of TX - 100 (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

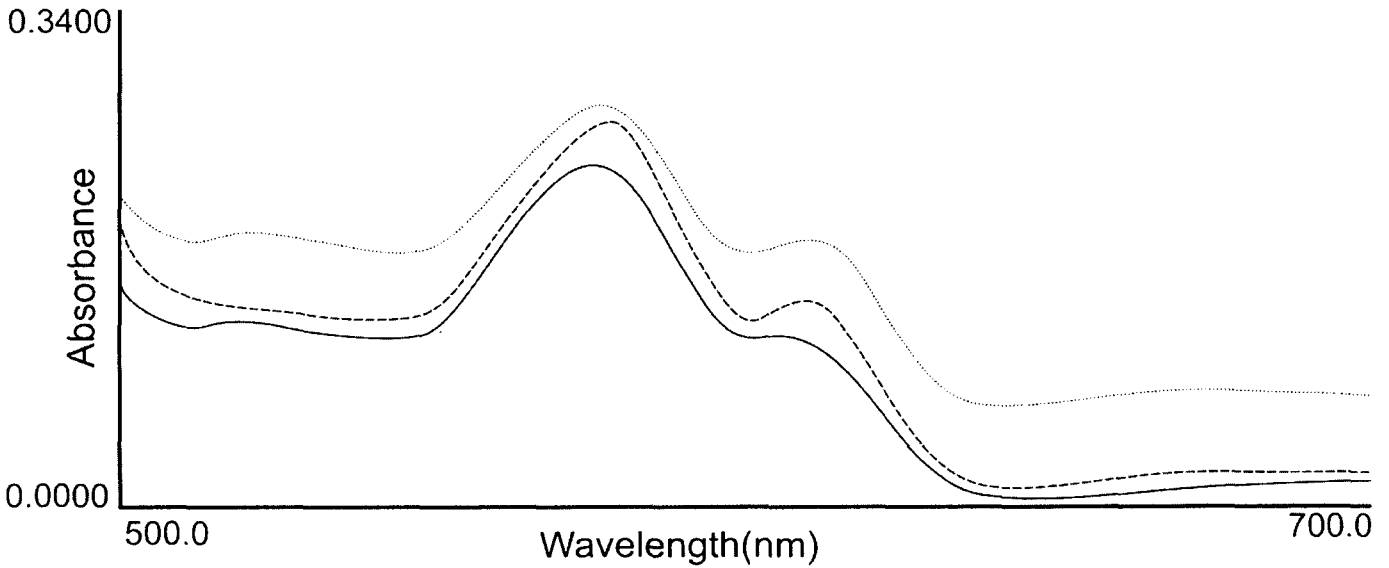


Figure: 4.2.6.b.(ii). **UV-Vis Overlay Spectra (Q- Band) of Mn[T(naphthyl)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of TX - 100 (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

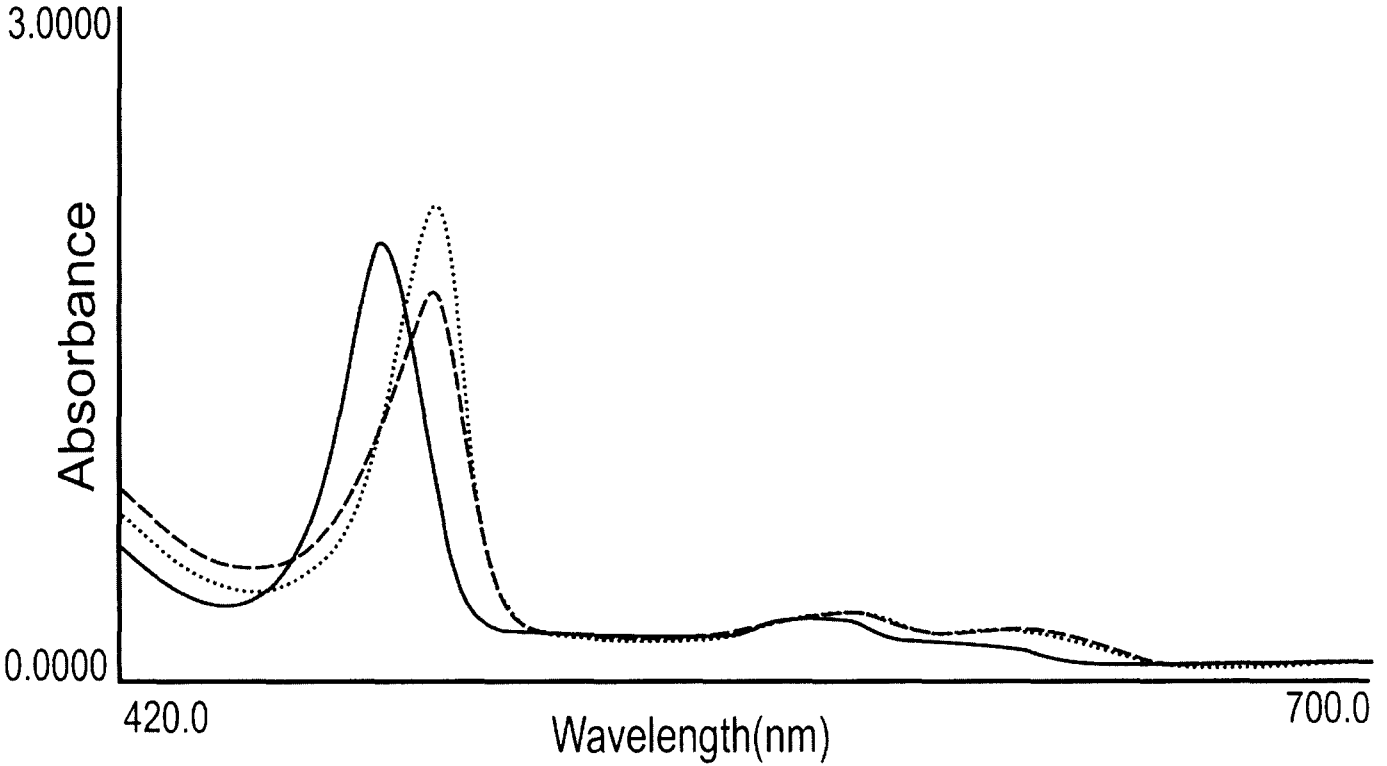


Figure:4.2.6.c. **UV-Vis Overlay Spectra of Mn[T(naphthyl)P]OAc (10^{-5}M in $CHCl_3$)(——); in the presence of CTAB (10^{-1}M in $CHCl_3$) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

REFERENCES:

1. J.H. Fendler, *Science*, **223**, 886 (1984).

2. J.H. Fendler, *Annu. Rev. Phys. Chem.*, **35**, 137 (1984).

3. R.G. Weiss, V. Ramamurthy, G.S. Hammond, *Acc. Chem. Res.*, **26**, 530 (1993).

4. K. Kalyansundaram, *Photochemistry in micro heterogeneous systems*, Acad. Press, New York, 1991.

5. N.C. Maiti, S. Mazumdar and N. Periasamy, *J. Phys. Chem.*, **99**, 10708 – 10715 (1995).

6. R. Matsuoka, T.Yui, R. Sasai, K. Takagi, H. Inoue, *Mol.Cryt.Lig.Cryst.*, **341**, 333 (2000).

7. *The Porphyrin Hand book*, Edited by K.M. Kadish, K.M. Smith, R. Guilard, Acad. Press, New York, 1999.

8. K. Yamashita, N. Kihara, H.Shimidzu and H. Suzuki, *Photochem. Photobiol.*, **35**, 1 (1982).

9. R.B. Beswick, C.W. Pitt, *Chem.Phys.Lett.*, **143**, 589 (1988).

10. N.C. Maiti, S. Mazumdar, N. Periasamy, *J.Phys.Chem.B*, **102**, 1528 (1998).

11. A. Osuka, K. Maruyama, *J.Am.Chem.Soc.*, **110**, 4454 (1988).

12. T. Nagata, A. Osuka, K. Maruyama, *J.Am.Chem.Soc.*, 112, 3054 (1988).

13. J.A. Shelnutt, M.M. Dobey, D.J. Sattenlee, *J. Phys. Chem.*, **88**, 4980 (1984).

14. J. A. Shelnutt, *J. Phys. Chem.*, **88**, 4988 (1984).

15. S. Mazumdar, *J. Phys. Chem.*, **94**, 5947 (1994).

CHAPTER – 5

CYCLIC VOLTAMMETRIC STUDIES OF SOME MANGANESE PORPHYRINS IN SURFACTANT MEDIUM

CHAPTER - 5

5.1. INTRODUCTION

In surfactant medium, metalloporphyrins maybe encapsulated, mono dispersed[1-9] or aggregated within the interlayer spaces of the micelles[10]. The response of the metalloporphyrin to electrochemical processes will depend on the surrounding environment and will be reflected in the voltammogram. In order to know the redox behaviour of the manganese porphyrins (not soluble in aqueous medium) in the surfactant medium, cyclic voltammetric measurements are carried out. Only the positive scans are monitored.

5.2. RESULTS:

5.2.1. Mn[T(2-OMeP)P]OAc:

Results are summarized in the Table: 5.A. 10^{-3}M solution of Mn[T(2-OMeP)P]OAc in chloroform exhibits two one electron redox couples with $E_{½}$ values 1.101V and 1.365V. Both redox couples correspond to porphyrin ligand oxidations (Figure: 5.2.1.a).

IN SDS MEDIUM:

The Voltammogram exhibits two redox couples with their $E_{½}$ values 1.154V and 1.337V. The $E_{½}$ value corresponding to the first ligand oxidation is slightly higher by 53 mV, while the second oxidation is slightly lower by 28mV (Figure: 5.2.1.b).

IN TX – 100 MEDIUM :

The Voltammogram could not be resolved in TX – 100 medium (Figure: 5.2.1.c).

IN CTAB MEDIUM:

The Voltammogram could not be resolved in CTAB medium (Figure: 5.2.1.d).

5.2.2. Mn[T(4-OMeP)P]OAc:

Results are summarized in the Table: 5.B. The voltammogram in chloroform exhibits two one – electron

redox couples with their $E_{½}$ values 0.9795 V and 1.2615 V (Figure: 5.2.2.a). No metal centered redox couple could be resolved.

IN SDS MEDIUM:

The voltammogram exhibits two one – electron redox couples with $E_{½}$ values 1.0725V and 1.3025V. The $E_{½}$ values are shifted more positively. The $E_{½}$ (1) value corresponding to the first oxidation is shifted positively by 0.093 V while the $E_{½}$ (2) corresponding to the second oxidation is positively shifted by 0.041V (Figure: 5.2.2.b).

IN TX – 100 MEDIUM:

The Voltammogram could not be resolved in TX – 100 medium.

IN CTAB MEDIUM:

The Voltammogram could not be resolved in CTAB medium.

5.2.3. Mn[T(2-MeP)P]OAc:

The voltammogram exhibits two one – electron redox couples with $E_{½}$ values 1.033V and 1.285V (Table: 5.C). No metal centered redox couple could be observed (Figure: 5.2.3.a).

IN SDS MEDIUM:

The voltammogram exhibits two redox couples with $E_{½}$ values 1.105V and 1.35V (Figure: 5.2.3.b). The $E_{½}$ values are shifted towards more positive side. The $E_{½}$ (1) is shifted positively by 0.072V while $E_{½}$ (2) is shifted positively by 0.065V.

IN TX – 100 MEDIUM:

The Voltammogram could not be resolved in TX – 100 medium.

IN CTAB MEDIUM:

The Voltammogram could not be resolved in this case.

5.2.4. Mn[T(3-MeP)P]OAc:

In chloroform, the voltammogram exhibits two redox couples with $E_{½}$ values 1.165V and 1.45V (Table: 5.D). No metal centered redox couple could be observed. The redox couples correspond to porphyrin ligand oxidations. (Figure: 5.2.4.a).

IN SDS MEDIUM:

Two redox couples with $E_{½}$ values 1.175V and 1.465V (Figure: 5.2.4.b). The $E_{½}$ values are slightly shifted towards positive side. The $E_{½}$ (1) is shifted by 0.010V while $E_{½}$ (2) is shifted by 0.015 V.

IN TX – 100 MEDIUM:

The Voltammogram could not be resolved in this medium.

IN CTAB MEDIUM:

The Voltammogram could not be resolved in CTAB medium.

5.2.5. Mn[T(4-MeP)P]OAc:

The voltammogram in chloroform consists of two redox couples (Figure:5.2.5.a) with their corresponding $E_{½}$ values of 1.095V and 1.40V. The two $E_{½}$ values correspond to ligand oxidations. No metal centered oxidation could be observed (Table: 5.E).

IN SDS MEDIUM:

The voltammogram consists of two redox couples (Figure: 5.2.5.b.) with $E_{½}$ values of 1.135V and 1.35V. The first oxidation potential is shifted slightly towards the positive side by 0.040V while the second oxidation potential is slightly lowered by 0.050V.

IN TX – 100 MEDIUM:

The Voltammogram could not be resolved in this medium.

IN CTAB MEDIUM:

Here the Voltammogram could not be resolved.

5.2.6. Mn[T(naphthyl)P]OAc:

In chloroform it gives a voltammogram comprises of two redox couples (Figure: 5.2.6.a) with $E_{½}$ values 0.9525V and 1.3285V (Table:5.F). These two potentials correspond to the first and second ligand oxidations. No metal oxidations are observed.

IN SDS MEDIUM:

The voltammogram exhibits two redox couples with $E_{½}$ values 1.0765V and 1.38V. Both $E_{½}$ values are shifted positively. $E_{½}$ (1) is shifted by 0.124V while the $E_{½}$ (2) is shifted by 0.052V (Figure: 5.2.6.b).

IN TX – 100 MEDIUM:

Here the Voltammogram could not be resolved.

IN CTAB MEDIUM:

The Voltammogram could not be resolved in CTAB medium.

5.3. DISCUSSION:

In the SDS medium only the ligand oxidations are observed and no metal centered redox couples are observed. The ligand oxidations are found to be slightly shifted towards the positive side (higher side). The voltammogram does not indicate the presence of dimer but the two redox couples indicate the oxidations of monomeric porphyrins. Further, the voltammogram indicates that the metal ion is not available for the redox process. The higher $E_{1/2}$ values is indicative of a conformation closer to planar form. It is most likely that the porphyrin is outside the micelle.

5.4. CONCLUSION:

From the cyclic voltammetric studies the following observations are made:

(i) It is most likely that metalloporphyrins are mono dispersed in the interlayer spaces of the micelles.

(ii) The central metal ion is interacting strongly with the charged surface of the micelles and hence is not available for the redox processes.

(iii) Due to restricted space, the porphyrin molecules could be in a planar like structure.

TABLE 5.A. : REDOX POTENTIALS OF Mn[T(2-OMeP)P]OAc AT ROOM TEMPERATURE
SOLVENT : CHLOROFORM
CONCENTRATION : 10^{-3}M
SUPPORTING ELECTROLYTE : TBAP
REFERENCE ELECTRODE : Ag/AgCl
SCAN RATE : 0.1 (V/s)

COMPOUNDS		$E_{pa}(1)$ (V)	$E_{pa}(2)$ (V)	$E_{pc}(1)$ (V)	$E_{pc}(2)$ (V)	$E_{1/2}(1)$ (V)	$E_{1/2}(2)$ (V)	ΔE_1 (V)	ΔE_2 (V)
Mn[T(2-OMeP)P]OAc	In Chloroform	1.152	1.420	1.050	1.310	1.101	1.365	0.102	0.110
	With SDS (10^{-1}M in CH_3OH)	1.205	1.373	1.103	1.301	1.154	1.337	0.102	0.072
	With TX – 100	-	-	-	-	-	-	-	-
	With CTAB (10^{-1}M in $CHCl_3$)	-	-	-	-	-	-	-	-

TABLE 5.B. : REDOX POTENTIALS OF Mn[T(4-OMeP)P]OAc AT ROOM TEMPERATURE
SOLVENT : CHLOROFORM
CONCENTRATION : 10^{-3}M
SUPPORTING ELECTROLYTE : TBAP
REFERENCE ELECTRODE : Ag/AgCl
SCAN RATE : 0.1 (V/s)

COMPOUNDS		$E_{pa}(1)$ (V)	$E_{pa}(2)$ (V)	$E_{pc}(1)$ (V)	$E_{pc}(2)$ (V)	$E_{1/2}(1)$ (V)	$E_{1/2}(2)$ (V)	ΔE_1 (V)	ΔE_2 (V)
Mn[T(4-OMeP)P]OAc	In Chloroform	1.125	1.40	0.834	1.123	0.9795	1.2615	0.291	0.277
	With SDS (10^{-1}M in CH_3OH)	1.175	1.402	0.970	1.203	1.0725	1.3025	0.205	0.199
	With TX – 100	-	-	-	-	-	-	-	-
	With CTAB (10^{-1}M in $CHCl_3$)	-	-	-	-	-	-	-	-

TABLE 5.C. : REDOX POTENTIALS OF Mn[T(2-MeP)P]OAc AT ROOM TEMPERATURE
SOLVENT : CHLOROFORM
CONCENTRATION : 10^{-3}M
SUPPORTING ELECTROLYTE : TBAP
REFERENCE ELECTRODE : Ag/AgCl
SCAN RATE : 0.1 (V/s)

COMPOUNDS		$E_{pa}(1)$ (V)	$E_{pa}(2)$ (V)	$E_{pc}(1)$ (V)	$E_{pc}(2)$ (V)	$E_{1/2}(1)$ (V)	$E_{1/2}(2)$ (V)	ΔE_1 (V)	ΔE_2 (V)
Mn[T(2-MeP)P]OAc	In Chloroform	1.07	1.32	0.996	1.25	1.033	1.285	0.074	0.070
	With SDS (10^{-1}M in CH_3OH)	1.16	1.40	1.05	1.30	1.105	1.35	0.110	0.100
	With TX – 100	-	-	-	-	-	-	-	-
	With CTAB (10^{-1}M in $CHCl_3$)	-	-	-	-	-	-	-	-

TABLE 5.D. : REDOX POTENTIALS OF Mn[T(3-MeP)P]OAc AT ROOM TEMPERATURE
SOLVENT : CHLOROFORM
CONCENTRATION : 10^{-3}M
SUPPORTING ELECTROLYTE : TBAP
REFERENCE ELECTRODE : Ag/AgCl
SCAN RATE : 0.1 (V/s)

COMPOUNDS		$E_{pa}(1)$ (V)	$E_{pa}(2)$ (V)	$E_{pc}(1)$ (V)	$E_{pc}(2)$ (V)	$E_{1/2}(1)$ (V)	$E_{1/2}(2)$ (V)	ΔE_1 (V)	ΔE_2 (V)
Mn[T(3-MeP)P]OAc	In Chloroform	1.33	1.57	1.0	1.33	1.165	1.45	0.330	0.240
	With SDS (10^{-1}M in CH_3OH)	1.33	1.58	1.02	1.35	1.175	1.465	0.310	0.230
	With TX – 100	-	-	-	-	-	-	-	-
	With CTAB (10^{-1}M in $CHCl_3$)	-	-	-	-	-	-	-	-

TABLE 5.E. : REDOX POTENTIALS OF Mn[T(4-MeP)P]OAc AT ROOM TEMPERATURE
SOLVENT : CHLOROFORM
CONCENTRATION : 10^{-3}M
SUPPORTING ELECTROLYTE : TBAP
REFERENCE ELECTRODE : Ag/AgCl
SCAN RATE : 0.1 (V/s)

COMPOUNDS		$E_{pa}(1)$ (V)	$E_{pa}(2)$ (V)	$E_{pc}(1)$ (V)	$E_{pc}(2)$ (V)	$E_{1/2}(1)$ (V)	$E_{1/2}(2)$ (V)	ΔE_1 (V)	ΔE_2 (V)
Mn[T(4-MeP)P]OAc	In Chloroform	1.22	1.50	0.97	1.30	1.095	1.40	0.250	0.200
	With SDS (10^{-1}M in CH_3OH)	1.22	1.38	1.05	1.32	1.135	1.35	0.170	0.060
	With TX – 100	-	-	-	-	-	-	-	-
	With CTAB (10^{-1}M in $CHCl_3$)	-	-	-	-	-	-	-	-

TABLE 5.F. : REDOX POTENTIALS OF Mn[T(naphthyl)P]OAc AT ROOM TEMPERATURE
SOLVENT : CHLOROFORM
CONCENTRATION : 10^{-3}M
SUPPORTING ELECTROLYTE : TBAP
REFERENCE ELECTRODE : Ag/AgCl
SCAN RATE : 0.1 (V/s)

COMPOUNDS		$E_{pa}(1)$ (V)	$E_{pa}(2)$ (V)	$E_{pc}(1)$ (V)	$E_{pc}(2)$ (V)	$E_{1/2}(1)$ (V)	$E_{1/2}(2)$ (V)	ΔE_1 (V)	ΔE_2 (V)
Mn[T(naphthyl)P]OAc	In Chloroform	1.027	1.363	0.878	1.294	0.9525	1.3285	0.149	0.069
	With SDS (10^{-1}M in CH_3OH)	1.150	1.424	1.003	1.336	1.0765	1.38	0.147	0.088
	With TX – 100	-	-	-	-	-	-	-	-
	With CTAB (10^{-1}M in $CHCl_3$)	-	-	-	-	-	-	-	-

