# ELECTROCATALYTIC REDUCTION OF TOXIC ORGANOHALIDES IN SURFACTANT MICROSTRUCTURES

## CHRISTOPHER KIVUTI REUBEN

**B.Sc. Honors, University of Nairobi, 1991**

**A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry at the University of Nairobi 1994.**
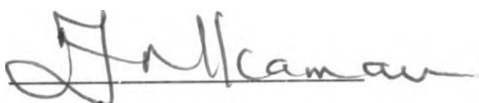
# DECLARATION

I declare that this thesis is my original work and has not been presented for a degree in any other University. The research was accomplished in the Chemistry Department at the University of Nairobi.

**KIVUTI, C.R.**
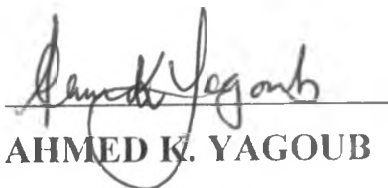
This thesis has been submitted for examination with our approval as University supervisors.

Major supervisor:

**DR. GEOFFREY N. KAMAU**

Associate supervisor:

**DR. AHMED K. YAGOUB**

**CHEMISTRY DEPARTMENT**

**UNIVERSITY OF NAIROBI**

1994

## DEDICATION

To my parents, Reuben Njue Njobuthi and Peliphetua Njuri Ndwiga, who have always believed that children deserve a splendid Education and they have been right. Thanks for your remarkable commitment, love and encouragement.

# ACKNOWLEDGEMENT

# ABSTRACT

In a bicontinuous conductive media of 23:34:43 didodecyldimethylammonium bromide DDAB/n-dodecane/water microemulsion (% by wt.), controlled potential electrolysis was performed at the two diffusion controlled reduction waves of copper phthalocyanine tetrasulphonic acid, tetrasodium (CuPcTS) in absence and in presence of added 1,2-dibromobutane as substrate   From the data obtained, it is possible to establish the mechanism for electrocatalytic reduction of vicinal dihalides in surfactant media.   The results suggest that vicinal dihalides are reduced to the olefin and the mediator is reoxidized from the active $CuPcTS^{6-}$ state to the   $CuPcTS^{5-}$ or $CuPcTS^{4-}$ state. In the presence of catalyst the reduction of the organohalides occurs at potentials lower than that of direct reduction.

Linear sweep voltammetric study indicate that p-chlorophenol is better reduced in isotropic water/acetonitrile media than in the DDAB microemulsion media by copper phthalocyanine mediated electrocatalytic dehalogenation.   A tentative reason is that in microemulsion reaction occurs via adsorbed film of the surfactant containing both the catalyst and the substrate. In acetonitrile/water media such an environment is not present.

A new approach to studies involving destruction of toxic recalcitrant organohalide pollutants has been suggested.   This involves a correlation between molecular mechanics and quantum mechanics calculated parameters with observed voltammetric half-wave potentials.   Such an approach has been applied for a few model organohalides.   A linear relationship has been obtained between voltammetric half-wave potentials and theoretically calculated parameters such as heats of formation and lowest unoccupied molecular orbitals (LUMOs).   A forward step suggested for the future involves understanding the lowering of the overpotential phenomena by mediators (catalysts) for reductive dehalogenation of organohalides.

UV/VIS spectroscopic studies for copper phthalocyanine tetrasulphonic acid, tetrasodium in both aqueous and microemulsion media reflected a high degree of

aggregation for this complex in water as compared to microemulsion media. This suggests possible compartmentalization of CuPcTS catalyst in microemulsion. A higher extent of aggregation was found for CuPcTS catalyst in aqueous media, in presence of added tetraethylammonium bromide salt.

In buffered aqueous media, voltammetric reduction of copper phthalocyanine tetrasulphonic acid tetrasodium was found to be pH dependent. A positive shift in reduction potentials was found with decrease in pH. Thus, control of pH could give another handle on  lowering of the overpotential phenomena for reduction of toxic orghanohalides by copper phthalocyanine tetrasulphonate mediator (catalyst).

# CHAPTER 1

## INTRODUCTION:

For several years now one of the most highly published class of environmental pollutants has been pesticides [1]. The use of chemicals to control pests dates to the ancient Greeks, who used sulphur against insects and salt (sodium chloride) against weeds [2]. The "first generation of pesticides" comprised naturally occurring organic compounds [2].