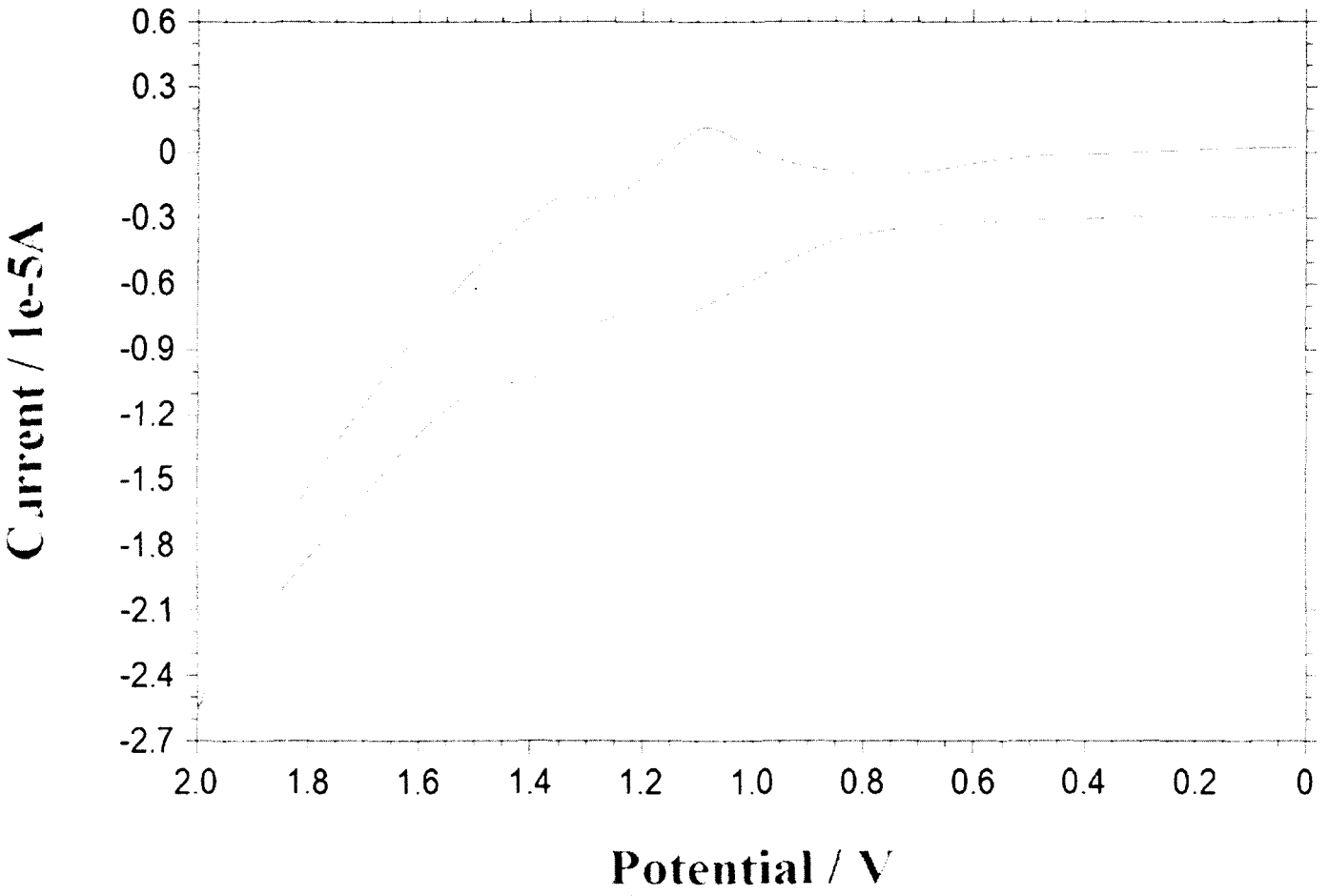


Figure:5.2.1.a. **Cyclic Voltammogram of Mn[T(2-OMeP)P]OAc (10^{-3}M in $CHCl_3$) containing 0.1M TBAP at Room Temperature.**

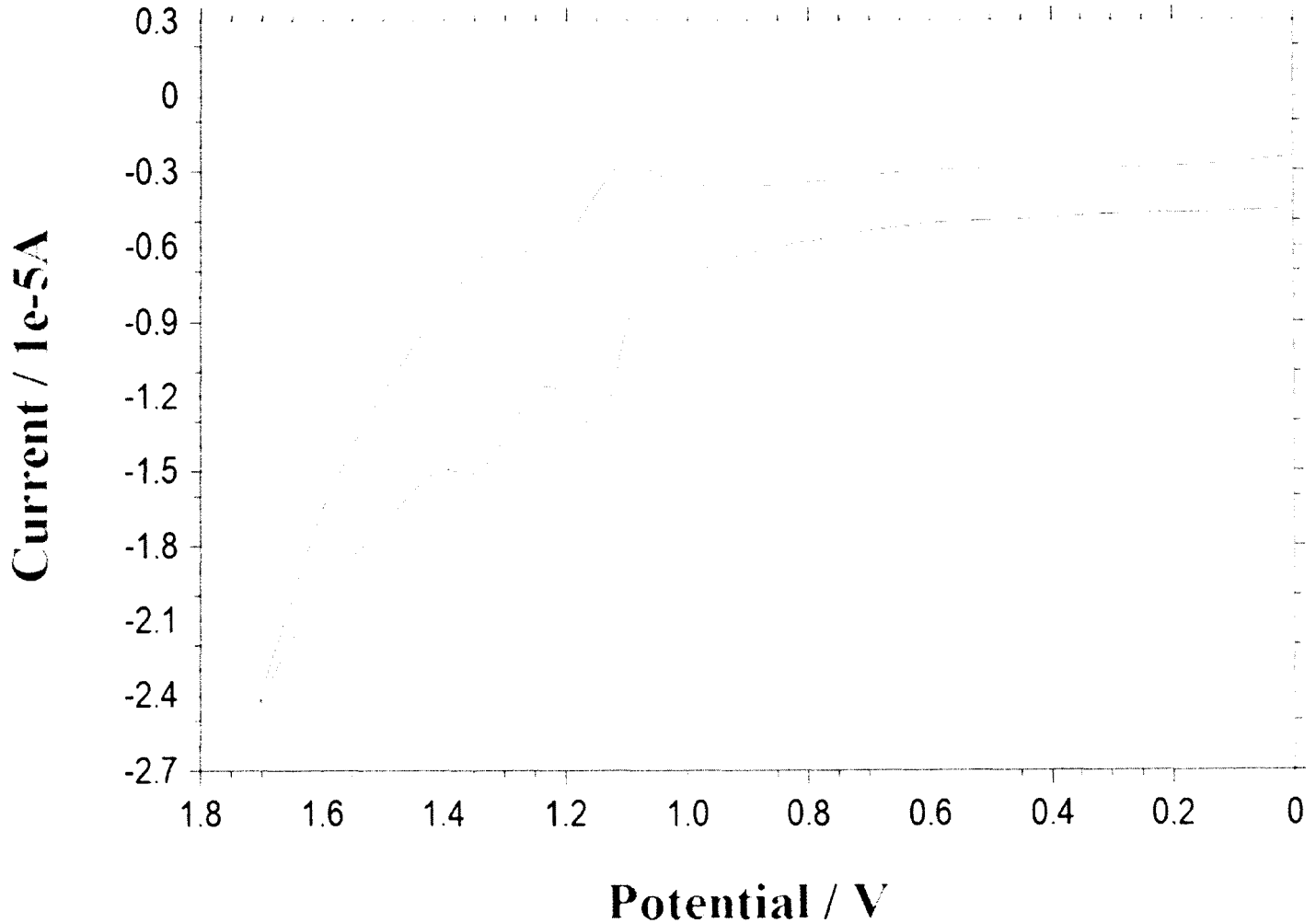


Figure:5.2.1.b. **Cyclic Voltammogram of Mn[T(2-OMeP)P]OAc (10^{-3}M in $CHCl_3$) containing 0.1M TBAP in SDS medium (10^{-1}M in CH_3OH) at Room Temperature.**

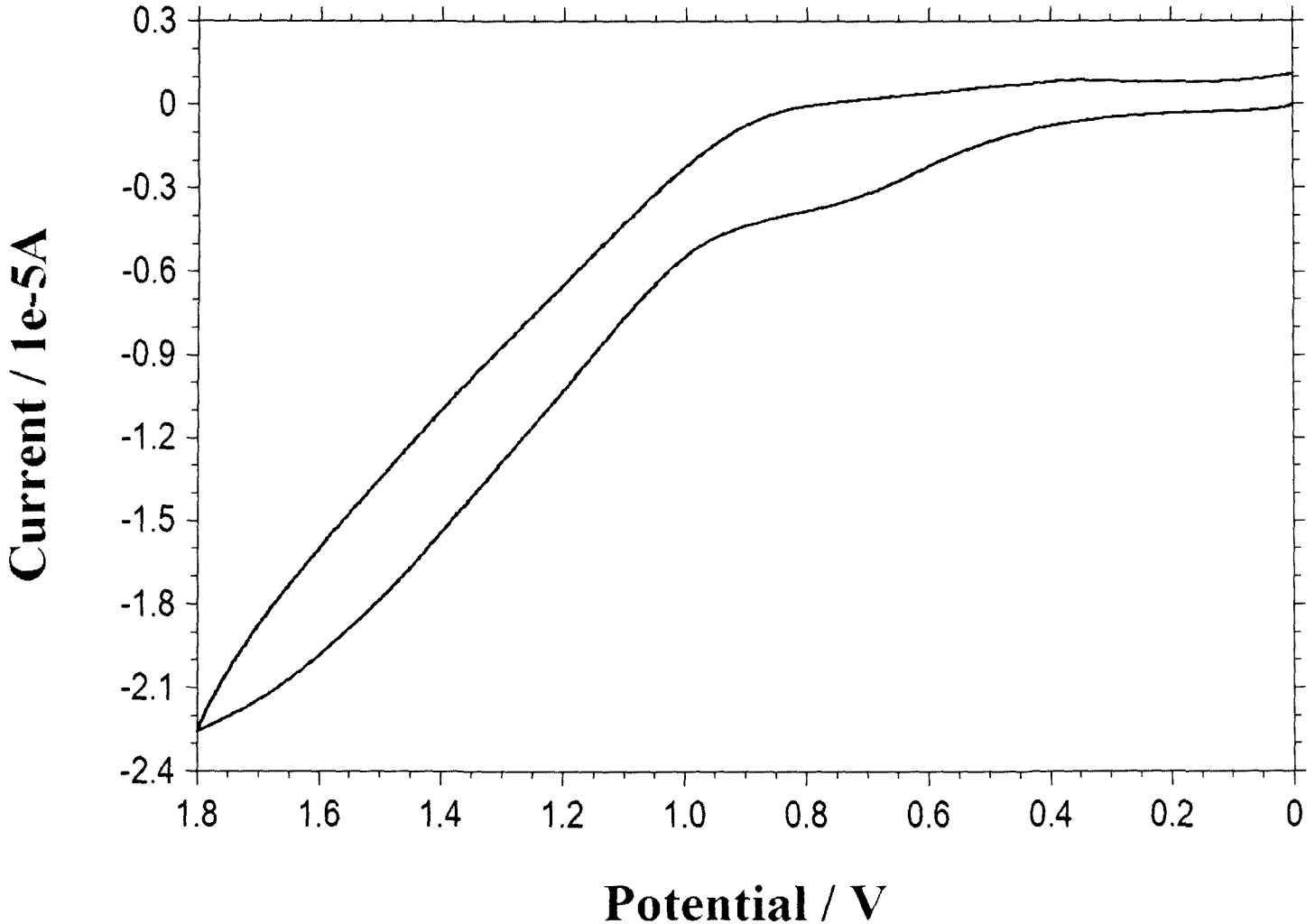


Figure:5.2.1.c. **Cyclic Voltammogram of Mn[T(2-OMeP)P]OAc (10^{-3}M in $CHCl_3$) containing 0.1M TBAP in TX - 100 *medium at Room Temperature.***

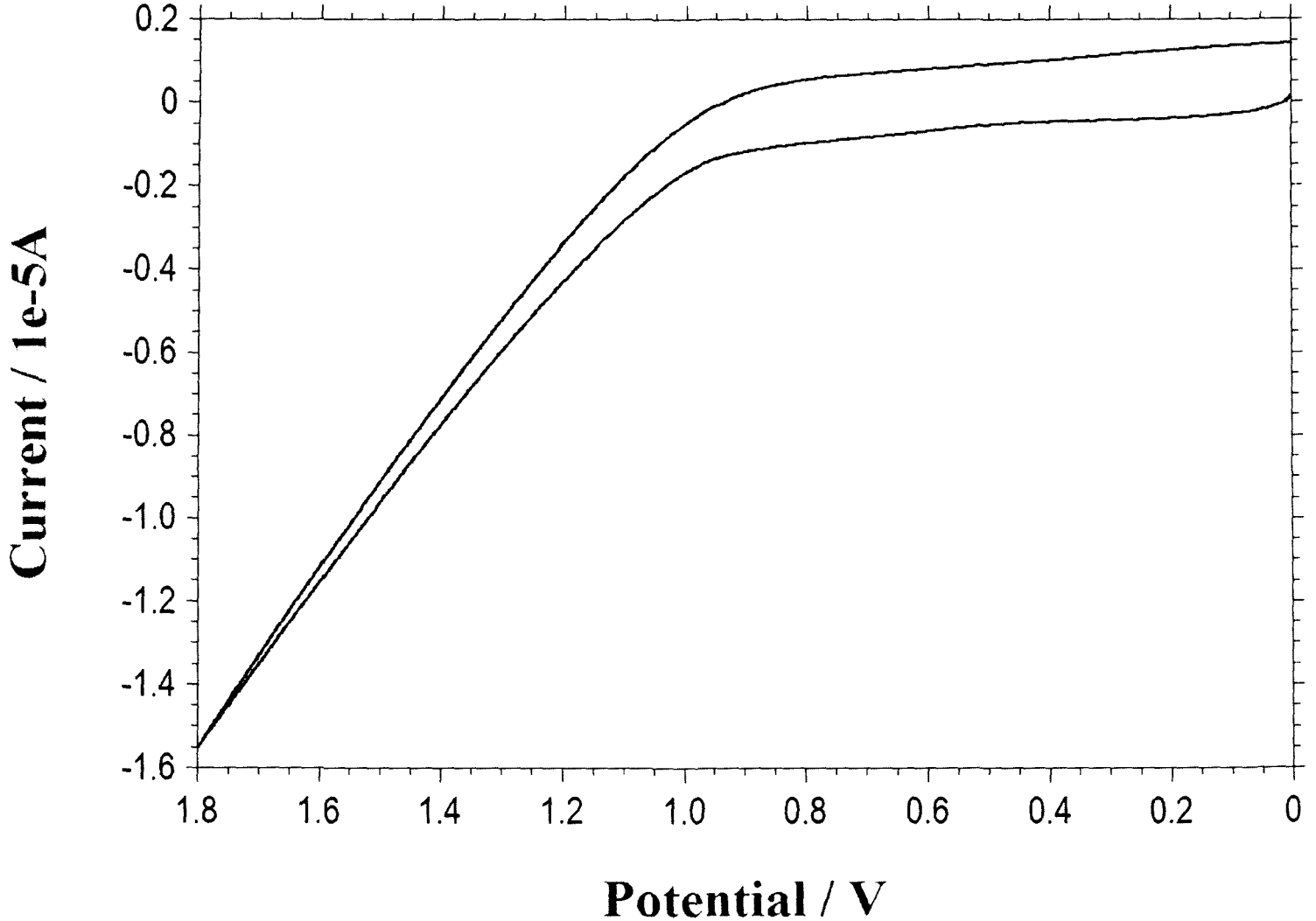


Figure:5.2.1.d. **Cyclic Voltammogram of Mn[T(2-OMeP)P]OAc (10^{-3}M in $CHCl_3$) containing 0.1M TBAP in CTAB (10^{-1}M in $CHCl_3$) medium at Room Temperature.**

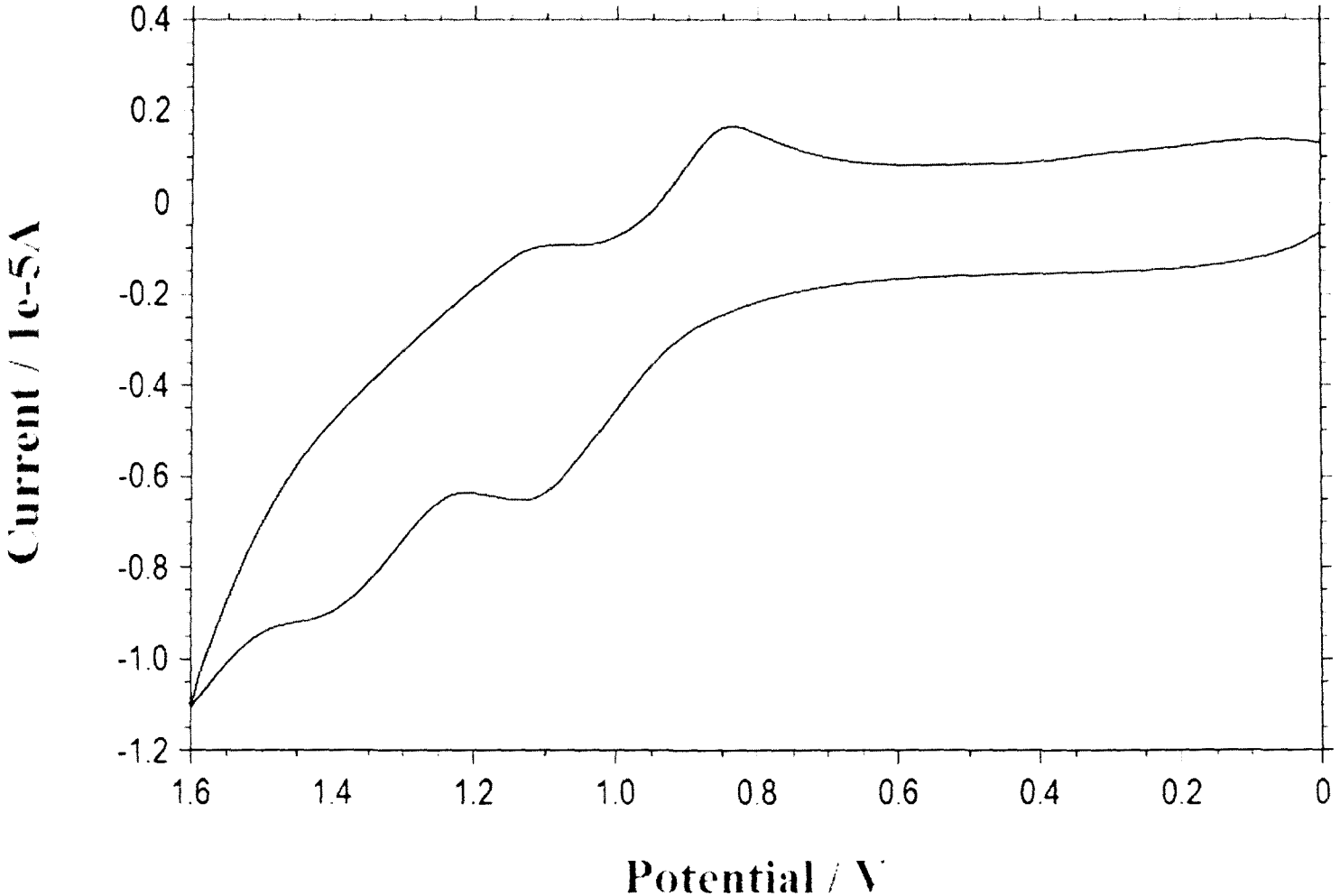


Figure:5.2.2.a. **Cyclic Voltammogram of Mn[T(4-OMeP)P]OAc (10^{-3}M in $CHCl_3$) containing 0.1M TBAP at Room Temperature.**

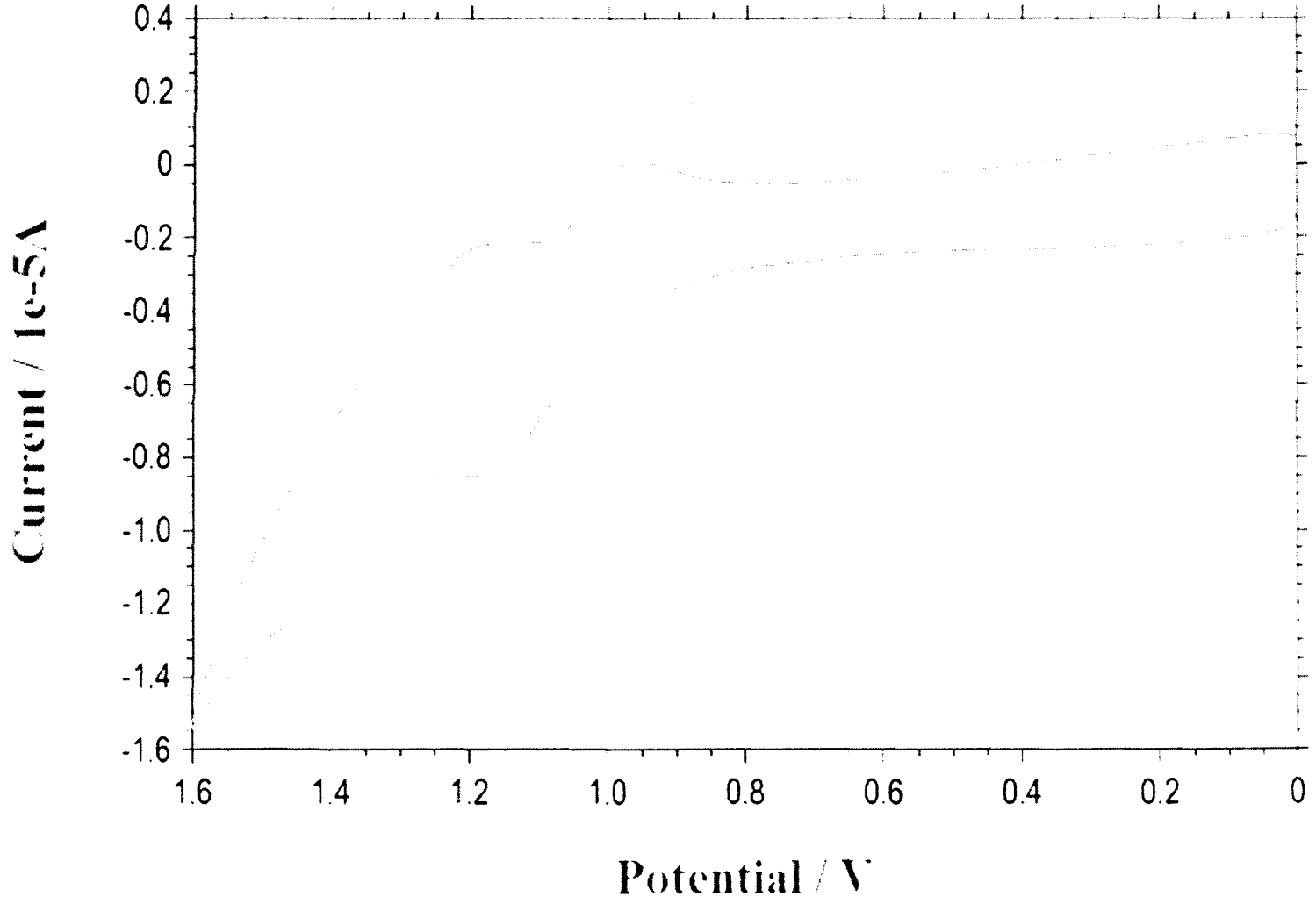


Figure:5.2.2.b. **Cyclic Voltammogram of Mn[T(4-OMeP)P]OAc (10^{-3}M in $CHCl_3$) containing 0.1M TBAP in SDS medium (10^{-1}M in CH_3OH) at Room Temperature.**

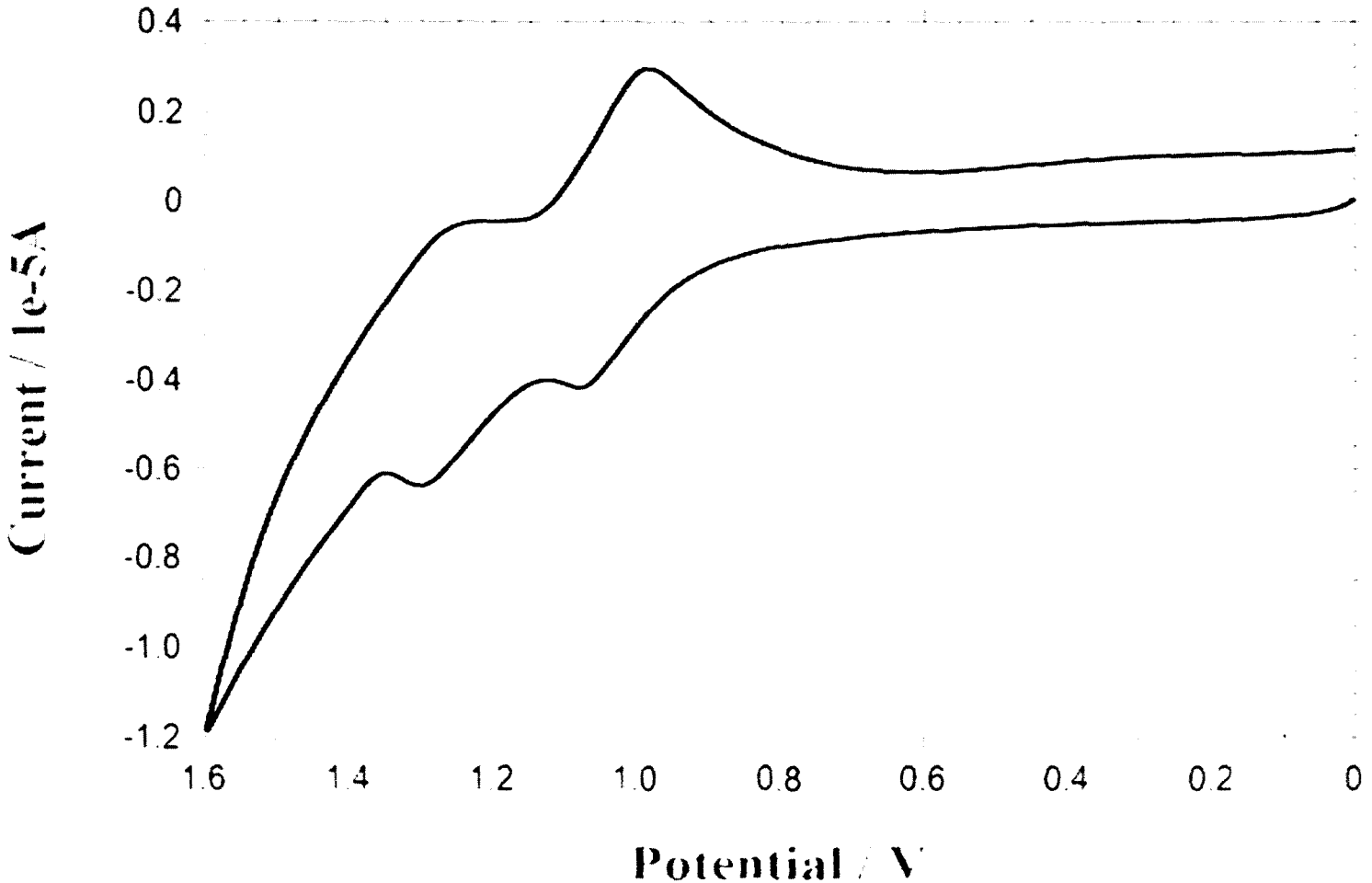


Figure:5.2.3.a. **Cyclic Voltammogram of Mn[T(2-MeP)P]OAc (10^{-3}M in $CHCl_3$) containing *0.1M* TBAP at Room Temperature.**

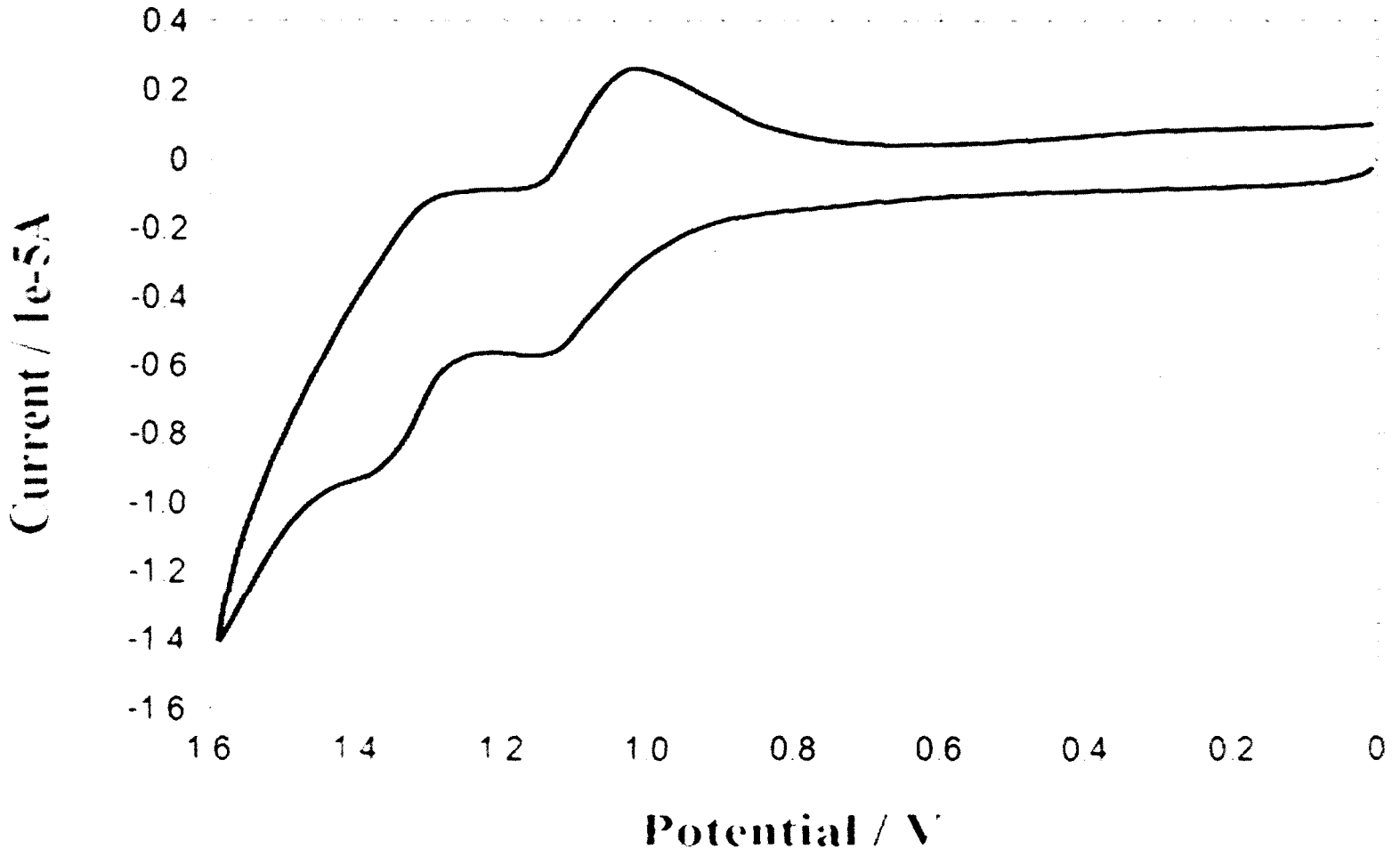


Figure:5.2.3.b. **Cyclic Voltammogram of Mn[T(2-MeP)P]OAc (10^{-3}M in $CHCl_3$) containing 0.1M TBAP in SDS medium (10^{-1}M in CH_3OH) at Room Temperature.**

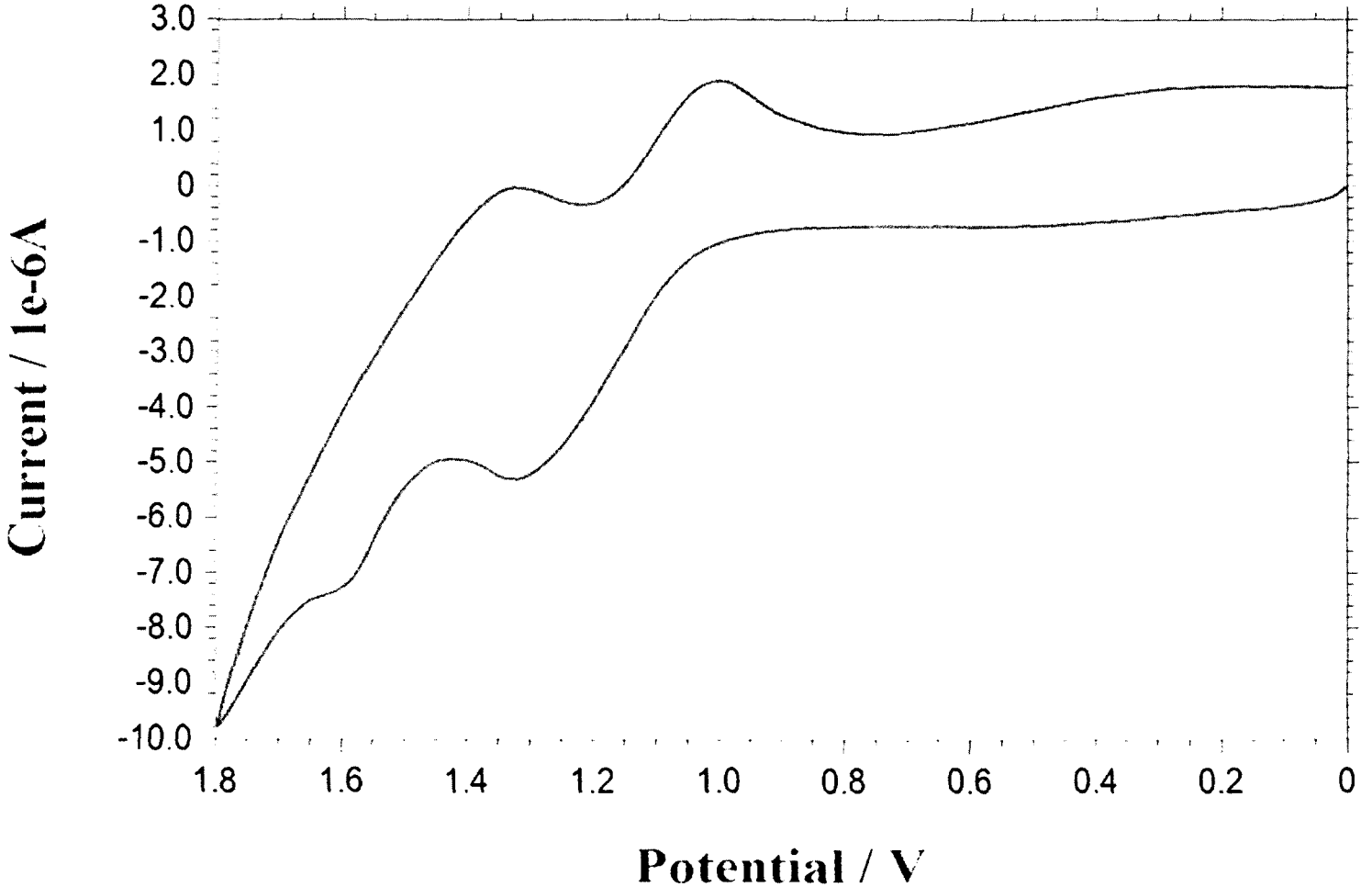


Figure:5.2.4.a. **Cyclic Voltammogram of Mn[T(3-MeP)P]OAc (10^{-3}M in $CHCl_3$) containing 0.1M TBAP at Room Temperature.**

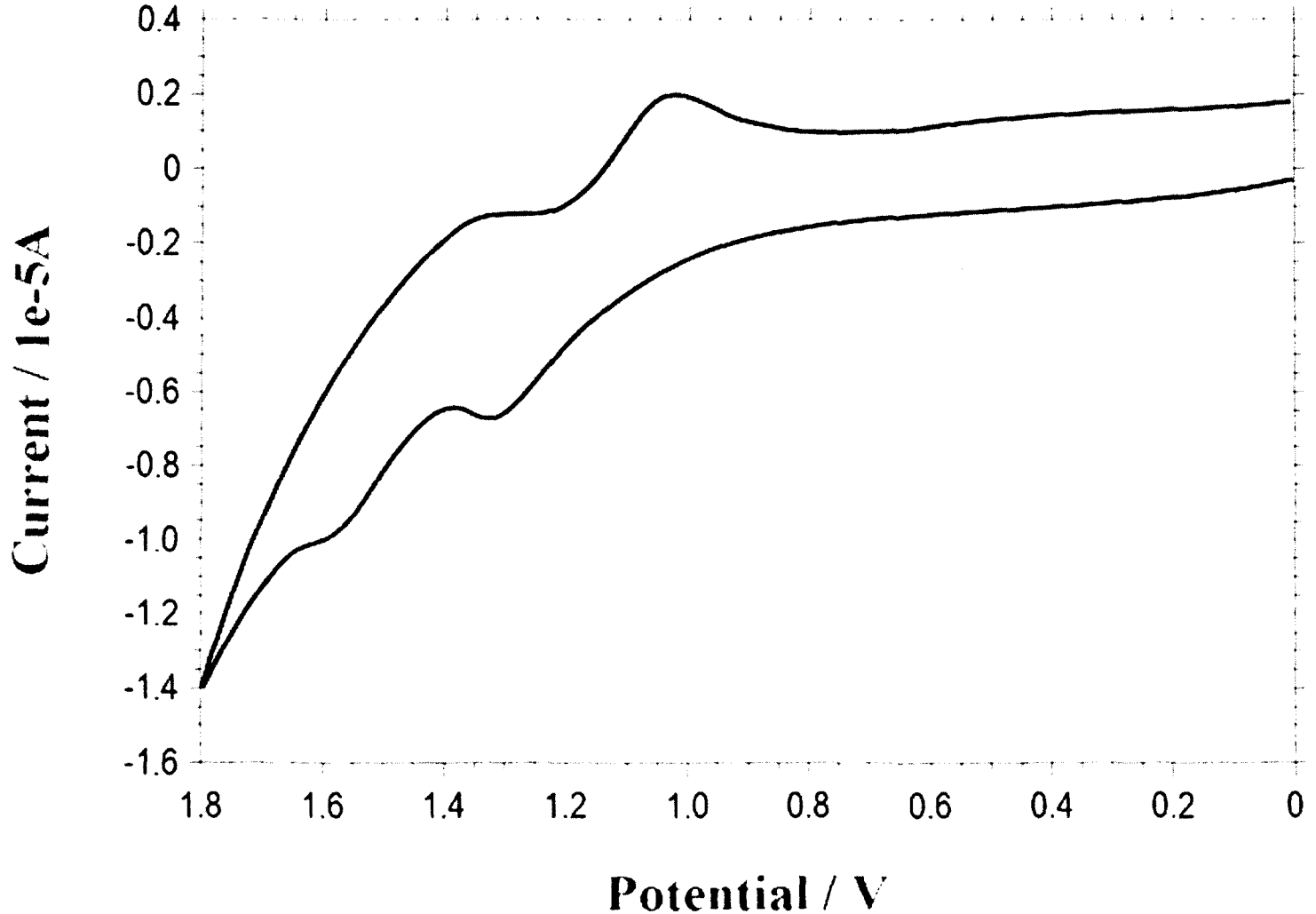


Figure:5.2.4.b. **Cyclic Voltammogram of Mn[T(3-MeP)P]OAc (10^{-3}M in $CHCl_3$) containing 0.1M TBAP in SDS medium (10^{-1}M in CH_3OH) at Room Temperature.**

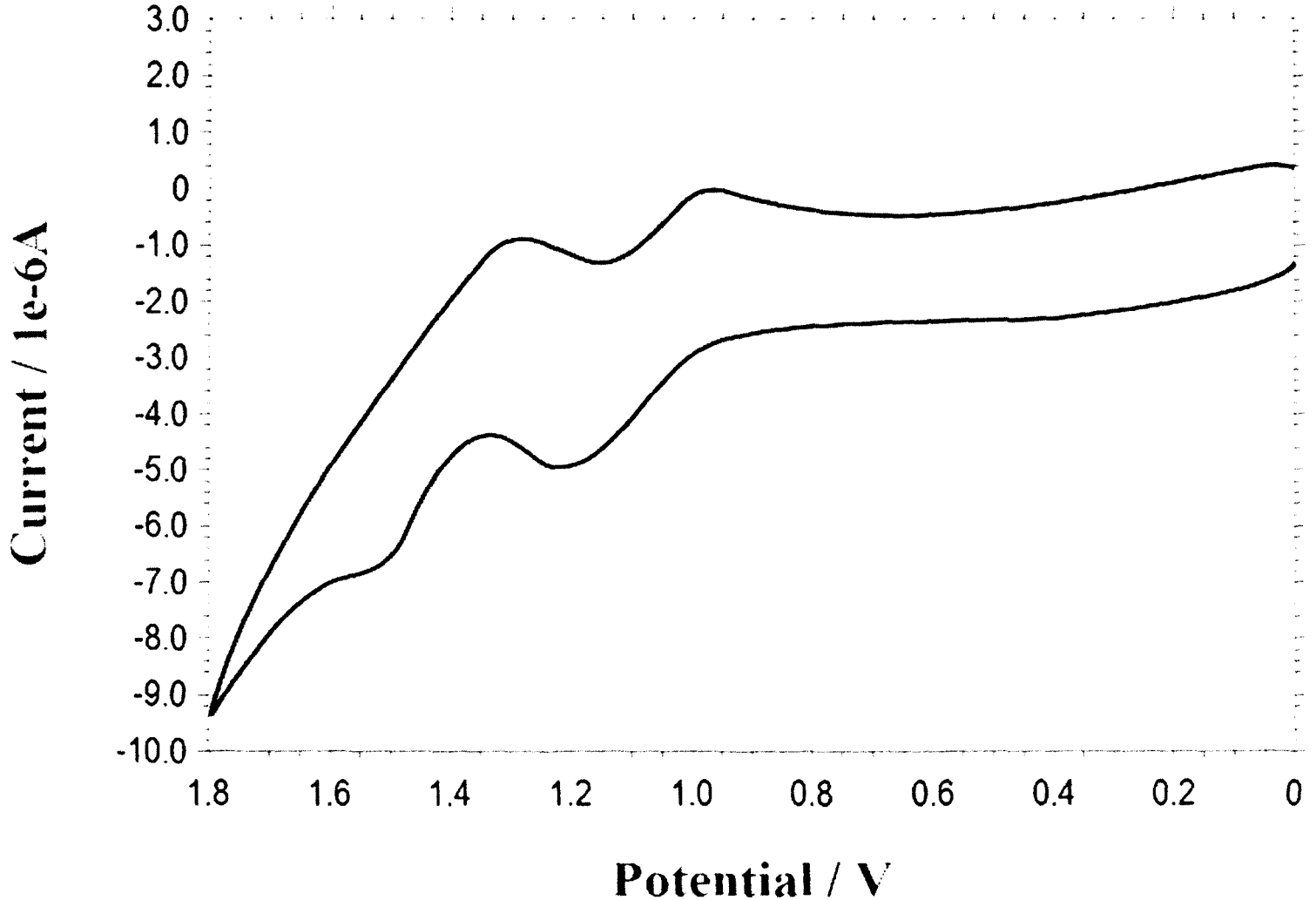


Figure:5.2.5.a. **Cyclic Voltammogram of Mn[T(4-MeP)P]OAc (10^{-3}M in $CHCl_3$) containing 0.1M TBAP at Room Temperature.**