In 1939 a Swiss named Paul Mueller discovered that the compound dichlorodiphenyltrichloroethane (mercifully called DDT) killed insects. This caused a revolution in pest control. The use of synthetic (man made) chemical pesticides, many of which do not occur in nature have greatly increased. DDT was cheap, relatively nonpoisonous to mammals (according to knowledge at that time), and astonishingly more effective against almost all insects than any previously known control method. DDT had dramatic early success in word war II. It was used to kill mosquitoes, lice and fleas in tropical islands and consequently saved millions from death due to malaria and yellow fever. It forestalled a threatened typhus epidemic in the allied Army in Italy, and by increasing crop production, it eased the threat of starvation for many. During the war other synthetic pesticides were developed [2].

It is not surprising that few questioned the rapidly increasing use of pesticides in the 1940's and 1950's, the "Golden Age of Pesticides", even when their use was ineffective, as for example, when applied in a futile effort to control Dutch elm disease. But by the end of 1950's, troubles began to appear. Insect resistance was widespread, and it became evident that DDT and related chemicals, killed much more than insects. In 1962 biologist, Rachel Carson published a best-selling book, silent spring, which detailed the harmful aspects of the pesticides. Her book began a period of environmental concern, and it received both lavish praise and vicious criticism. Ten years later, the side effects of DDT

had caused enough harm and concern so that its use in the United States was banned beginning in 1973 [2].

Man-made pesticidal chemicals can be detected by chemical analysis in almost every part of the world [3]. While the domains of some pollutants tend to be restricted, pesticide contamination has found its way to every corner of our environment, soils where they are adsorbed on minerals and other substances; sediments where pesticides can be further concentrated by solvent extraction as a result of petrochemical pollution; water including drinking water, lakes, ponds, rivers, streams, and ground waters as well as the oceans [1].

The chlorinated hydrocarbons do not occur in nature and consequently are not integrated into the biogeochemical cycles [2]. These poisons are cumulative in the body and there is no "physiological equilibrium" that limits their levels in the body [1]. The carbon-chlorine bond is very strong and does not react with water or components of the soil. As a result this class of pesticides is very persistent, lifetimes of 20 years or more in the environment having been demonstrated in careful tests [2]. Chlorinated hydrocarbon insecticides act as central nerve toxins, inducing paralysis, convulsions, and ultimately death. They are nonselective broad-spectrum pesticides, capable of attacking any organism with a central nervous system [2].

Many of the paths that these dangerous chemicals follow in our environment lead back to us to our food and to our own bodies [1]. In as much as man is now top predator on this planet, any chemical that concentrates in a food chain represent a particular hazard to him [1].

Pesticides are not the only chlorinated hydrocarbons that are known causes of environmental disruption. Polychlorinated biphenyls (PCBs), a group of compounds in which chlorine replaces hydrogen in the biphenyl molecule, have become widely dispersed in the environment during the last 40 years [2]. As a class of compounds PCBs are very stable to heat, acids and bases. Their stability and insulating ability led to wide uses, and in fact, more than 90% of all power capacitors contains PCBs and approximately 5% of the

transformers are PCB filled [4]. Because of their chemical similarity to pesticides, PCBs are often created during the manufacture of pesticides and remains as accidental contaminants [2].

PCBs get into the environment through accidental leaks, waste disposal, and the weathering of materials containing them. In the eastern united states, PCBs are about ten times more prevalent than DDT in the atmosphere, in the water, and in the fatty tissues of organisms. Levels of 3 ppm are often found in sediments near cities, and mature trout in Cayuga lake, near Ithaca, New York, have over 20 ppm. Ospreys may be more contaminated than other wildlife; near long Island sound osprey eggs contains PCB levels up to 2000 ppm. Even polar bears contain measurable amount [2]. As much as 29 parts of PCB per billion have been found in tissues of the general population. The known toxic effects of PCBs in humans include acne-like skin eruption (Chloracne), pigmentation of the skin and nails, excessive eye discharge, swelling of eyelids and distinctive hair follicles, PCBs are known to cause cancer in test animals and suspected of being carcinogenic in humans [4].

Biological oxidations are electrophilic in nature, and substituent groups which lower the electron density at a reaction site will decrease the reaction rate. Enzyme catalysis is carried out by lowering the level of energy necessary in the substrate for the reaction. Electron manipulation is a requirement for a catalytic activity. The high-risk, persistent chlorinated hydrocarbons are non-polar compounds and these bind to surfactant aggregates, thus, they are excellent substrates for attempting rate enhancements [5].