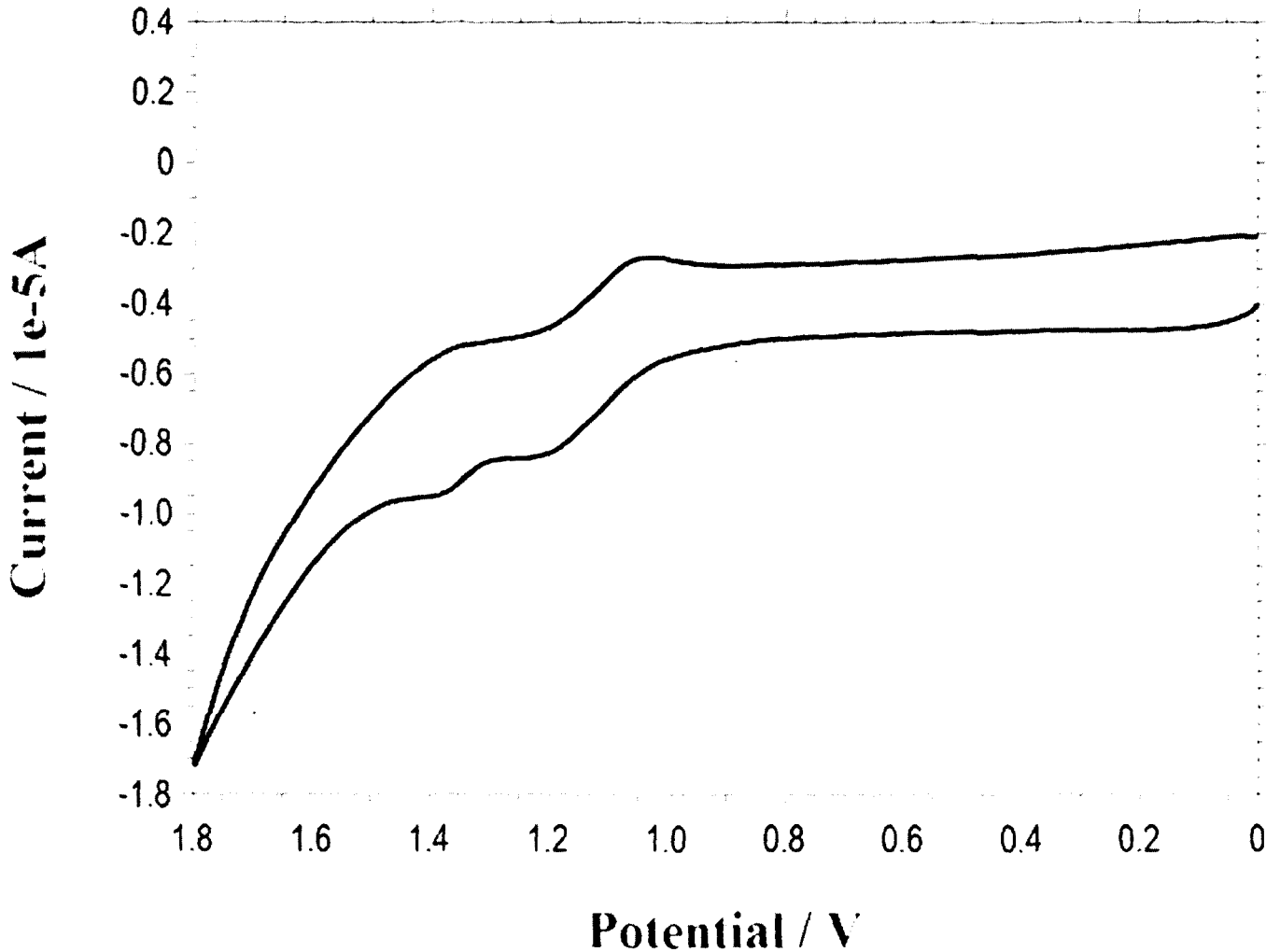


Figure:5.2.5.b. **Cyclic Voltammogram of Mn[T(4-MeP)P]OAc (10^{-3}M in $CHCl_3$) containing 0.1M TBAP in SDS medium (10^{-1}M in CH_3OH) at Room Temperature.**

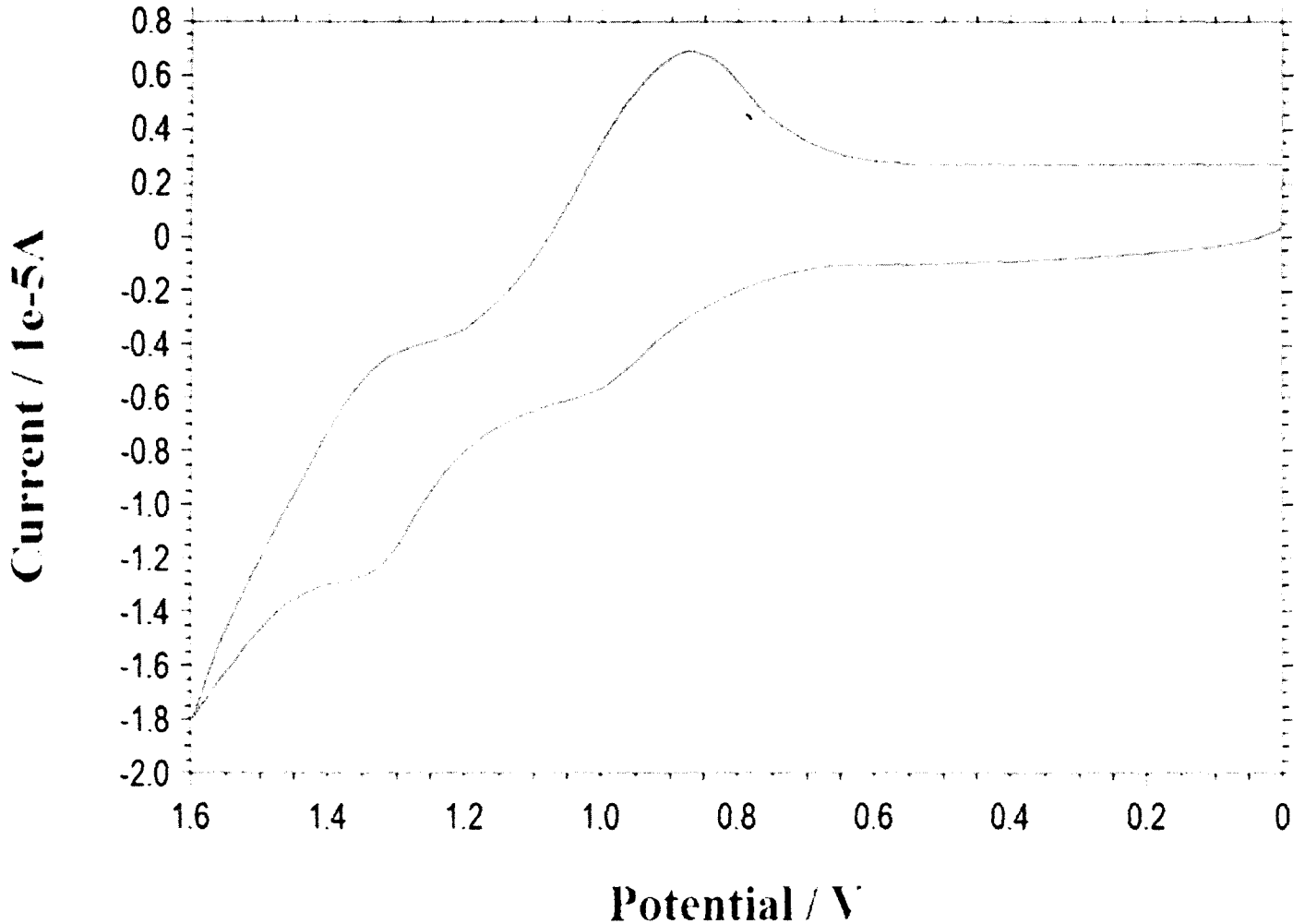


Figure:5.2.6.a. **Cyclic Voltammogram of Mn[T(naphthyl)P]OAc (10^{-3}M in $CHCl_3$) containing 0.1M TBAP at Room Temperature.**

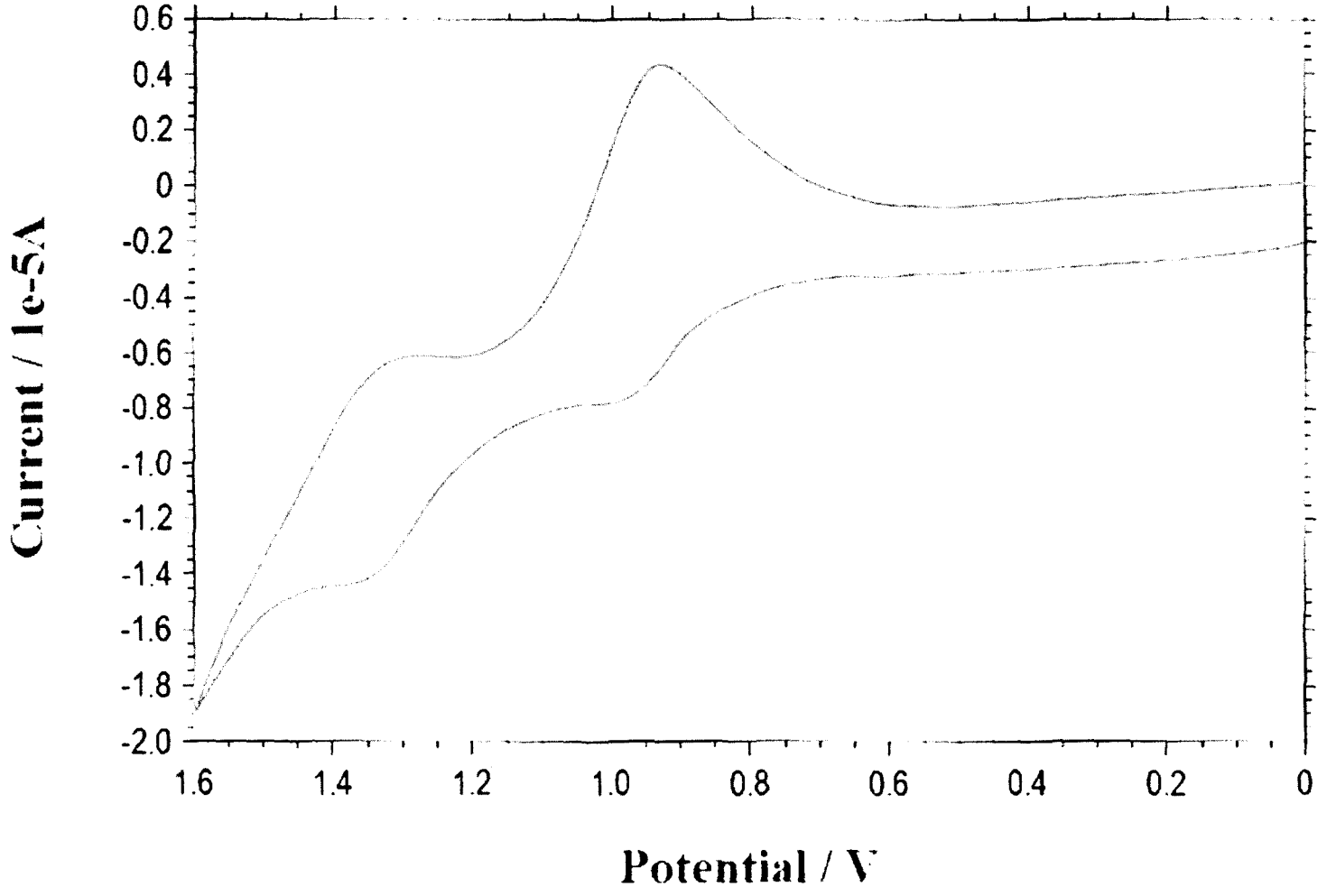


Figure:5.2.6.b. **Cyclic Voltammogram of Mn[T(naphthyl)P]OAc (10^{-3}M in $CHCl_3$) containing 0.1M TBAP in SDS medium (10^{-1}M in CH_3OH) at Room Temperature.**

REFERENCES

1. K.M. Kadish, B.G. Maiya, C. Araullo, R. Guilard, *Inorg. Chem.*, **28**, 2725- 2731 (1989).

2. K.M. Kadish, B.G. Maiya, C. Araullo - Mc Adams, *J. Phys. Chem.*, **95**, 427-431 (1991).

3. M.J. Minch, G.R. Lamar, *J. Phys. Chem.*, **86**, 1400 – 1406 (1982).

4. O.K. Medhi, S. Mazumdar, S. Mitra, *Inorg. Chem.*, **28**, 3243-3248 (1989).

5. S. Mazumdar, O.K. Medhi, S. Mitra, *J. Chem. Soc. Dalton Trans.*, 1057 – 1061 (1990).

6. S. Mazumdar, *J. Chem Soc. Dalton trans.*, 2091-2096 (1991).

7. S. Mazumdar, *J. Phys. Chem.*, **94**,5947-5953 (1990).

8. S. Mazumdar, O.K. Medhi, S. Mitra, *Inorg. Chem.*, **27**, 7 (14), 2541 – 2543 (1988).

9. M. Vermathen, E.A. Louie, A.B. Chodosh, S. Reid and U. Simonis, *Langmuir*, **16**, 210 – 221 (2000).

10. L.A. Lucia, T. Yui, R. Sasai, S. Takagi, K. Takagi, H. Yoshida, D.G. Whitten and H. Inoue., *J. Phys. Chem. B*, **107**, 3789 – 3797 (2003).

CHAPTER – 6

UV – VISIBLE

AND

CYCLIC VOLTAMMETRIC

STUDIES OF SOME

ZINC AND COPPER

PORPHYRINS

IN

SURFACTANT MEDIUM

CHAPTER – 6

This chapter presents the investigations of some zinc and copper porphyrins in non aqueous micellar medium by UV-Visible spectroscopy and Cyclic Voltammetry.

6.1. RESULTS:

6.1.1. UV-VISIBLE STUDIES:

6.1.1.a. Zn[T(4-OMeP)P]:

10^{-5}M solution of Zn[T(4-OMeP)P] in chloroform exhibits a soret band at 427nm and the Q band at 556nm. (Table 6.A.)

IN SDS MEDIUM:

The soret band remains at 427nm while the Q band shift slightly to 599nm (3nm, red shift). There is no appreciable changes. Addition of 0.3 mol of triethylamine has no effect on the spectrum. [Figure: 6.1.1.a.(i)]

IN TX – 100 MEDIUM :

The soret band shows slight red shift while the Q band shows small red shift. The soret band shifts from 427nm to 429nm (2nm shift) while the Q band shifts from 556nm to 558nm (2nm shift). Addition of 0.3 moles of triethylamine has no effect on the spectra. [Figure 6.1.1.a.(ii)].

IN CTAB MEDIUM :

The soret band occurs at 428nm and the Q band occurs at 558nm. Practically, there is no change in the UV-Visible spectrum. Addition of 0.3 mol of triethylamine shows slight red shift. The soret band shifts from 427nm to 429nm (2nm shift) while the Q band shifts from 556nm to 562nm (6nm shift) [Figure 6.1.1.a.(iii)].

6.1.1.b. Zn[T(naphthyl)P]:

In Chloroform the spectrum consists of a soret band at 428nm and a Q band at 556nm (Table 6.B.).

IN SDS MEDIUM:

Practically, there is no change in the UV-Visible spectra. Addition of 0.3 mol of triethylamine does not change the spectra. [Figure 6.1.1.b.(i)].

IN TX – 100 MEDIUM:

No change is observed in the spectra in the presence of TX – 100 surfactant. Addition 0.3 moles of triethylamine shows slight red shift. The soret band shifts to 431nm (3nm shift) while the Q band shifts from 556nm to 559nm (3nm shift). [Figure 6.1.1.b.(ii)].

IN CTAB MEDIUM:

There is no appreciable change in the spectrum. Addition of 0.3 moles of triethylamine exhibit slight red shift. The soret band shifts from 428nm to 432nm (4nm shift) and the Q band shifts from 556nm to 560nm (4nm shift) [Figure 6.1.1.b.(iii)].

6.1.1.c. Cu[T(4-OMeP)P]:

The UV-Visible absorption spectra exhibits the soret band at 419nm and the Q band at 541nm (Table 6.C.).

IN SDS MEDIUM:

No change is the spectrum is observed except dilution effect. Addition of 0.3 moles of triethylamine has no effect on the spectrum [Figure 6.1.1.c.(i)].

IN TX – 100 MEDIUM :

There is no change in the absorption spectrum. Addition of 0.3 mol of triethylamine shows no effect on the spectrum. [Figure 6.1.1.c.(ii)].

IN CTAB MEDIUM:

In CTAB medium also no appreciable changes are observed except dilution effect. Addition of 0.3 mol of triethylamine shows no appreciable changes on the UV-Visible spectrum. [Figure 6.1.1.c.(iii)].

6.1.1.d. Cu[T(naphthyl)P]:

The UV-Visible absorption spectrum in chloroform exhibits a soret band at 420nm and the Q band at 540nm. (Table 6.D.).

IN SDS MEDIUM:

There is no change in the spectrum. Addition of 0.3 moles of triethylamine has no effect. [Figure 6.1.1.d.(i)].

IN TX – 100 MEDIUM:

No change in the spectrum is observed. Addition of 0.3 moles of triethylamine has no effect on the spectrum. [Figure 6.1.1.d.(ii)].

IN CTAB MEDIUM:

There is no change in the UV-Visible spectrum. Addition of 0.3 moles of triethylamine shows no effect [Figure 6.1.1.d.(iii)].

6.2. DISCUSSION:

UV-Visible spectra remain invariant in SDS, TX – 100 and CTAB media in most cases. However, a red shift of the Q band for Zn[T(4-OMeP)P] in TX – 100 medium is observed (3nm shift). In CTAB medium also a slight red shift of the Q band is observed (6nm). This could be due to dimer formation. In this case most probably J – type dimer[3,4]. Slight red shift is also observed for Zn[T(Naphthyl)P] in TX – 100, the shift is 3nm where as in CTAB the shift is 4nm. This also points to a possible formation of dimer (J – type). In the case of zinc porphyrins, addition of triethylamine does not show much effect on the spectra. It implies that amine is not accessible to the zinc ion of the porphyrin in the surfactant environment.

6.3. CONCLUSION:

From the UV-Visible studies no significant observation can be made. However, red shift in some cases implies dimerisation[3].

6.4. CYCLIC VOLTAMMETRIC STUDIES:

6.4.1. RESULTS:

6.4.1.a. Zn[T(4-OMeP)P]:

The voltammogramn of 10^{-3}M solution of Zn[T(4-OMeP)P] in chloroform exhibits two redox couples with $E_{½}$ values 0.623V and 0.9955V [Figure 6.4.1.a.(i)]. The results are summarized in the Table 6.E.

IN SDS MEDIUM:

The voltammogram exhibits three redox couples [Figure 6.4.1.a.(ii)] with $E_{½}$ values 0.625V, 0.9955V and 1.285V.

IN TX-100 MEDIUM:

The voltammogram could not be resolved in TX – 100 medium.

IN CTAB MEDIUM:

The voltammogram could not be resolved in this case.

6.4.1.b. Zn[T(Naphthyl)P]:

In chloroform, the voltammogram consists of two redox couples [Figure 6.4.1.b.(i)] with $E_{½}$ values 0.6975V and 0.951V (Table 6.F.).

IN SDS MEDIUM :

The voltammogram exhibits three redox couples [Figure 6.4.1.b.(ii)] with $E_{½}$ values 0.645V, 0.99V and 1.225V.

IN TX – 100 MEDIUM:

The voltammogram could not be resolved.

IN CTAB MEDIUM:

The voltammogram could not be resolved.

6.4.1.c. Cu[T(4-OMeP)P]:

In chloroform the compound exhibits a voltammogram which consists of two redox couples with $E_{½}$ values of 0.84V and 1.24V [Table 6.G.), Figure 6.4.1.c.(i)].

IN SDS MEDIUM:

Two redox couples are observed with $E_{½}$ values of 0.805V and 1.175V. The first $E_{½}$ value is lower by 0.035V while the second $E_{½}$ value is lower by 0.065V [Figure 6.4.1.c.(ii)].

IN TX- 100 MEDIUM.

The voltammogram could not be resolved in this medium.

IN CTAB MEDIUM:

The voltammogram could not be resolved in CTAB medium

6.4.1.d. Cu[T(naphthyl)P]:

10^{-3}M solution of Cu[T(naphthyl)P] in chloroform gives a voltammogram which consists of two redox couples [Figure 6.4.1.d.(i)]. Their $E_{½}$ values are 0.705V and 1.29V (Table 6.H.)

IN SDS MEDIUM:

The voltammogram presents three redox couples [Figure 6.4.1.d.(ii)] with $E_{½}$ values 0.96V, 1.145V and 1.345V.

IN TX- 100 MEDIUM.

The voltammogram could not be resolved in this medium.

IN CTAB MEDIUM:

The voltammogram could not be resolved in CTAB medium.

6.5. DISCUSSION[1-5]:

The three redox couples observed in the SDS medium corresponds to ligand oxidations. However, we do not observe three redox couples in the voltammogram of the metalloporphyrins in chloroform without SDS. The most possible reason for observing three redox couples in SDS medium is the formation of metalloporphyrin dimmers. In the case of Cu[T(4-OMeP)P] the $E_{1/2}$ values are slightly lower. This is essentially due to dimerisation. The red shift observed earlier in the UV-Visible spectra is supplemented by the Cyclic Voltammetric results. On the contrary, in TX-100 and in CTAB media voltammograms could not be resolved. Perhaps porphyrins are not readily available in those two media. Maybe due to encapsulation.

6.6. CONCLUSION:

From the Cyclic Voltammetric studies the following observations are made:

(i) In SDS medium zinc and copper porphyrins aggregate forming dimmers, most probably J – type.

(ii) Zinc and copper porphyrins acts as guest in SDS medium and form dimmers within the inter layer spaces of the micelles.

TABLE 6.A. : UV- VIS ABSORPTION SPECTRAL DATA OF Zn[T(4-OMeP)P] AT ROOM TEMPERATURE
SOLVENT : CHLOROFORM
CONCENTRATION : 10^{-5}M

COMPOUND		B- BAND	Q – BANDS
Zn[T(4-OMeP)P]	In Chloroform	427(1.705)	556(0.057)
	With SDS (10^{-1}M in CH_3OH)	427(1.604)	559(0.067)
	With SDS and Triethylamine	427(1.596)	559(0.062)
	With TX - 100	429(1.55)	558(0.117)
	With TX - 100 and Triethylamine	429(1.486)	558(0.114)
	With CTAB (10^{-1}M in $CHCl_3$)	428(1.395)	558(0.063)
	With CTAB and Triethylamine	429(1.406)	562(0.071)

TABLE 6.B. : UV- VIS ABSORPTION SPECTRAL DATA OF Zn[T(naphthyl)P] AT ROOM TEMPERATURE
SOLVENT : CHLOROFORM
CONCENTRATION : 10^{-5}M

COMPOUND		B- BAND	Q – BANDS
Zn[T(naphthyl)P]	In Chloroform	428(2.298)	556(0.1124)
	With SDS (10^{-1}M in CH_3OH)	428(2.084)	558(0.325)
	With SDS and Triethylamine	428(2.038)	558(0.350)
	With TX - 100	428(2.298)	556(0.1124)
	With TX - 100 and Triethylamine	431(1.4687)	559(0.142)
	With CTAB (10^{-1}M in $CHCl_3$)	429(1.872)	557(0.097)
	With CTAB and Triethylamine	432(1.8505)	560(0.097)

TABLE 6.C. : UV- VIS ABSORPTION SPECTRAL DATA OF Cu[T(4-OMeP)P] AT ROOM TEMPERATURE
SOLVENT : CHLOROFORM
CONCENTRATION : 10^{-5}M

COMPOUND		B- BAND	Q – BANDS
Cu[T(4-OMeP)P]	In Chloroform	419 (2.470)	541(0.121)
	With SDS (10^{-1}M in CH_3OH)	419(2.134)	541(0.036)
	With SDS and Triethylamine	419(2.102)	540(0.111)
	With TX - 100	418(1.955)	541(0.104)
	With TX - 100 and Triethylamine	419(1.945)	540(0.103)
	With CTAB (10^{-1}M in $CHCl_3$)	420(2.215)	541(0.122)
	With CTAB and Triethylamine	418(2.234)	541(0.123)

TABLE 6.D. : UV- VIS ABSORPTION SPECTRAL DATA OF Cu[T(naphthyl)P] AT ROOM TEMPERATURE
SOLVENT : CHLOROFORM
CONCENTRATION : 10^{-5}M

COMPOUND		B- BAND	Q – BANDS
Cu[T(naphthyl)P]	In Chloroform	420 (2.041)	540(0.135)
	With SDS (10^{-1}M in CH_3OH)	419(1.728)	540(0.127)
	With SDS and Triethylamine	419(1.689)	540(0.124)
	With TX - 100	420(1.655)	540(0.125)
	With TX - 100 and Triethylamine	420(1.633)	540(0.129)
	With CTAB (10^{-1}M in $CHCl_3$)	420(1.99)	540(0.161)
	With CTAB and Triethylamine	419(2.002)	540(0.151)

TABLE 6.E. : REDOX POTENTIALS OF Zn[T(4-OMeP)P] AT ROOM TEMPERATURE
SOLVENT : CHLOROFORM
CONCENTRATION : 10^{-3}M
SUPPORTING ELECTROLYTE : TBAP
REFERENCE ELECTRODE : Ag/AgCl
SCAN RATE : 0.1 (V/s)

COMPOUNDS		$E_{pa}(1)$ (V)	$E_{pa}(2)$ (V)	$E_{pa}(3)$ (V)	$E_{pc}(1)$ (V)	$E_{pc}(2)$ (V)	$E_{pc}(3)$ (V)	$E_{1/2}(1)$ (V)	$E_{1/2}(2)$ (V)	$E_{1/2}(3)$ (V)	ΔE_1 (V)	ΔE_2 (V)	ΔE_3 (V)
Zn[T(4-OMeP)P]	In Chloroform	0.785	1.151	-	0.461	0.840	-	0.623	0.9955	-	0.324	0.311	-
	With SDS (10^{-1}M in CH_3OH)	0.750	1.16	1.47	0.50	0.83	1.10	0.625	0.995	1.285	0.250	0.330	0.370
	With TX – 100	-	-	-	-	-	-	-	-	-	-	-	-
	With CTAB (10^{-1}M in $CHCl_3$)	-	-	-	-	-	-	-	-	-	-	-	-

TABLE 6.F. : REDOX POTENTIALS OF Zn[T(naphthyl)P] AT ROOM TEMPERATURE
SOLVENT : CHLOROFORM
CONCENTRATION : 10^{-3}M
SUPPORTING ELECTROLYTE: TBAP
REFERENCE ELECTRODE : Ag/AgCl
SCAN RATE : 0.1 (V/s)

COMPOUNDS		$E_{pa}(1)$ (V)	$E_{pa}(2)$ (V)	$E_{pa}(3)$ (V)	$E_{pc}(1)$ (V)	$E_{pc}(2)$ (V)	$E_{pc}(3)$ (V)	$E_{1/2}(1)$ (V)	$E_{1/2}(2)$ (V)	$E_{1/2}(3)$ (V)	ΔE_1 (V)	ΔE_2 (V)	ΔE_3 (V)
Zn[T(naphthyl)P]	In Chloroform	0.745	0.998	-	0.650	0.904	-	0.6975	0.951	-	0.095	0.094	-
	With SDS (10^{-1}M in CH_3OH)	0.740	1.10	1.30	0.550	0.88	1.15	0.645	0.99	1.225	0.190	0.220	0.150
	With TX – 100	-	-	-	-	-	-	-	-	-	-	-	-
	With CTAB (10^{-1}M in $CHCl_3$)	-	-	-	-	-	-	-	-	-	-	-	-

TABLE 6.G. : REDOX POTENTIALS OF Cu[T(4-OMeP)P] AT ROOM TEMPERATURE
SOLVENT : CHLOROFORM
CONCENTRATION : 10^{-3}M
SUPPORTING ELECTROLYTE : TBAP
REFERENCE ELECTRODE : Ag/AgCl
SCAN RATE : 0.1 (V/s)

COMPOUNDS		$E_{pa}(1)$ (V)	$E_{pa}(2)$ (V)	$E_{pc}(1)$ (V)	$E_{pc}(2)$ (V)	$E_{1/2}(1)$ (V)	$E_{1/2}(2)$ (V)	ΔE_1 (V)	ΔE_2 (V)
Cu[T(4-OMeP)P]	In Chloroform	0.97	1.40	0.71	1.08	0.84	1.24	0.260	0.320
	With SDS (10^{-1}M in CH_3OH)	0.94	1.31	0.67	1.04	0.805	1.175	0.270	0.270
	With TX – 100	-	-	-	-	-	-	-	-
	With CTAB (10^{-1}M in $CHCl_3$)	-	-	-	-	-	-	-	-

TABLE 6.H. : REDOX POTENTIALS OF Cu[T(naphthyl)P] AT ROOM TEMPERATURE
SOLVENT : CHLOROFORM
CONCENTRATION : 10^{-3}M
SUPPORTING ELECTROLYTE : TBAP
REFERENCE ELECTRODE : Ag/AgCl
SCAN RATE : 0.1 (V/s)

COMPOUNDS		$E_{pa}(1)$ (V)	$E_{pa}(2)$ (V)	$E_{pa}(3)$ (V)	$E_{pc}(1)$ (V)	$E_{pc}(2)$ (V)	$E_{pc}(3)$ (V)	$E_{1/2}(1)$ (V)	$E_{1/2}(2)$ (V)	$E_{1/2}(3)$ (V)	ΔE_1 (V)	ΔE_2 (V)	ΔE_3 (V)
Cu[T(naphthyl)P]	In Chloroform	0.74	1.32	-	0.67	1.26	-	0.705	1.29	-	0.070	0.060	-
	With SDS (10^{-1}M in CH_3OH)	1.04	1.20	1.42	0.88	1.09	1.27	0.96	1.145	1.345	0.160	0.110	0.150
	With TX – 100	-	-	-	-	-	-	-	-	-	-	-	-
	With CTAB (10^{-1}M in $CHCl_3$)	-	-	-	-	-	-	-	-	-	-	-	-

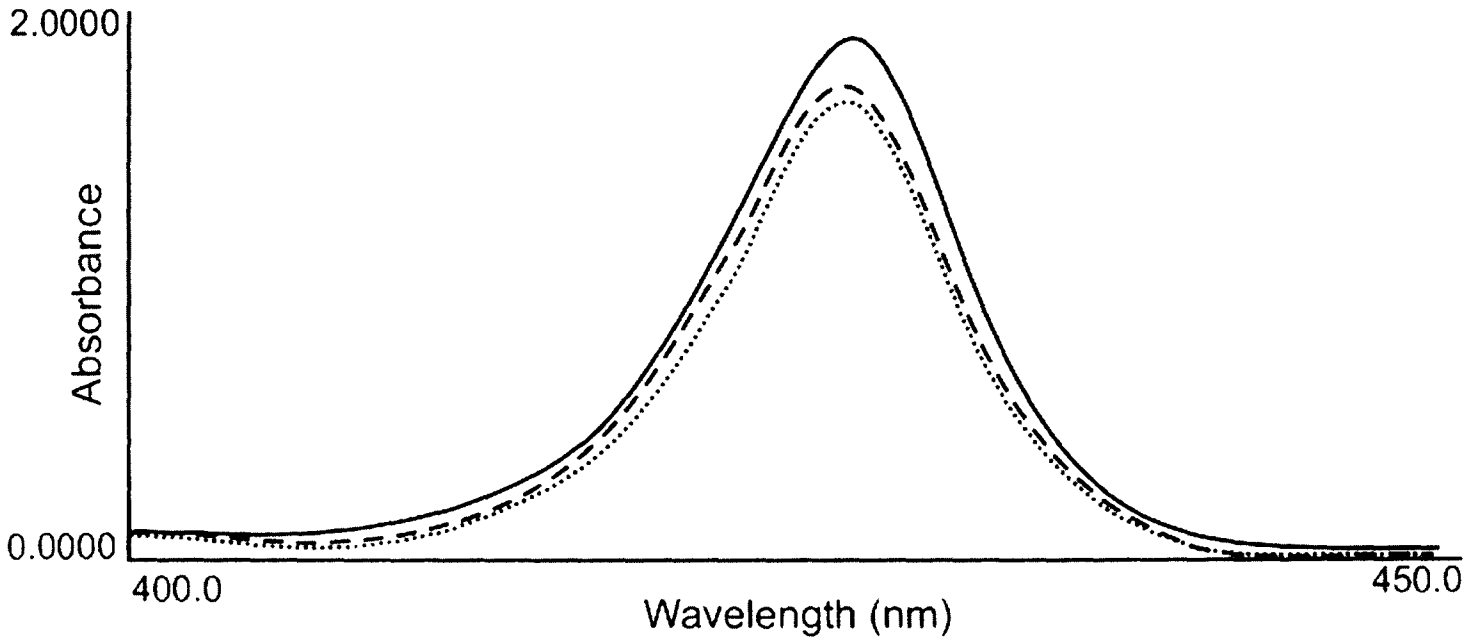


Figure: 6.1.1.a.(i). **UV-Vis Overlay Spectra (B- Band) of Zn[T(4-OMeP)P] (10^{-5}M in $CHCl_3$)(——); in the presence of SDS (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

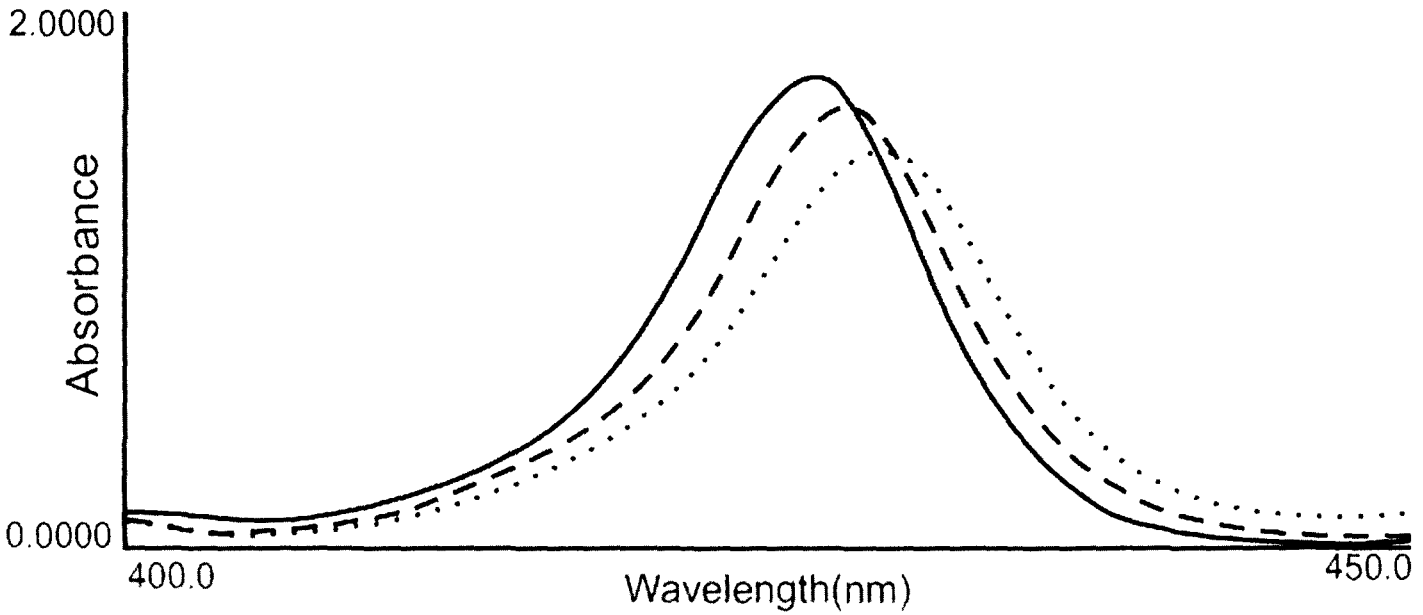


Figure: 6.1.1.a.(ii). **UV-Vis Overlay Spectra (B- Band) of Zn[T(4-OMeP)P] (10^{-5}M in $CHCl_3$)(———); in the presence of TX-100 (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

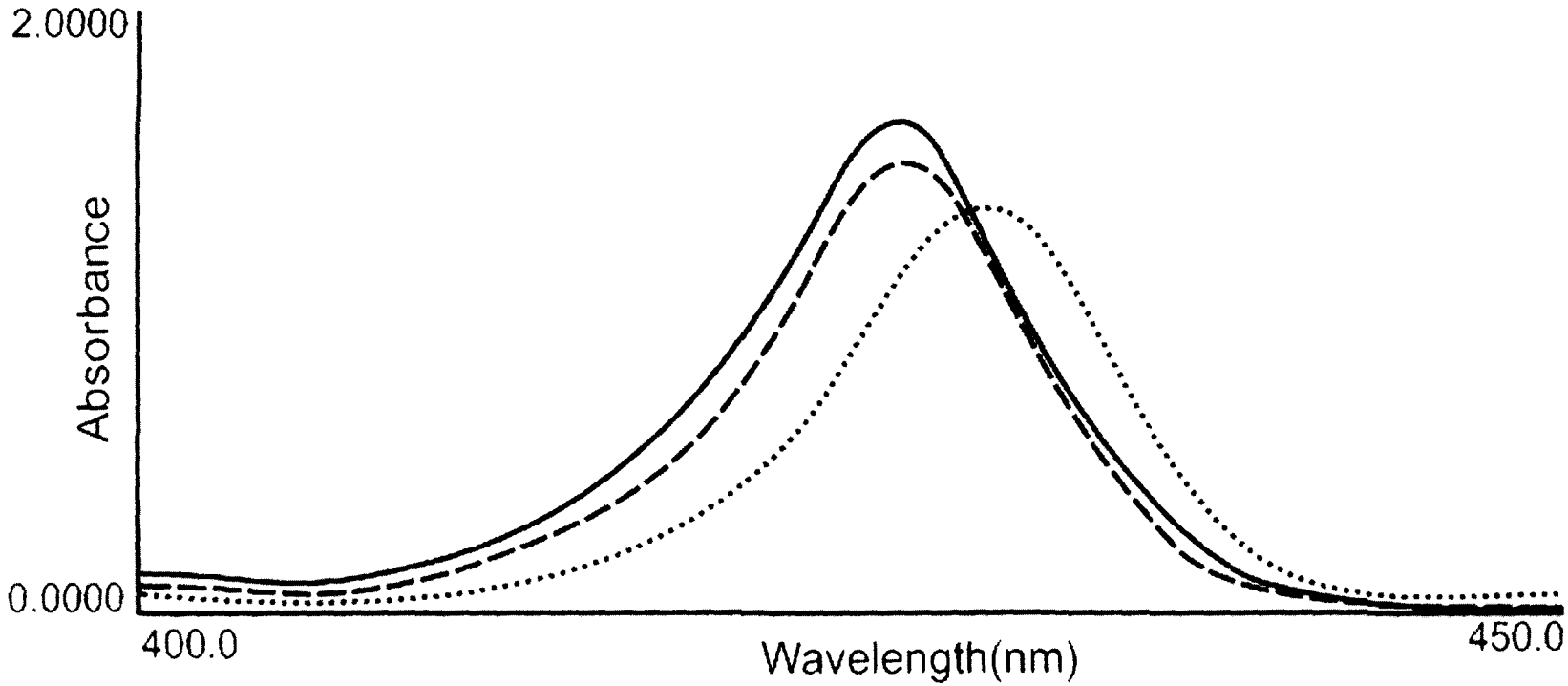


Figure: 6.1.1.a.(iii). **UV-Vis Overlay Spectra (B- Band) of Zn[T(4-OMeP)P] (10^{-5}M in $CHCl_3$)(——); in the presence of CTAB (10^{-1} M in $CHCl_3$) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

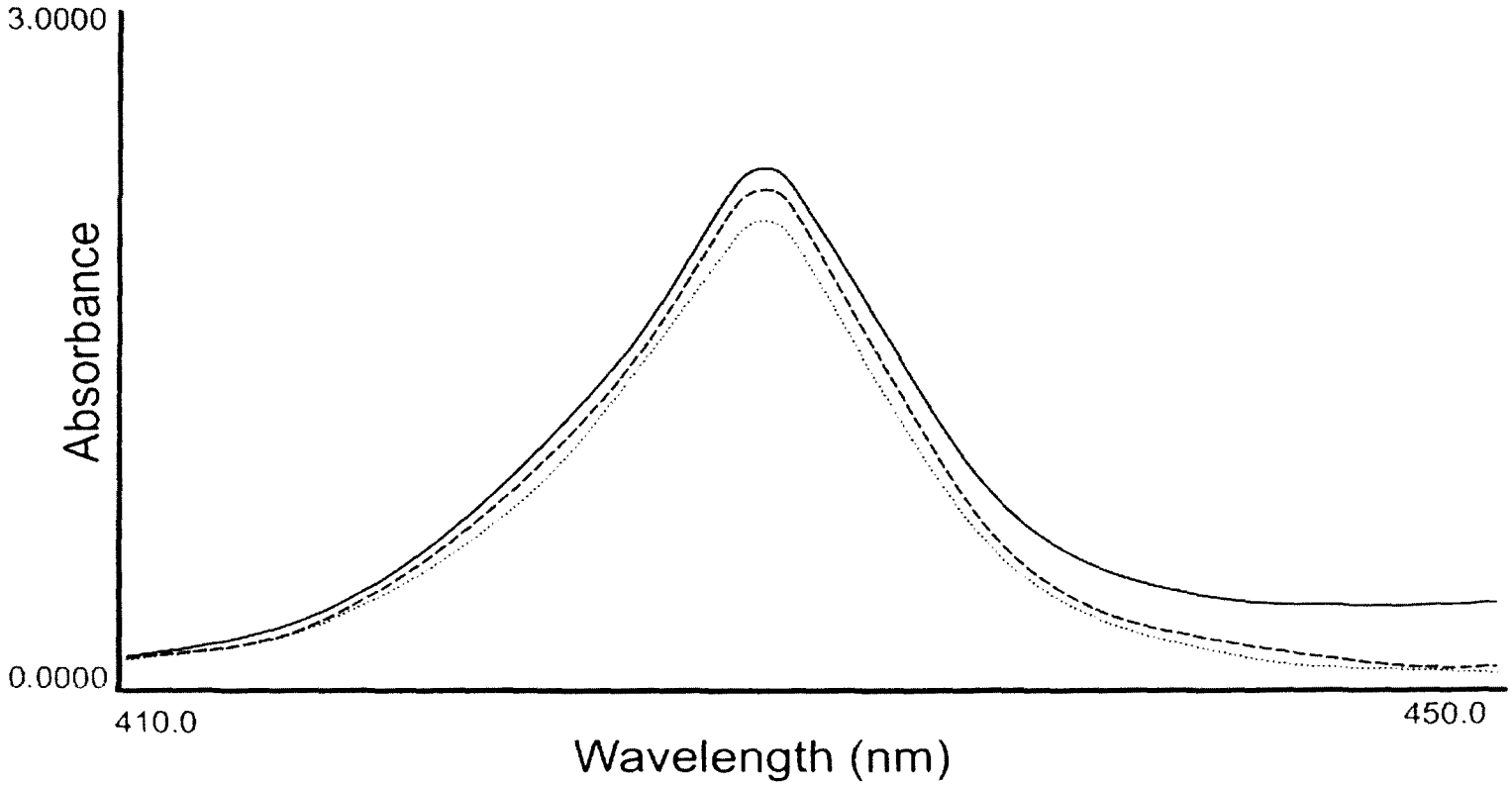


Figure: 6.1.1.b.(i). **UV-Vis Overlay Spectra (B- Band) of Zn[T(naphthyl)P] (10^{-5}M in $CHCl_3$)(———); in the presence of SDS (10^{-1}M in CH_3OH) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