Abatement of pollution, in fresh water and other aquatic environments, caused by pesticides and other recalcitrant organohalides, was tentatively the final goal of the present work. Electro-chemical catalytic methods were used to try and achieve this goal. A molecular and quantum mechanical approach to the problem was also attempted.

Electrochemical catalytic dehalogenation is an attractive alternative to widely used sodium naphthalide or borohydride assisted photolytic reductions [5]. Electrochemical catalysis in surfactant media does not require excess chemical reagents, is tolerant of water

and particles found with the pollutants, and can capitalize on modern advances in electrochemical engineering [5].

## 1.1 SPECIFIC AIMS:

Nature uses membrane-based microstructures which organize redox enzymes and reactants to provide living organisms with highly efficient redox processes. Micellar solutions and microemulsions contain surfactant aggregates which can be considered crude models for biological membranes [6]. Surfactant aggregates bind redox catalysts which are cycled at an electrode to their reactive forms. Taking reductions as an example, the electrochemically generated reduced form of an aggregate-bound catalyst can react with a nonpolar, organic substrate bound to hydrophobic regions of the same surfactant aggregate. Such organized systems are potential models for biological redox processes at membranes. Other advantages include providing non-toxic, aqueous media for organic redox reactions of nonpolar substrates, and enhancing rates of reactions due to compartmentalization of reactants in the aggregates [6].

Thermodynamically stable, optically clear mixtures of surfactant, water, and oil are called microemulsions [5]. Among the important properties of microemulsions is their ability to dissolve a variety of solutes of different polarities. Thus, a microemulsion can be used as a medium to bring together ionic and nonpolar reactants [7]. A case in point for electrochemistry is electrocatalysis, which can be used to amplify analytical sensitivity. In this technique, electrons are transferred between an electrode and a substrate whose electrode reaction is slow via a chemical mediator (catalyst) [7].

Rusling has given a detailed account on the use of surfactant microstructures in electrochemical catalysis [5]. Owlia, Wang and Rusling reported catalytic reduction of oil-soluble vicinal dihalides mediated by water-soluble vitamin $B_{12}$ in a w/o microemulsion [8]. Kamau, Hu and Rusling surveyed the reactivity of trans-1,2-dibromocyclohexane (t-DBC), 1,2-dibromobutane (DBB), and trichloroacetic acid (TCA) with copper and nickel phthalocyanine tetrasulphonate (MPcTS) mediators in bicontinuous microemulsions of

didodecyldimethylammonium bromide (DDAB) [9]. The metal phthalocyanines mediated these reductions similar to vitamin $B_{12}$, giving olefins from vicinal dihalides and acetic acid from haloacetic acids [10]. Both mediators were adsorbed onto glassy carbon electrodes from microemulsions and homogeneous water/acetonitrile [9]. Although these researchers were able to establish that addition of two electrons to M(II)PcTS was necessary, no mechanistic studies have so far been reported.

Thus, one of our main goal was to establish the mechanism of electrocatalytic reduction of organohalides in surfactant media. In our work, the mechanism for electrocatalytic reduction of 1,2-dibromobutane mediated by copper phthalocyanine tetrasulphonate (CuPcTS) in bicontinuous microemulsions of DDAB has been studied. Other important work involved a comparison of CuPcTS mediated electrochemical reduction of p-chlorophenol in bicontinuous microemulsions of DDAB and isotropic acetonitrile/water media. P-chlorophenol was studied as a model for electrocatalytic reduction of toxic pesticide intermediates. Standard procedures [5] were followed in this investigation. For both media, linear sweep voltammograms for the mediator, CuPcTS, were recorded in absence and in presence of added p-chlorophenol substrate. Better rate enhancements for the electrocatalytic reduction of p-chlorophenol were found for the homogeneous solution compared to the microemulsion media.

We began a new approach on studies involving reduction of toxic recalcitrant substances. This included a comparison of electrochemical reduction of these substrate (halogenated compounds) and their molecular and quantum mechanically calculated parameters. A challenge for the future will be to compare these parameters with those obtained for mediators such as CuPcTS. Such a comparison would throw more light into the mechanism of electron transfer between mediators and substrates as well as lowering of over potential phenomenon by the appropriate catalysts.

Thus the overall objectives of the current work are itemized below:

## 1.2 OBJECTIVES:

(i) Study new electrocatalytic procedures for an effective destruction of halogenated organic pollutants.

(ii)Optimize experimental design factor in order to attain significant faster rates of dehalogenation.

(iii)     Establish the mechanism for electrocatalytic reduction  of vicinal dihalides in surfactant microstructures mediated by copper phthalocyanine tetrasulphonate (CuPcTS).