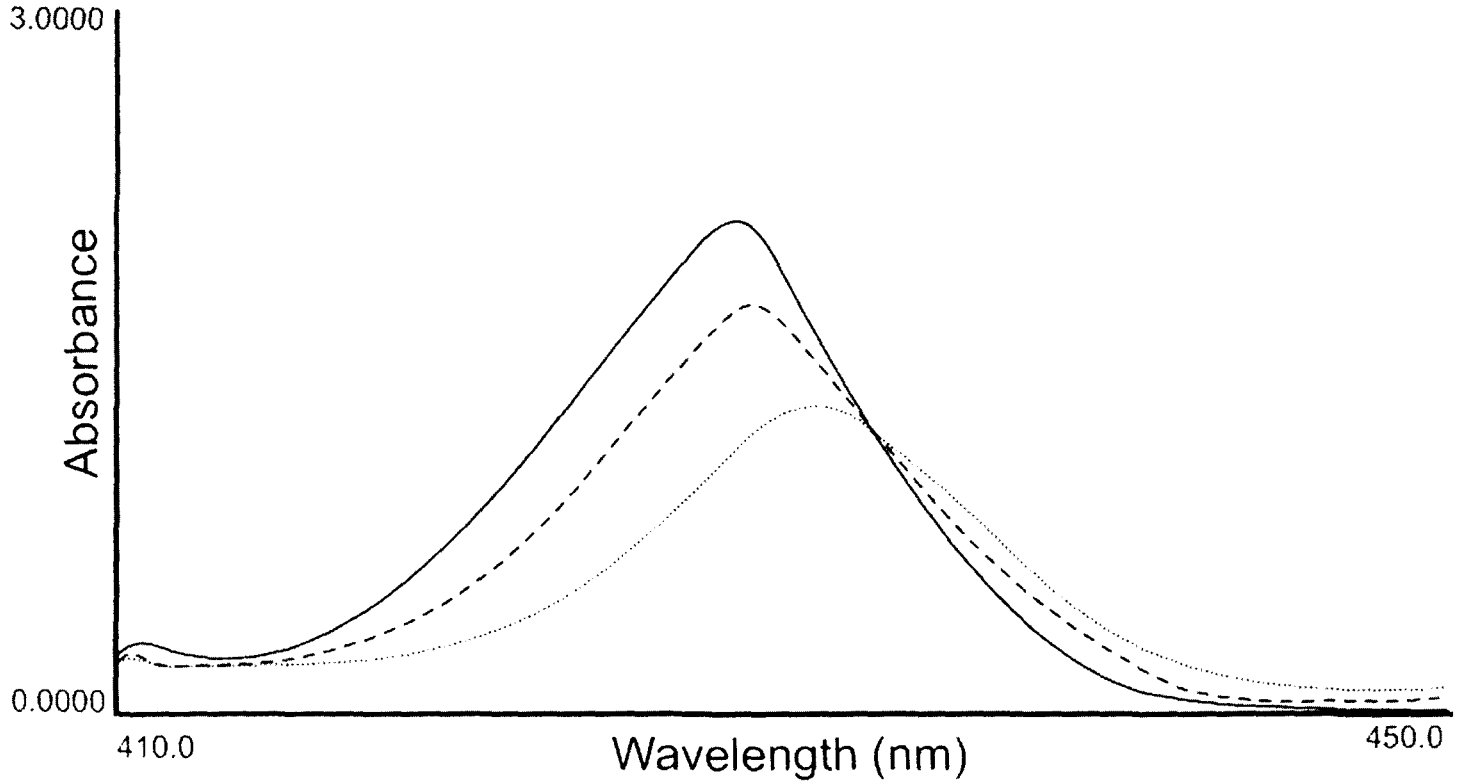


Figure: 6.1.1.b.(ii). **UV-Vis Overlay Spectra (B- Band) of Zn[T(naphthyl)P] (10^{-5}M in $CHCl_3$)(——); in the presence of TX-100 (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

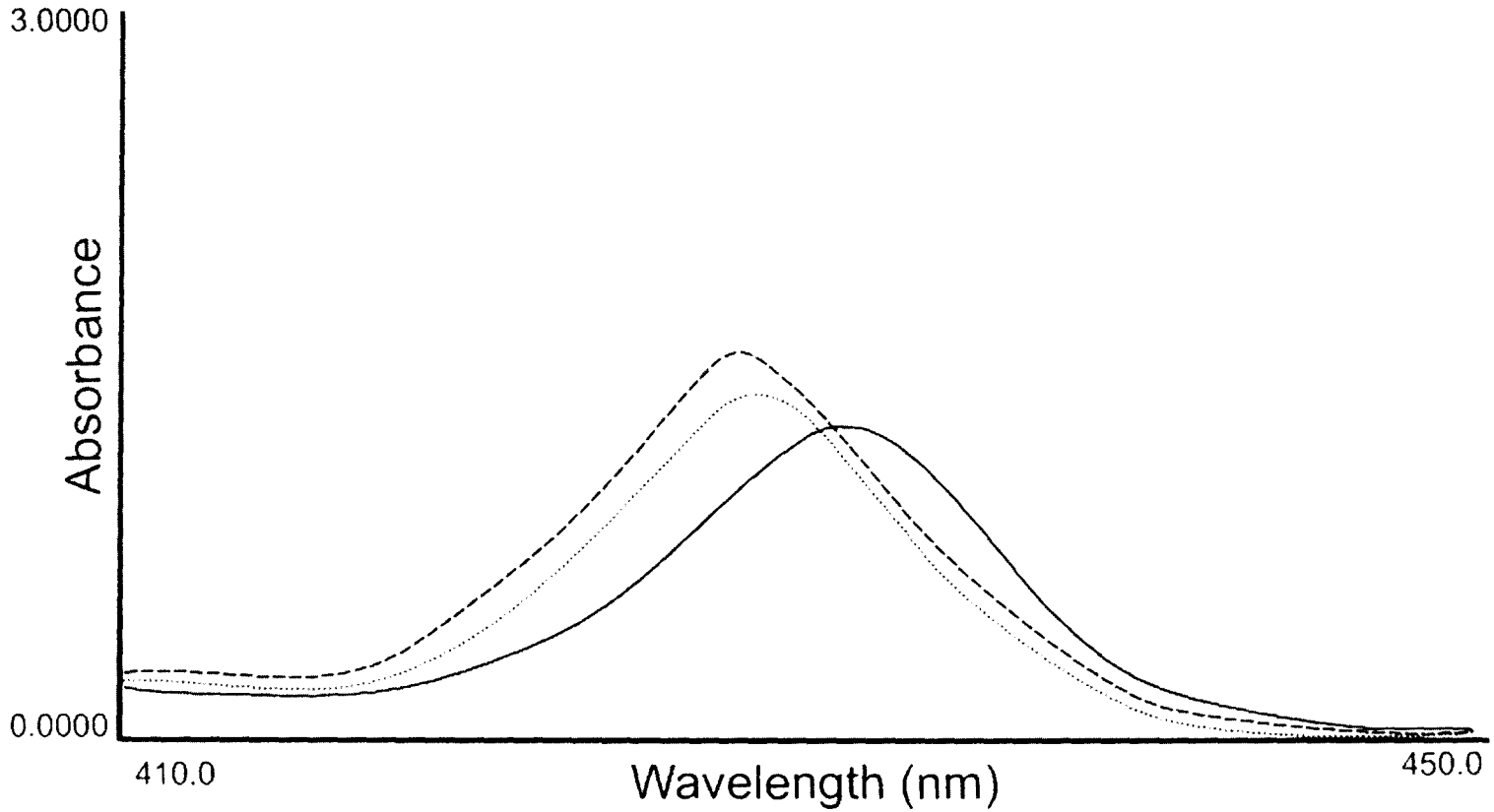


Figure: 6.1.1.b.(iii). **UV-Vis Overlay Spectra (B- Band) of Zn[T(naphthyl)P] (10^{-5}M in $CHCl_3$)(——); in the presence of CTAB (10^{-1}M in $CHCl_3$) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

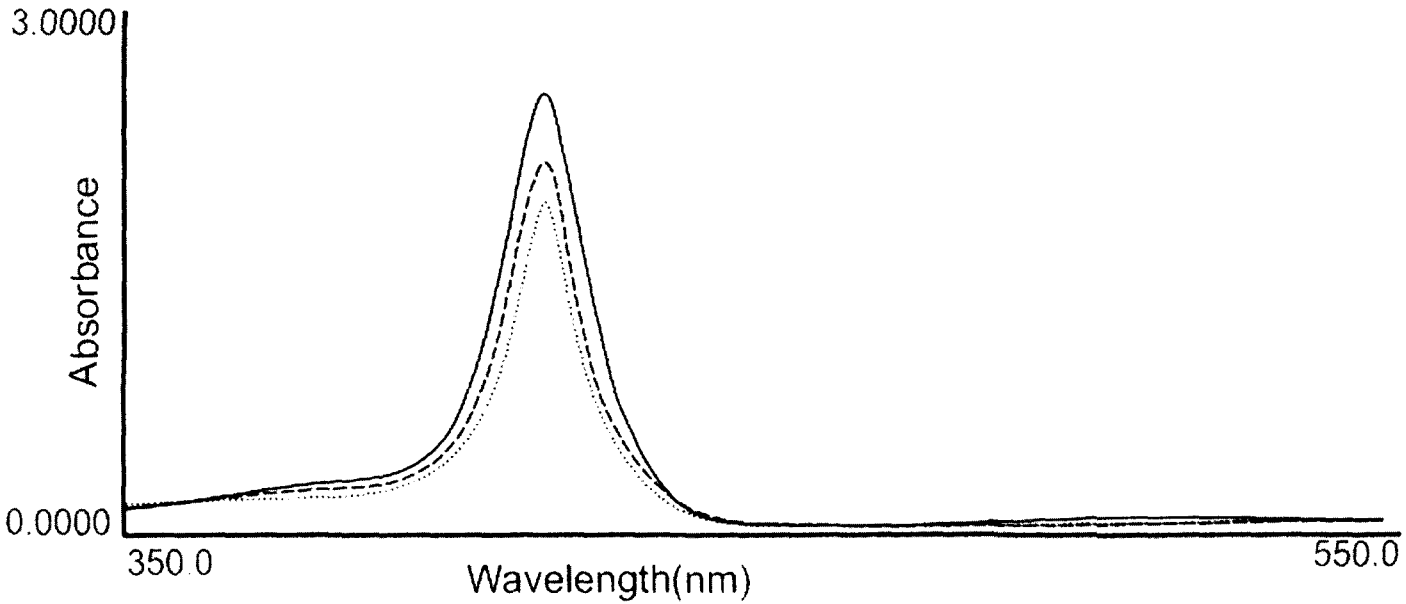


Figure: 6.1.1.c.(i). **UV-Vis Overlay Spectra (B- Band) of Cu[T(4-OMeP)P] (10^{-5}M in $CHCl_3$)(– – –); in the presence of SDS (10^{-1}M in CH_3OH) (———) and 0.3mol of triethylamine (·····) at Room Temperature.**

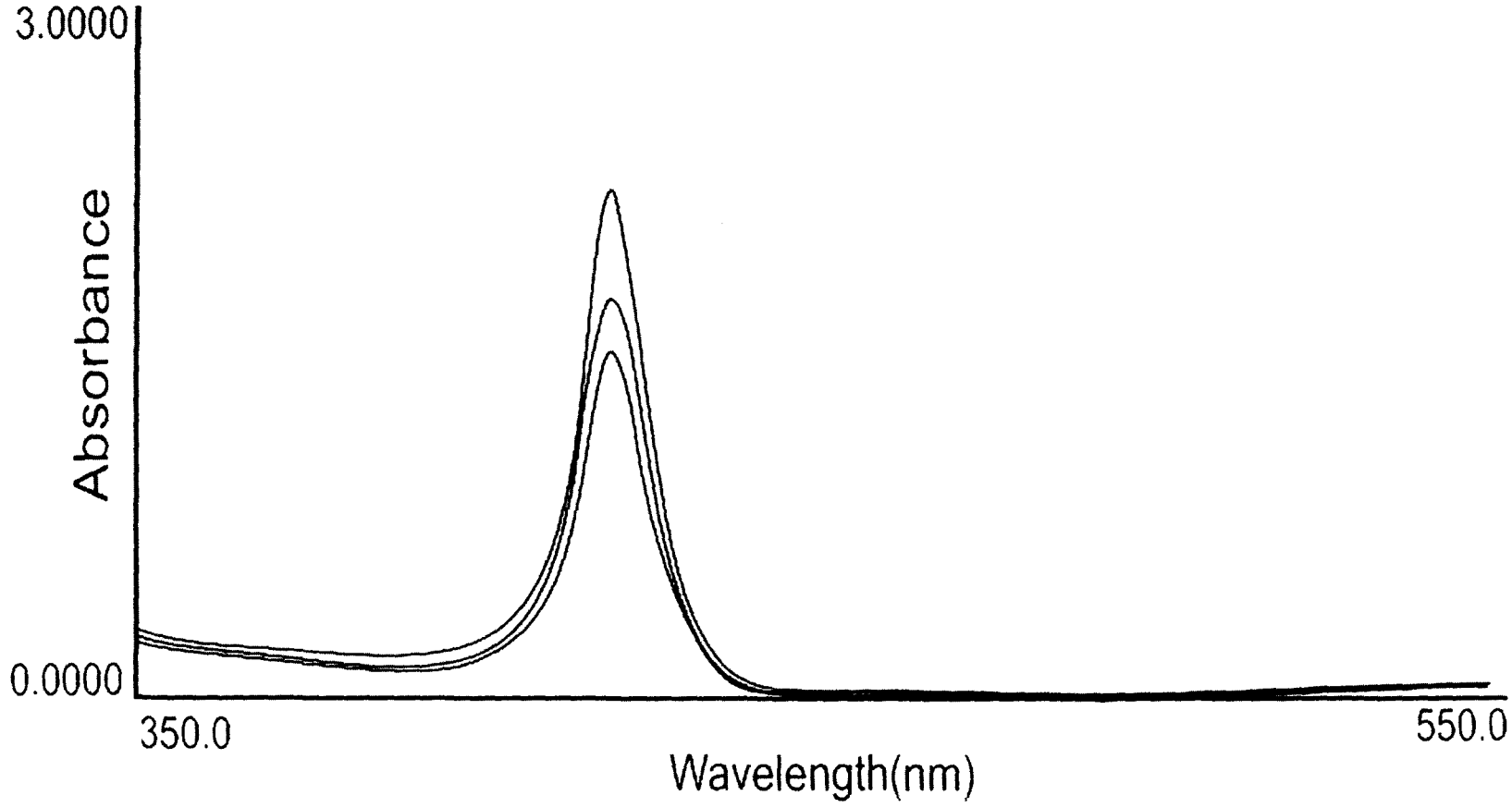


Figure: 6.1.1.c.(ii). **UV-Vis Overlay Spectra (B- Band) of Cu[T(4-OMeP)P] (10^{-5}M in $CHCl_3$)(——); in the presence of TX-100 (– – –) and 0.3mol of triethylamine (.....) at Room Temperature.**

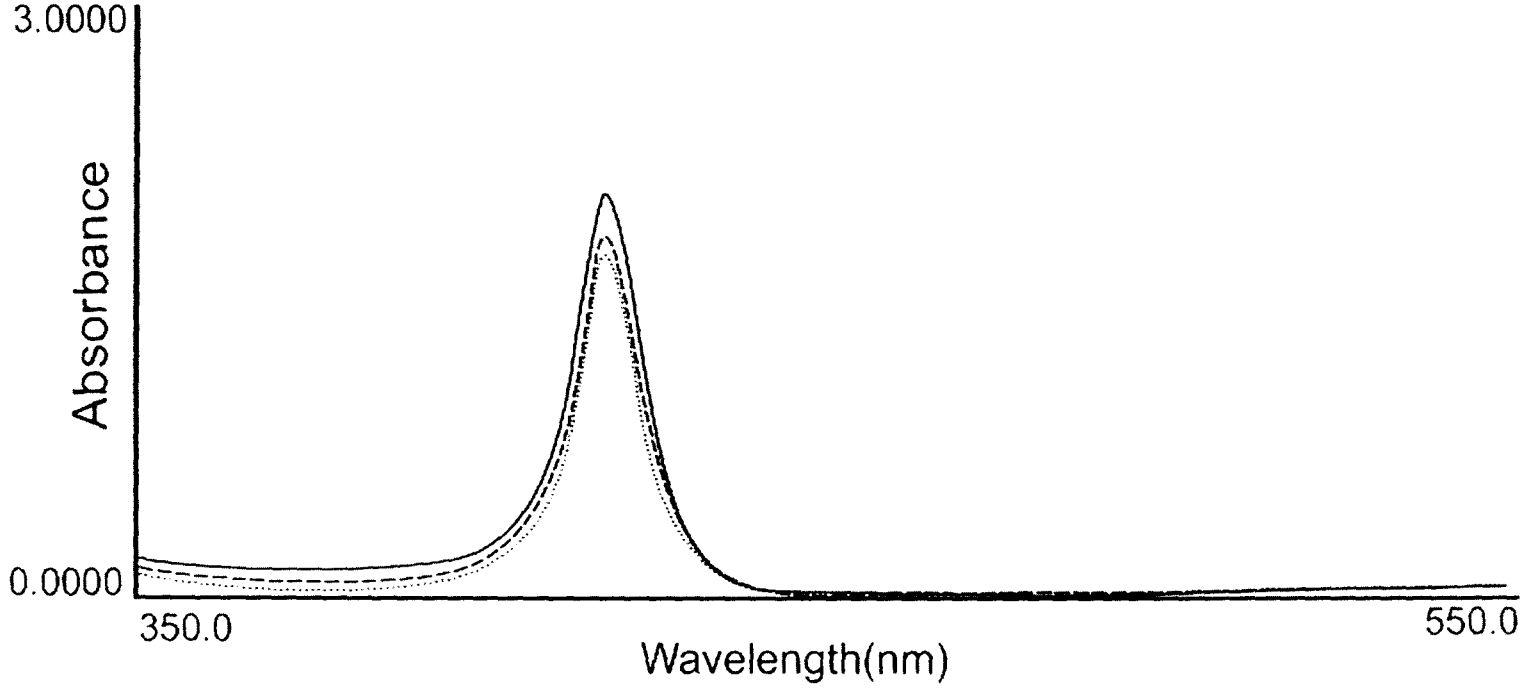


Figure: 6.1.1.*c*.(iii). **UV-Vis Overlay Spectra (B- Band) of Cu[T(4-OMeP)P] (10^{-5}M in $CHCl_3$)(——); in the presence of CTAB (10^{-1}M in $CHCl_3$) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

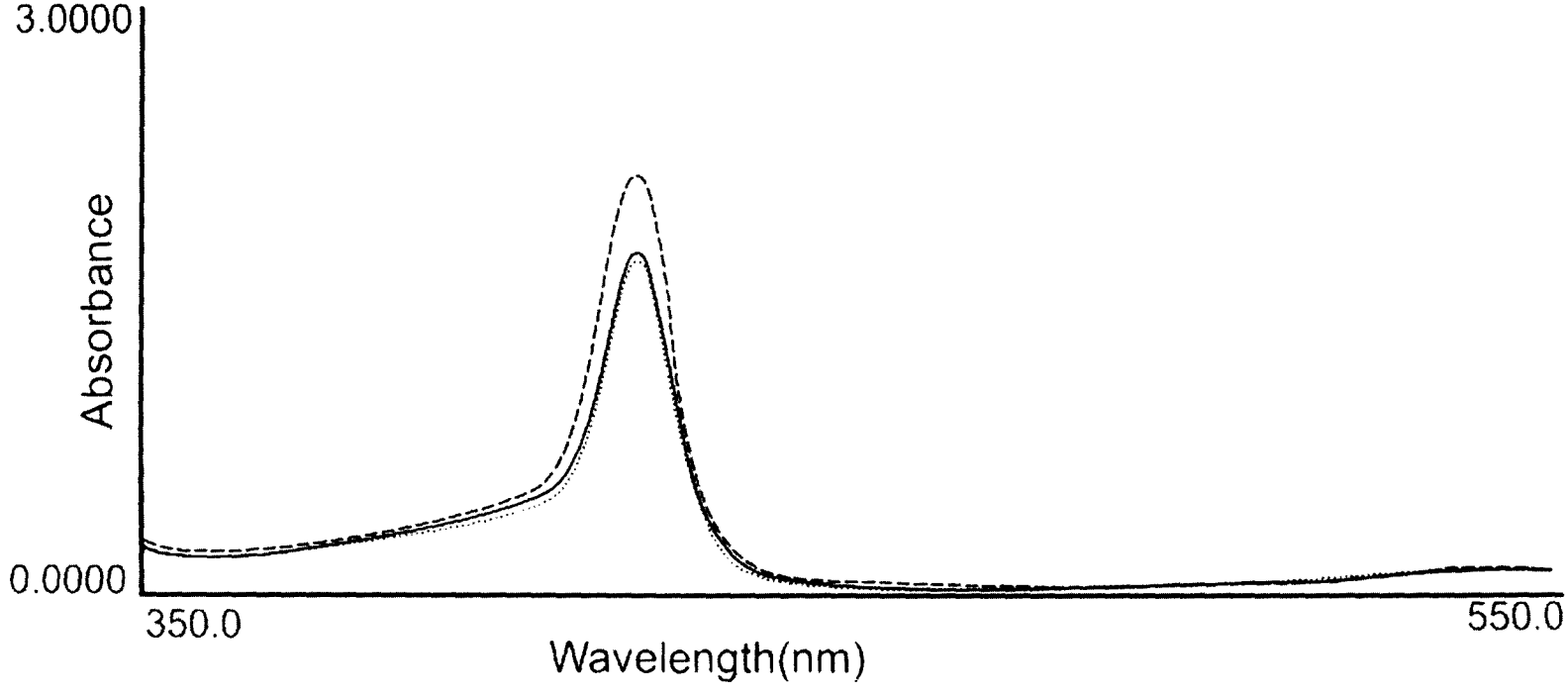


Figure: 6.1.1.d.(i). **UV-Vis Overlay Spectra (B- Band) of Cu[T(naphthyl)P] (10^{-5}M in $CHCl_3$)(– – –); in the presence of SDS (10^{-1}M in CH_3OH) (——) and 0.3mol of triethylamine (·····) at Room Temperature.**

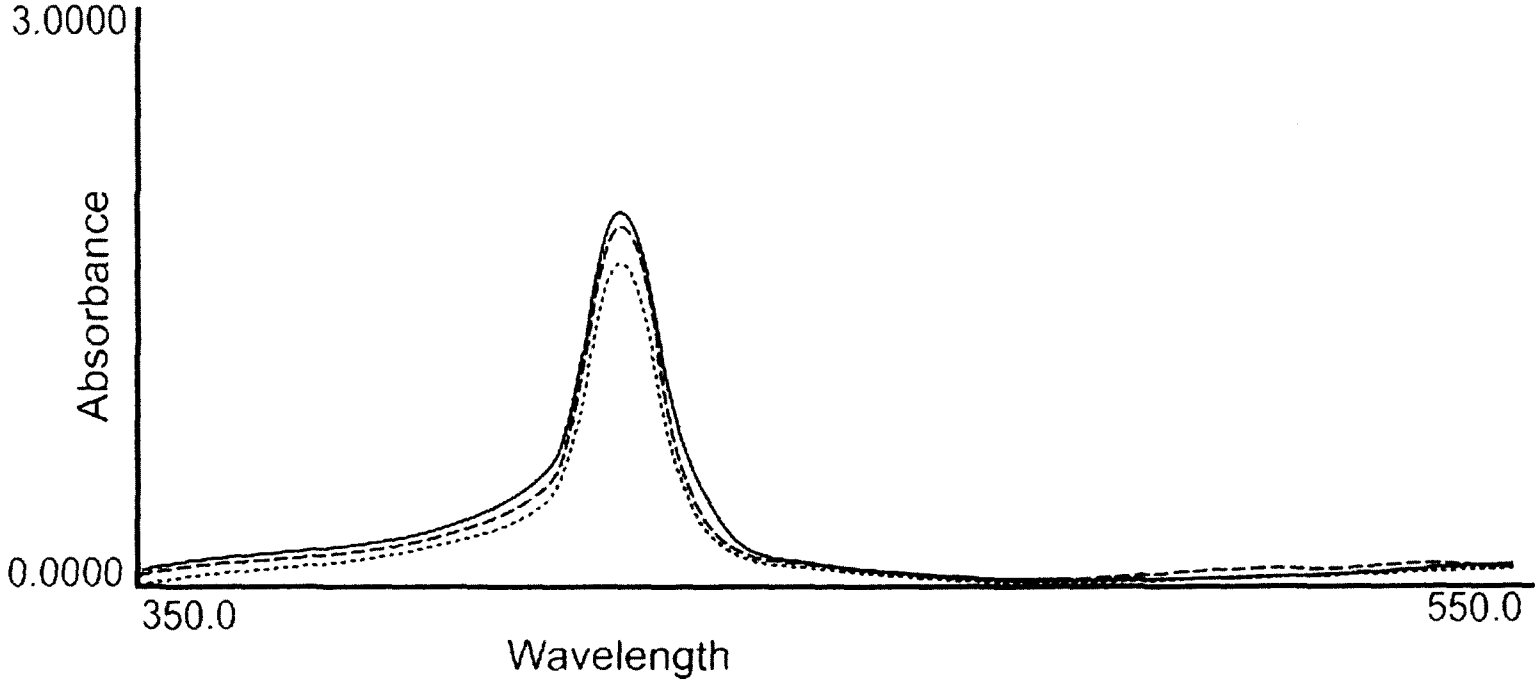


Figure: 6.1.1.d.(ii). **UV-Vis Overlay Spectra (B- Band) of Cu[T(naphthyl)P] (10^{-5}M in $CHCl_3$)(——); in the presence of TX-100 (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

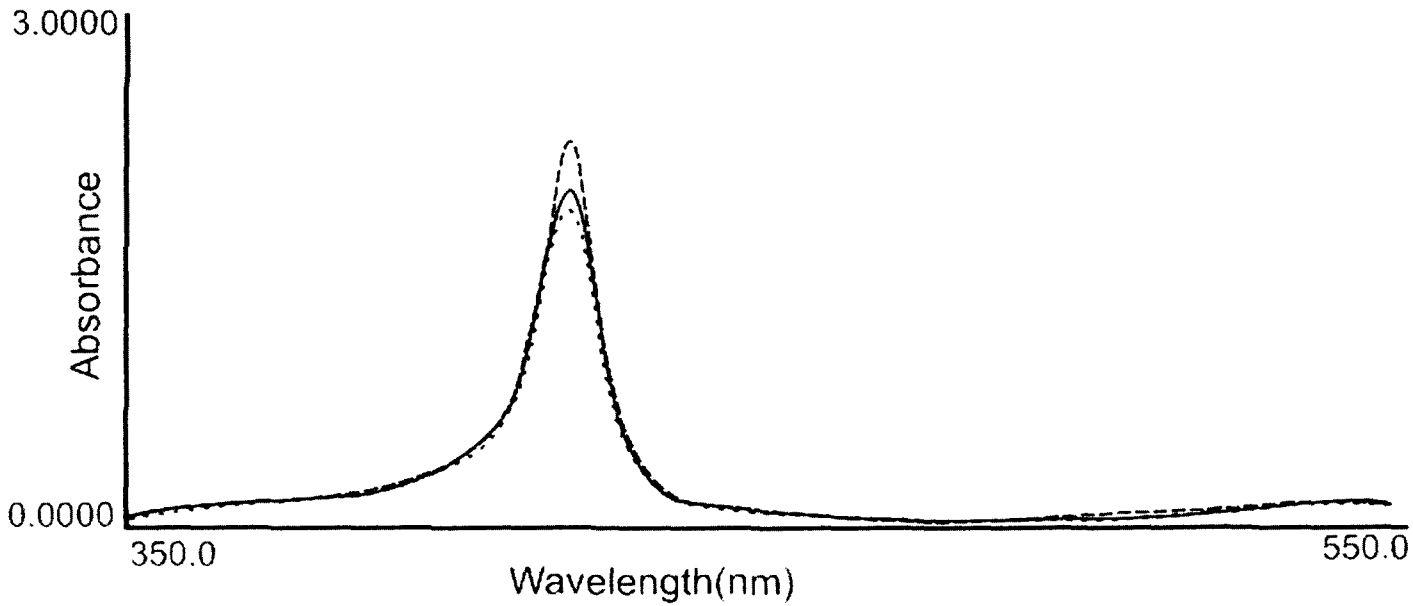


Figure: 6.1.1.d.(iii). **UV-Vis Overlay Spectra (B- Band) of Cu[T(naphthyl)P] (10^{-5}M in $CHCl_3$)(——); in the presence of CTAB (10^{-1}M in $CHCl_3$) (– – –) and 0.3mol of triethylamine (·····) at Room Temperature.**

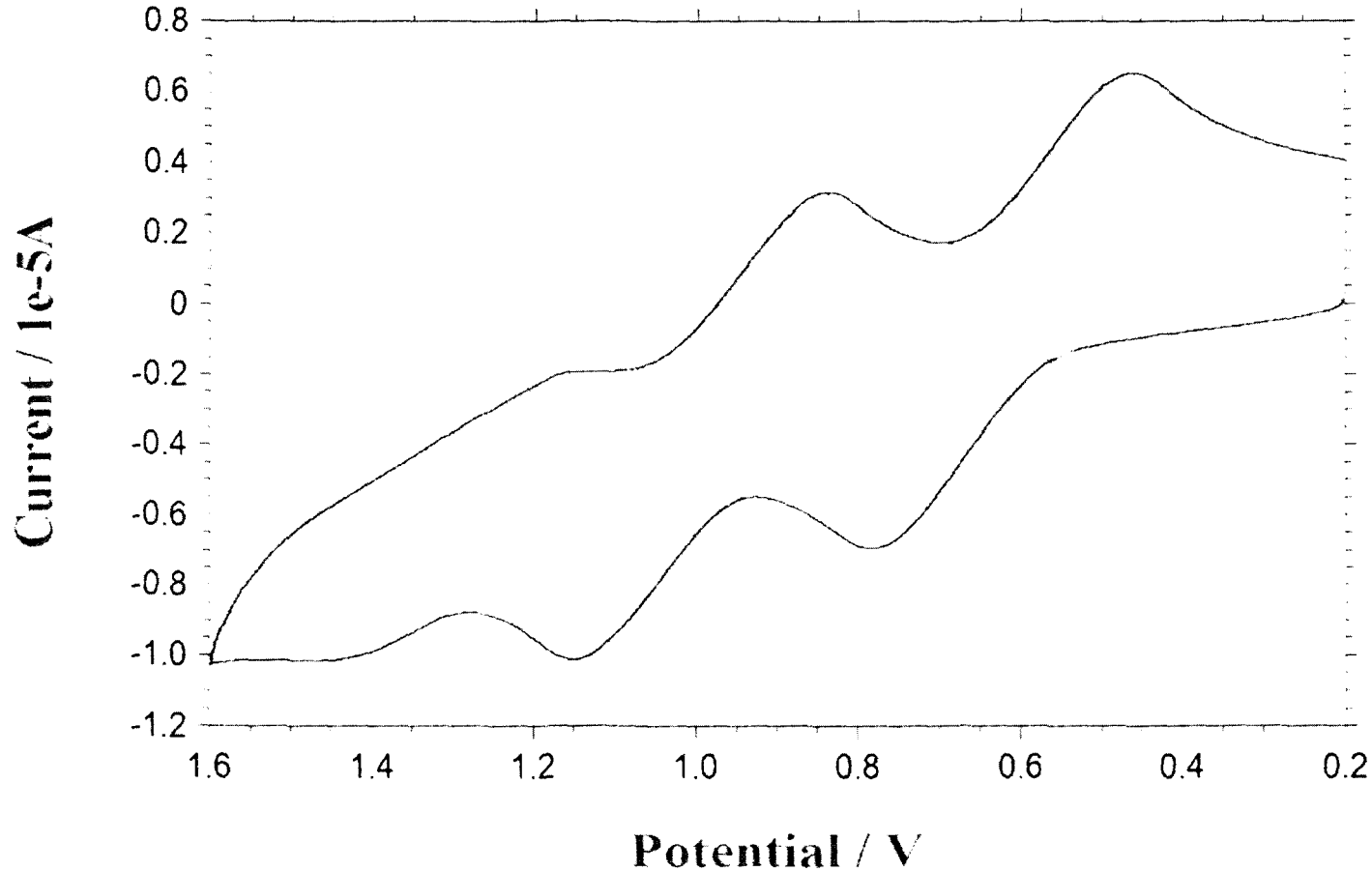


Figure: 6.4.1.a.(i). **Cyclic Voltammogram of Zn[(T-4OMeP)P] (10^{-3}M in $CHCl_3$) containing 0.1M TBAP at Room Temperature.**

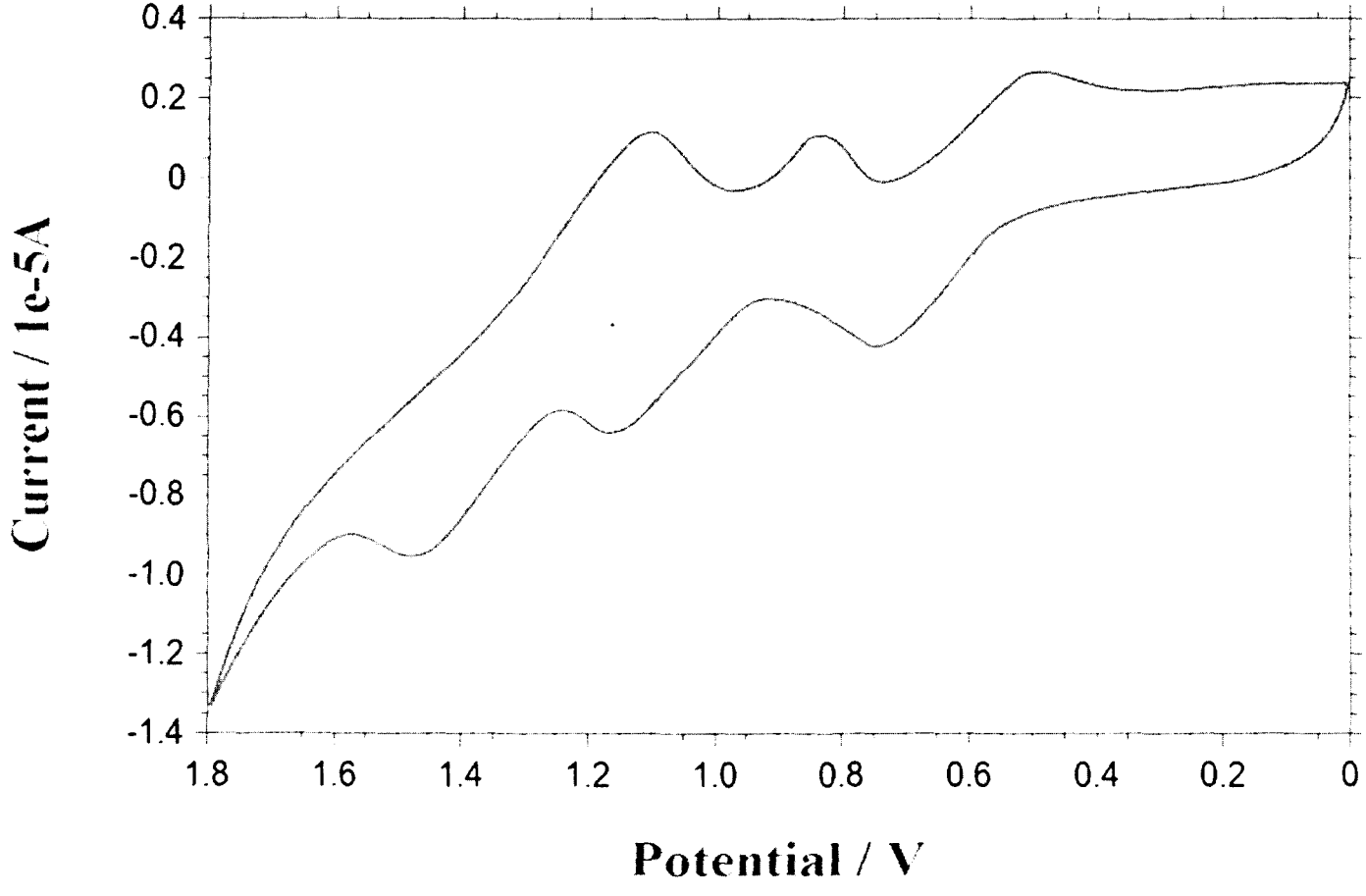


Figure: 6.4.1.a.(ii). **Cyclic Voltammogram of Zn[T(4-OMeP)P] (10^{-3}M in $CHCl_3$) containing 0.1M TBAP In SDS medium (10^{-1}M in CH_3OH) at Room Temperature.**

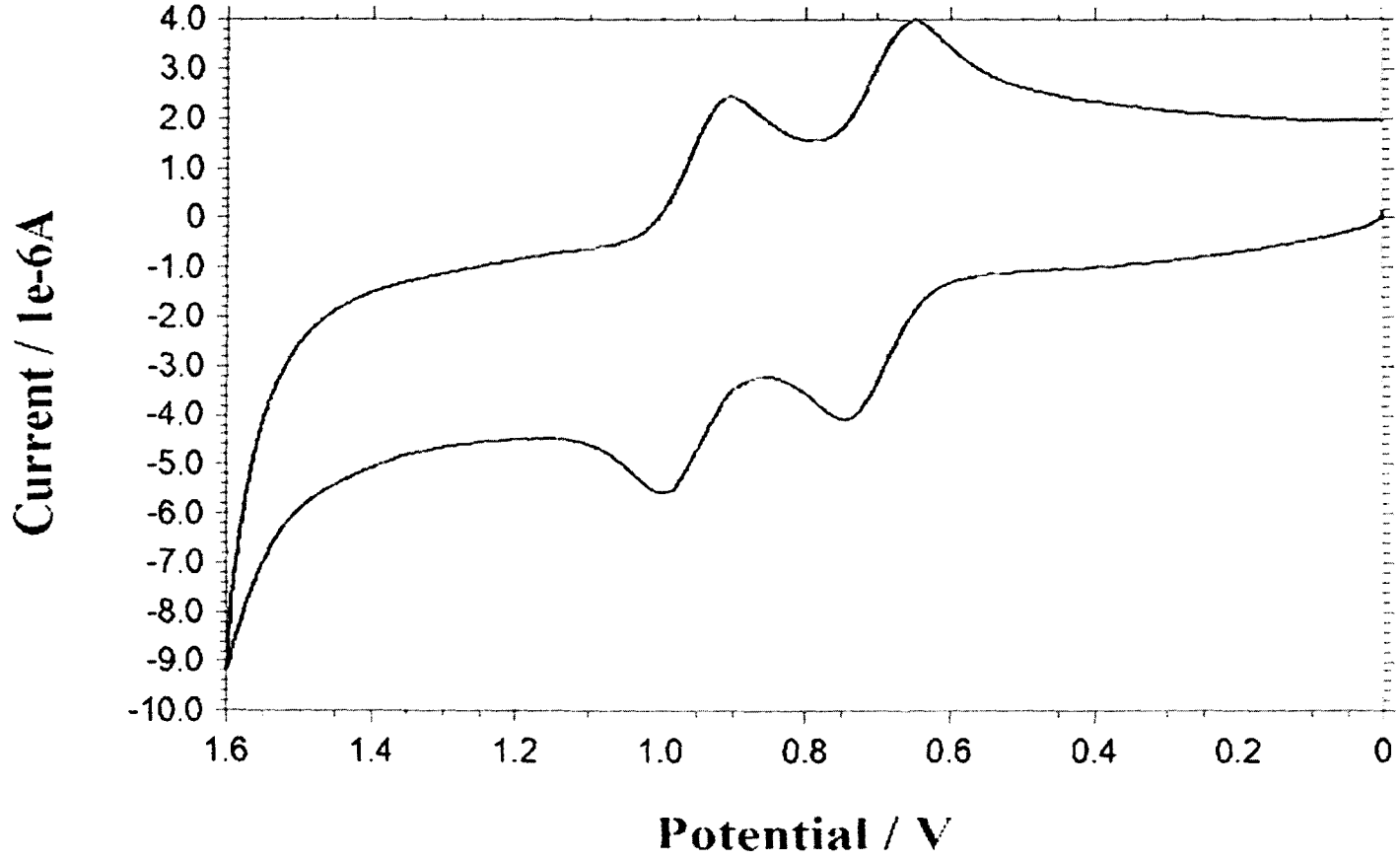


Figure: 6.4.1.b.(i). **Cyclic Voltammogram of Zn[T(naphthyl)P] (10^{-3}M in $CHCl_3$) containing 0.1M TBAP at Room Temperature.**

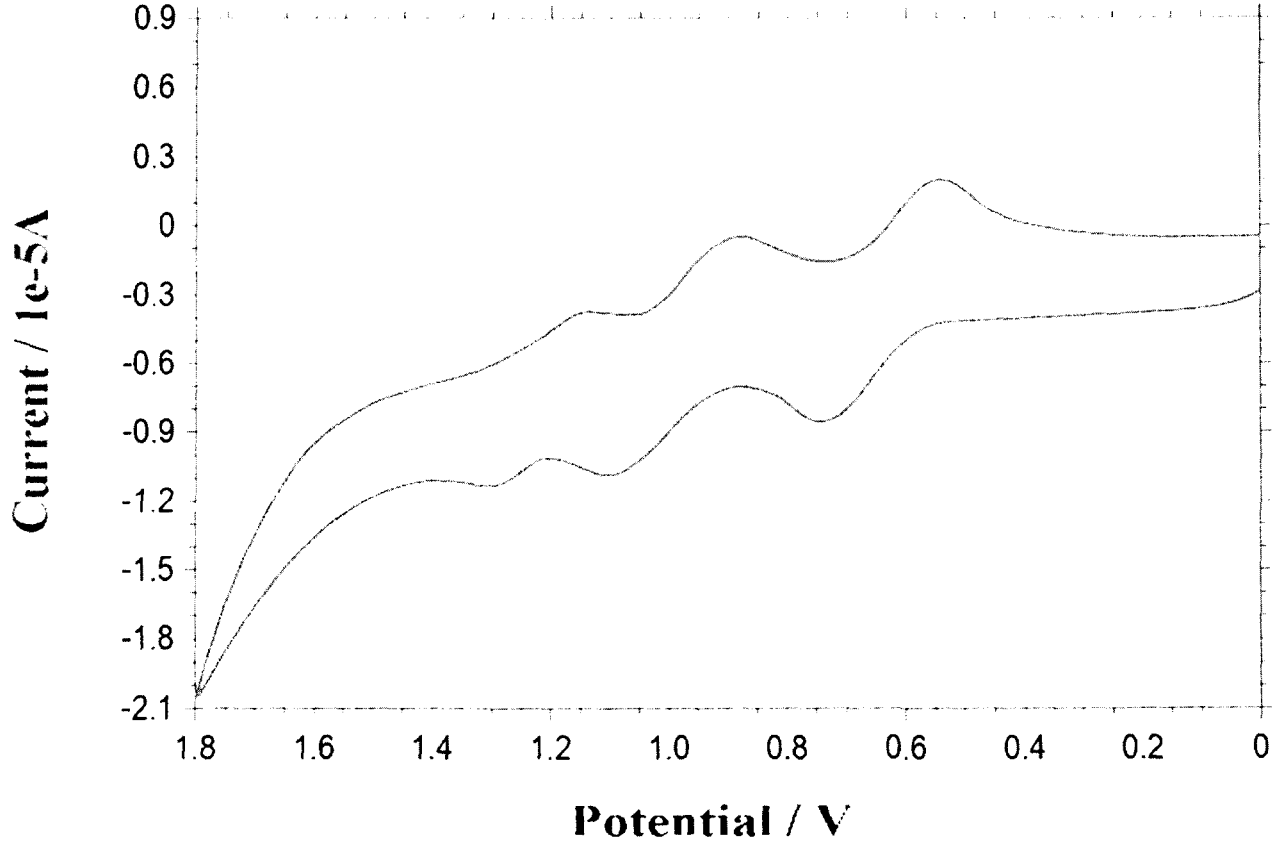


Figure: 6.4.1.b.(ii). **Cyclic Voltammogram of Zn[T(naphthyl)P] (10^{-3}M in $CHCl_3$) containing 0.1M TBAP In SDS medium (10^{-1}M in CH_3OH) at Room Temperature.**