(iv)     Use UV/VIS to study the behavior of catalyst in water and microemulsion.

(v)Compare electrocatalytic reduction of  p-chlorophenol in homogeneous solution and microemulsion.

(vi)     Compare the reduction potential of the substrate in the presence and absence of catalyst.

(vii)     Use microemulsion media to mimic biological reactions, which also provide synthetic route for organic compounds, generally needed by industries.

(viii)     Correlate electrochemical reducibility of organohalides to quantum and molecular mechanically calculated parameters.

(ix)     Use UV/VIS spectroscopic technique to monitor the mechanisms of electrocatalytic dehalogenation in microemulsion.

(x)Attempt to synthesize the phthalocyanine catalyst in the laboratory.


## 1.3   JUSTIFICATION AND NOVELTY OF WORK

Global environmental contamination with polychlorinated biphenyls (PCBs), polybrominated biphenyls (PBBs), and other halogenated organic compounds is a serious health problem [11].   Heavy industrial use of PCBs in electrical, heat-transfer, and hydraulic device, since the 1930's has resulted in widespread pollution with these compounds.   Extreme stability makes them resistant to environmental biodegradation.

PCBs are fat soluble, and therefore become more concentrated as they move up the food chain.

PCBs have been proven to be extremely toxic to humans; their effects include: reproductive malfunctions, chloracne, involution of lymphoid glands, edema, liver lesions, and death. More than 200 million kg of PCBs exist in working transformers and capacitors and an estimated 10 million kg are in storage [11].

Thus, there is an urgent need for biological and environmental interaction data, as well as the development of safe, economical and fast methods for their degradation. Currently, the two most widely used techniques for PCB decomposition are: (1) incineration and (2) reductive dechlorination with sodium naphthalide [11]. Incineration of PCBs requires the use of very high temperatures and combustion efficiencies greater than 99.9%. Such incinerators are expensive to build and to maintain, and can release acid and highly toxic dibenzo-p-dioxin onto the atmosphere. The sodium naphthalide process is not catalytic, and requires at least two naphthalide ions for each chloride removed, as well as the use of toxic and expensive organic solvents.

The use of surfactants in the form of micelles, microemulsions, bicontinuous microemulsions, and suspensions make electrocatalytic dehalogenation reactions possible in aqueous media. This entirely new approach will lead to less expensive, faster, and safer ways to decompose toxic pollutants. It is important that practical methods work in the presence of water, since most halogenated organics are found with water in the environment. Electrocatalytic dehalogenation requires only small amounts of catalyst, which is automatically recycled at the electrode. The ultimate product of the reaction is biphenyl, which can be reused by the chemical industry, or completely incinerated to carbon dioxide and water. Moreover, catalytic dehalogenation of vicinal dihalides leads to not only removal of toxicity but also recycle the olefin, which is required by industries.

## 1.4   DYNAMICS OF MEDIATED ELECTROCHEMICAL REACTIONS IN SURFACTANT MICROSTRUCTURES.

Surfactants are amphiphilic ions or molecules with charged or polar head groups and long hydrocarbon tails [5]. Two of their properties are useful in electrochemistry: adsorption at interfaces and aggregation into suppramolecular structures. Micelles are examples of surfactant aggregates. They are formed from soluble surfactants above a critical micelle concentration (CMC). Solutes can bind at the micelle-water interface (stern layer) and in hydrophobic region just below this interface [5].

Micellar catalysis has attracted increasing attention in recent years. This trend is based on the realization that many biochemical processes proceed in a microheterogeneous system which contains the organic and aqueous phases [12]. Although the general analogy between micellar and enzymatic catalysis has been repeatedly mentioned for some time, notable progress in micellar catalysis in relation to enzyme action has been made only in the past few years. The active part of enzymes is mostly located in a hydrophobic region [12]. Thus the attachment of enzyme-related functional groups to the hydrophobic core of micelles provides interesting enzyme-model systems. In fact, a variety of catalytic groups such as imidazole and thiol can be enormously activated in a hydrophobic microenvironment. A similar situation exists for coenzyme catalysis [12].

Micelles and other association colloids act as "microreactors" compartmentalizing and concentrating or separating and diluting reactants thereby altering, sometimes dramatically, apparent rate and equilibrium constants of chemical reactions [13]. For several decades, many researchers have explored the varied and often pronounced effects of micelles, synthetic and natural vesicles, monolayers, microemulsions, and polyelectrolytes on a wide variety of ground and excited state reactions and equilibria [13]. Rates of mediated electrochemical synthesis can be enhanced and controlled by surfactants adsorbed on electrodes.