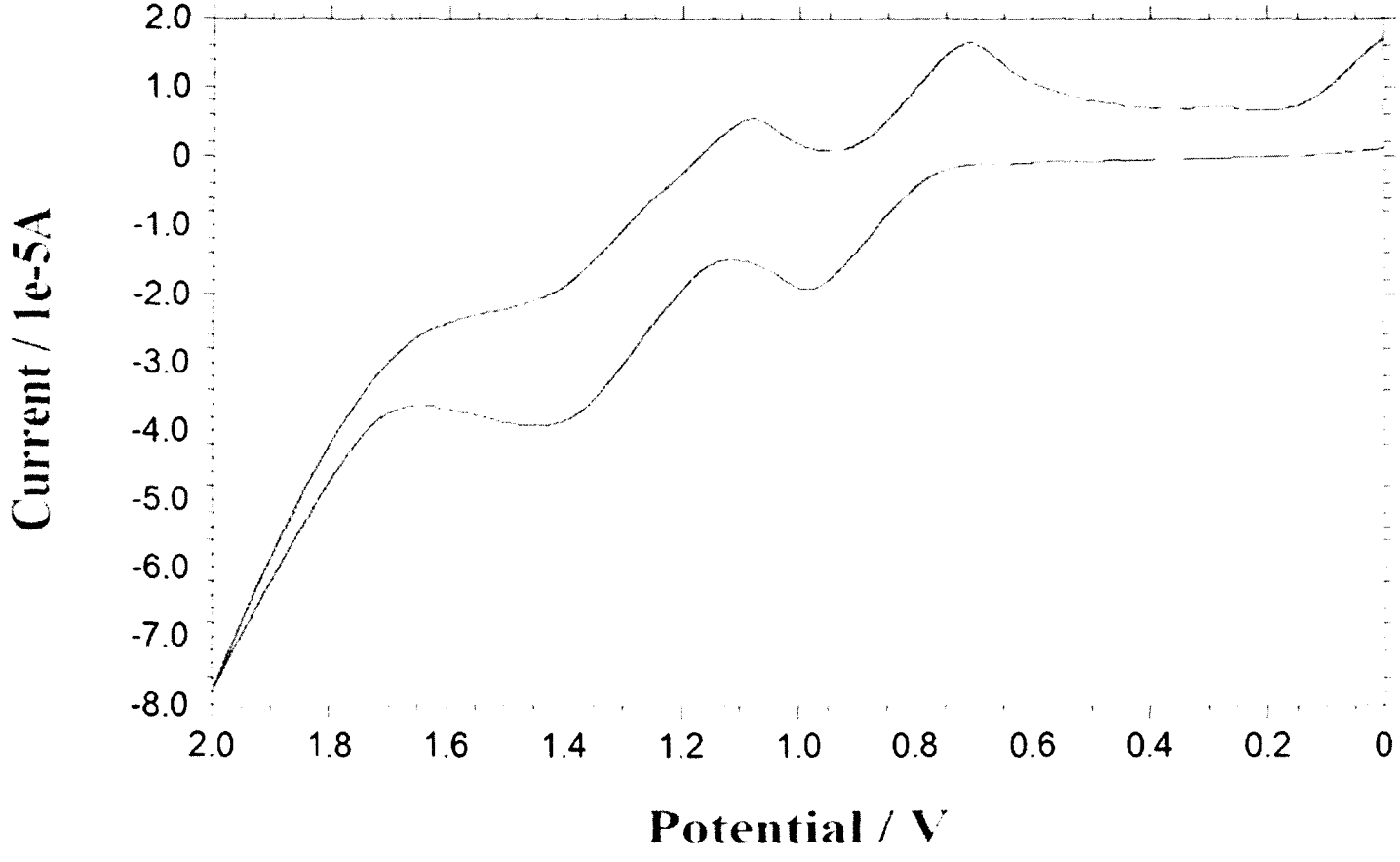


Figure: 6.4.1.c.(i). **Cyclic Voltammogram of Cu[T(4-OMeP)P] (10^{-3}M in $CHCl_3$) containing 0.1M TBAP at Room Temperature.**

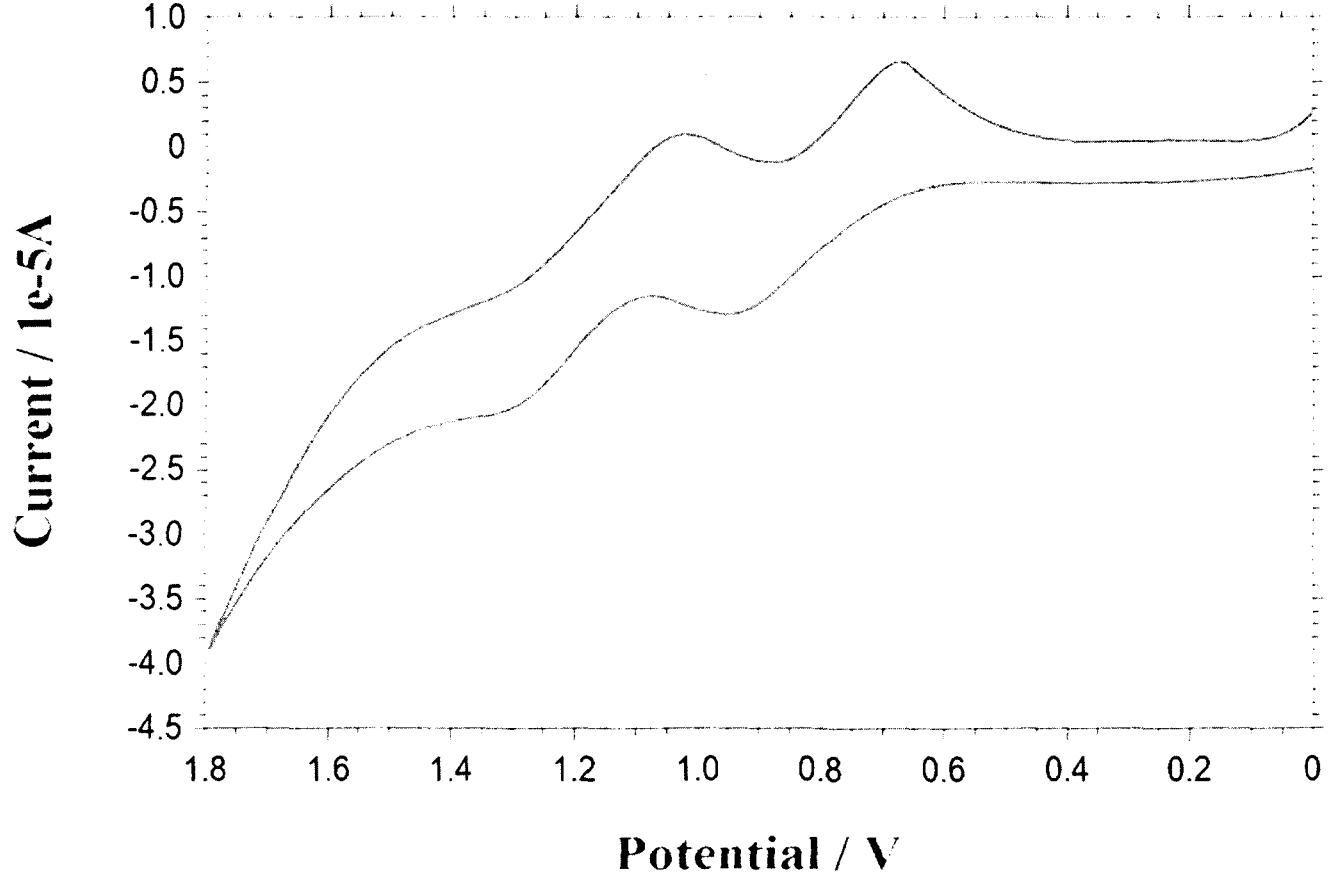


Figure: 6.4.1.c.(ii). **Cyclic Voltammogram of Cu[T(4-OMeP)P] (10^{-3}M in $CHCl_3$) containing 0.1M TBAP In SDS medium (10^{-1}M in CH_3OH) at Room Temperature.**

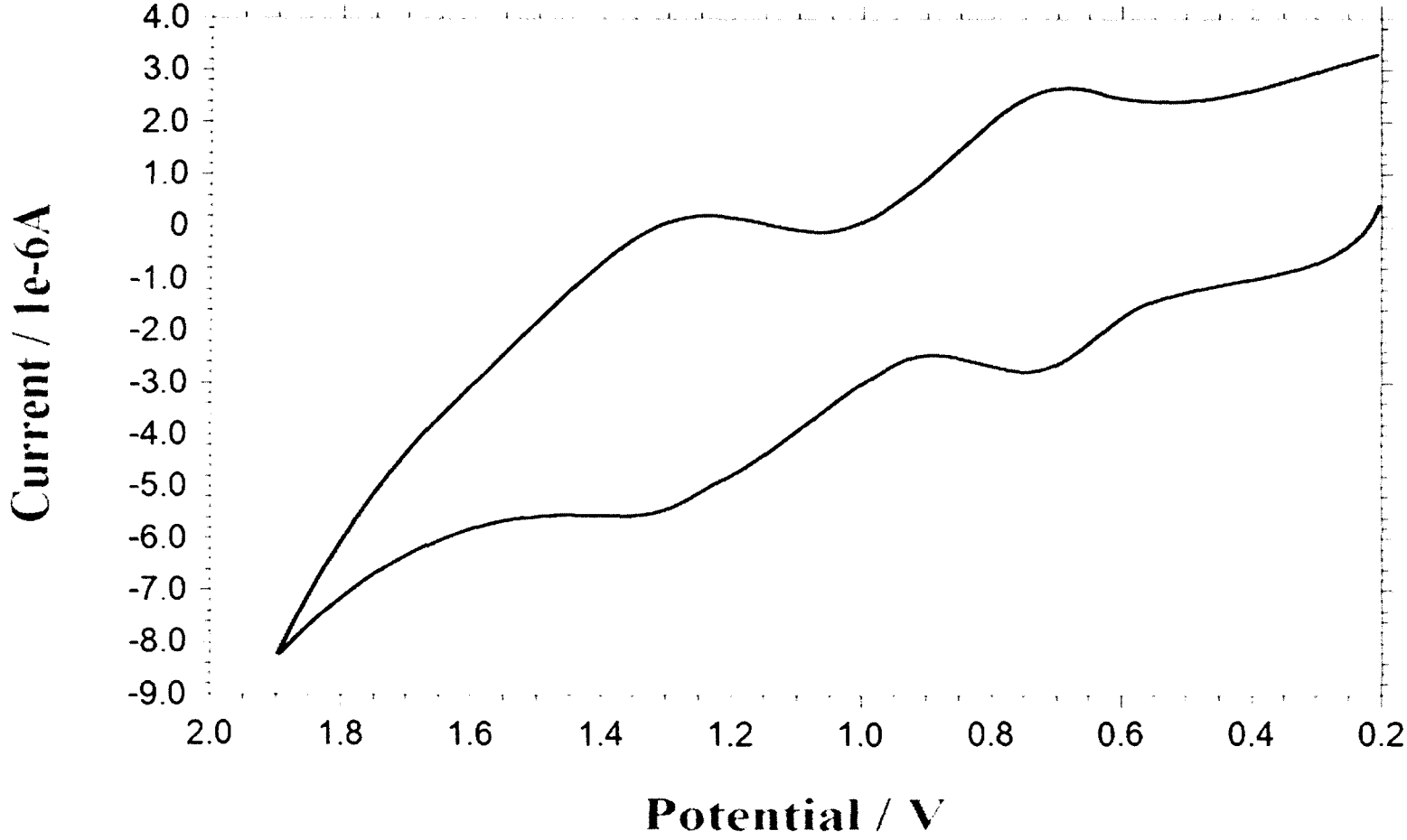


Figure: 6.4.1.d.(i). **Cyclic Voltammogram of Cu[T(naphthyl)P] (10^{-3}M in $CHCl_3$) containing 0.1M TBAP at Room Temperature.**

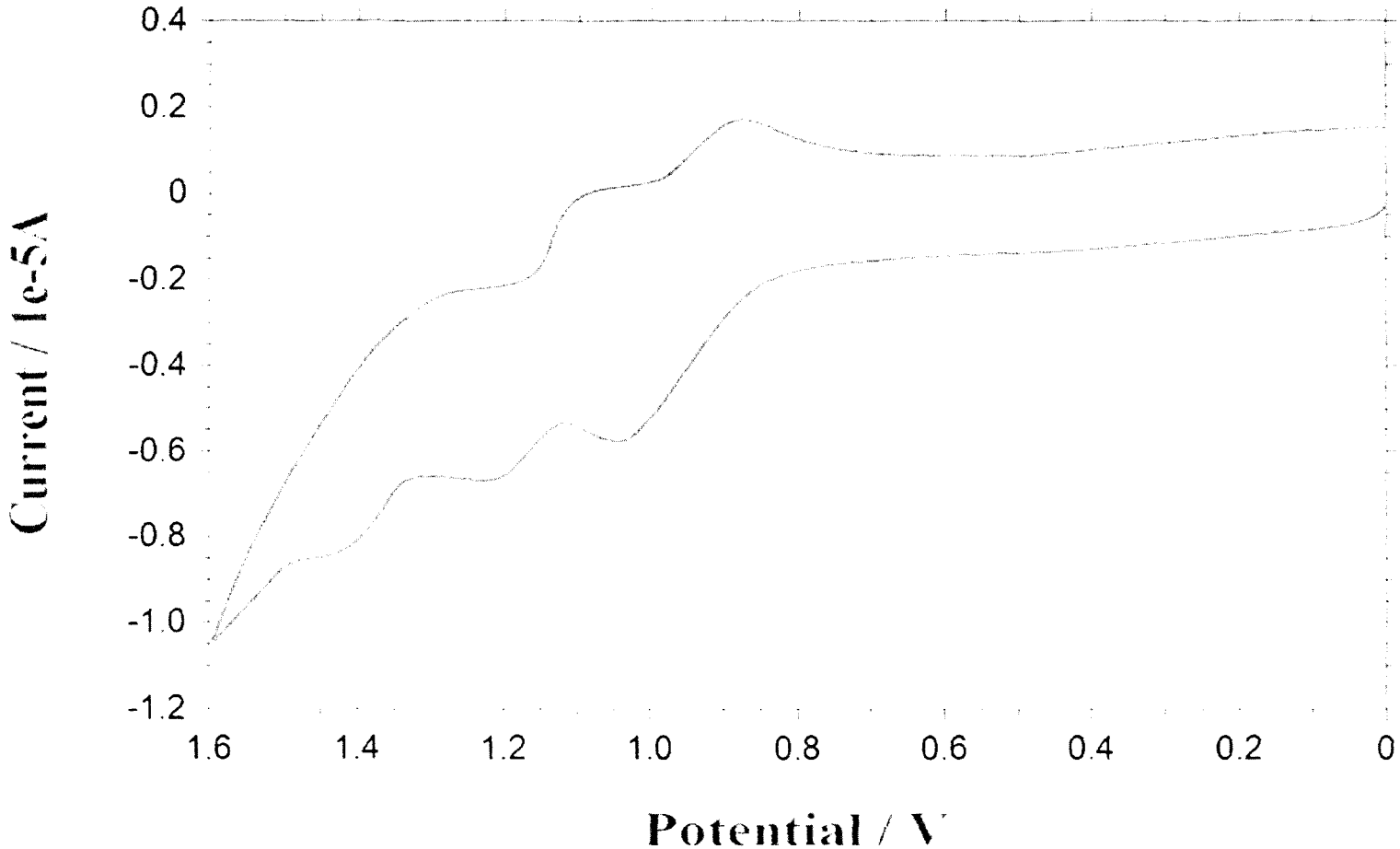


Figure: 6.4.1.d.(ii). **Cyclic Voltammogram of Cu[T(naphthyl)P] (10^{-3}M in $CHCl_3$) containing 0.1M TBAP In SDS medium (10^{-1}M in CH_3OH) at Room Temperature.**

REFERENCES:

1. A.P.H.J. Schenning, D.H.W. Hubert, M.C. Feiters, R.J.M. Nolte, *Langmuir*, **12**, 1572-1577 (1996).

2. J. Simplico, K. Schwenzer, F.Maenpa, *J. Am. Chem. Soc.*, **97**(25), 7319-7326 (1975).

3. L.A. Lucia, T. Yui, R. Sasai, S. Takagi, K. Takagi, H. Yoshida, D.G. Whitten and H. Inoue, *J. Phys. Chem. B,* **107**, 3789 – 3797 (2003).

4. D. Brault, C. Vever – Bizet, K. Kuzelova, *J. Photochem.. Photo Biol. B*, **20**, 191-195 (1993).

5. J. – H. Furhop, J. Mathieu, Angew. *Chem. Intl. Ed. Engl.*, **23**, 100-113 (1984).

SUMMARY

SUMMARY

This thesis entitled **"REDOX TUNING OF SOME METALLOPORPHYRINS IN MICELLAR MEDIUM"** discussed the information and results of investigations on the behaviour of some Metalloporphyrins in the presence of different surfactants. It consists of **six chapters**. We restrict our investigations to the determination of Critical Micellar Concentration (CMC) of some surfactants, UV – Visible absorption spectroscopy and Cyclic Voltammetric studies of some metalloporphyrins like Manganese, Zinc and Copper porphyrins in surfactant medium.

In the **Introduction**, biological functions of some metalloporphyrins and their uses in medicinal and pharmaceutical fields are briefly mentioned. Also, the importance to study the behaviour of metalloporphyrins in surfactant medium is highlighted in the Introduction.

A Brief Review on the studies of porphyrin in aqueous micellar medium is presented in **Chapter 1**. This review provides us the background information about the behaviour of porphyrins and their interactions in micellar

medium. Although this present work deals with the studies of metalloporphyrins in non-aqueous micellar medium, yet by knowing their behaviour in aqueous micellar media, it will give us an idea and help us to pursue our research investigation in the right direction.

Chapter 2 describes the details of the experimental procedures adopted for purification of solvents and chemicals, synthesis, purification and characterization of samples used during the course of our investigation. Besides this, brief description of CMC determination by different methods and some physical measurements are also presented.

Chapter 3 deals with the determination of CMC of SDS and CTAB surfactants by using the conductivity method and the Cyclic Voltammetry method.

For anionic surfactant, SDS, the CMC was determined by both the methods. In conductivity method, the CMC point was obtained graphically by plotting Conductivity, κ ($\Omega^{-1}m^{-1}$) Vs Concentration (M) and the

break point in the plot was taken as the CMC. For SDS solution in pure methanol, the CMC value obtained by Conductivity method is 6.4 x 10^{-3}M. In Cyclic Voltammetry method, the CMC point was obtained graphically by plotting Peak current, i_p (μA) Vs Concentration (M) and the break point in the plot was taken as the CMC point. From this method the CMC of SDS in pure methanol was found to be 6.0 x 10^{-3}M.

Similarly, the CMC of SDS in 1:1 mixture of methanol:chloroform was determined and found out to be 3.6 x 10^{-3}M.

The CMC of cationic surfactant, CTAB was determined by conductivity method only since the voltammogram of the redox active material used could not be resolved in the presence of CTAB. From the conductivity method the CMC of CTAB in chloroform was found to be 4.6 x 10^{-3}M.

The CMC of non-ionic surfactant, TX – 100 was taken as that reported in the literature

Chapter 4 describes the UV - Visible studies of some Manganese porphyrins in surfactant medium. All these manganese porphyrins exhibit similar spectral pattern in the same surfactant medium. The bands in SDS medium suffer blue shift and we attribute this observation to a possible replacement of the axial ligand OAc^- by the negatively charged head group of SDS and another possibility is the aggregation of porphyrin molecules resulting in dimerisation. The bands in TX – 100 are also blue shifted and this is attributed to the possible interaction between the manganese ion and the –OH group of TX – 100. In CTAB, the absorption bands suffer red shift and this could be due to the replacement of OAc^- by Br^- of the CTAB molecule. The UV – Visible spectra remain unchanged with the addition of triethylamine which means that the amine is not accessible by the metal ion. This points out to the fact that there is a strong interaction between the metal of the porphyrin and the surfactant which makes it unavailable for axial ligation with amine.

Chapter 5 discussed the Cyclic Voltammetric Studies of some manganese porphyrins in surfactant medium. In SDS medium only ligand oxidations are observed and are found to be on the higher side. No metal centered oxidation was observed which indicates that the metal ion is not available for the redox process. In TX – 100 and CTAB media, the voltammogram could not be resolved.

Chapter 6 describes the UV – Visible and Cyclic Voltammetric studies of some Zinc and Copper porphyrins in surfactant medium. The UV – Visible spectra remain invariant in SDS, TX – 100 and CTAB media in most cases. No significant conclusion can be drawn from here.

From Cyclic Voltammetric studies, the voltammograms of Zn[T(naphthyl)P] and Cu[T(naphthyl)P] exhibit three redox couples which are not observed in the voltammograms of these metalloporphyrins in chloroform in the absence of SDS. This observation is attributed to the possibility of dimer formation, probably J – type dimer. In TX – 100 and CTAB media, the voltammogram could not be resolved.