Microemulsions are clear, microheterogeneous, stable fluids made from oil, water and surfactant. They contain microdroplets or intertwined networks, of oil and water [10]. Among the important properties of microemulsions is their ability to dissolve significant amount of solutes of different types [7,10], low toxicity and low cost [7]. Thus, a microemulsion can be used as a medium to bring together ionic and nonpolar reactants. Control of the structural aspects of microemulsions offers the possibility of selecting reactant micro-environments to control chemical kinetics and reactivity for specific applications [7]. A case in point for electrochemistry is electrocatalysis, which can be used to amplify analytical signals. In this technique, electrons are transferred between an electrode and substrate whose electrode reaction is slow via a chemical mediator (catalyst) [7].

In contrast to w/o (water/oil) and o/w (oil/water) microemulsions, bicontinuous microemulsions conduct electricity [7]. In principle, they should be usable in electrochemical studies with electrodes of any size. Bicontinuous microemulsions offers unique properties for electrochemical studies, including the chance to study reductions and oxidations of nonpolar compounds in a continuous oil phase of nearly pure hydrocarbon with conventional sized electrodes [7].

Rusling and coworkers have recently showed that rates of mediated electrolytic dechlorination are greatly enhanced when they occur in a film of cationic surfactant adsorbed on an electrode [10]. In the reduction of 4-bromobiphenyl with 9-phenylanthracene as mediator, the apparent bimolecular rate was > 1000-fold larger in cationic surfactants adsorbed on Hg than in isotropic organic solvent [10]. Thus, rate enhancement and control of electrosynthesis by surfactant is well established.

Microemulsions have attracted wide interest as a possible low cost media for tertiary oil recovery, formation of very small semiconductor and polymer particles, production of ceramics, purification of biomacromolecules, drug delivery, and for enhancing rates of decomposition of toxic organic chemicals [10]. Applications derive from the microstructure and dynamics of these fluids. Properties can be tuned for specific

applications [10]. Substitution of a microemulsion for an organic solvent in mediated electrosynthesis has the following advantages:

(1)     high dissolving power for reactants of unlike polarities;

(2)     low toxicity;

(3)     low cost

(4)     surfactant films on electrodes to enhance rates of reaction;

(5)     recycling of components.

Electrolysis mediated by metal macrocycles have been used to make lactones, insect pheromones, prostoglandins, C-glycosides, optically active olefins and alcohols, bi-and tricyclic hydrocarbons and to remove protecting groups [10]. Mediated reactions are attractive for constant current industrial electrosynthesis because potential is controlled close to the mediators formal potential minimizing competing reactions such as reduction of $H^+$ or solvent.

## 1.5    CONTROL OF ELECTROCHEMICAL REACTIONS IN MICELLES.

In the early part of this century, adsorption of surface-active compounds on Hg electrodes was found to suppress unwanted convection such as polarographic maxima [5]. Research on the kinetics of electron transfer reactions at electrodes has been going on for the last century [14]. In 1952, Proske was the first to use micelles to solubilize nonpolar organic compounds in water for electrochemical measurements [15].

The past 10-15 years saw many new applications of surfactants in electrochemistry. For example, ion radicals produced at electrodes were stabilized by coulombic and hydrophobic interactions with micelles [15]. Reducible and oxidizable probes began to be used to measure diffusion in surfactant media [16]. Microstructure of amphiphiles adsorbed on electrodes were investigated [5,17]. Coatings of functional amphiphiles were prepared on electrodes by Langmuir-Blodget (LB) methods [18].

Over the same period, surfactant aggregates were used to separate charged products and retard back reactions in sensitized photolytic generation of hydrogen from water [5].

There are many examples of bimolecular thermal and photochemical reactions with enhanced rates in surfactant media [10]. In micellar solutions, the rate ($R_{obs}$) of a chemical reaction is taken as the sum of rates in the continuous aqueous phase ($R_w$) and the micellar "pseudophase" ($R_m$);

$$R_{obs} = R_w + R_m \quad \text{......... (1)}$$

For a bimolecular reaction between A and B, the simplest case is where both reactants exist entirely in micelles. The rate of reaction in the water phase is negligible and

$$R_{obs} = K_{obs} [A] [B] = K_m [A]_m [B]_m \text{......(2)}$$

Where rate constant $K_{obs}$ is computed on the basis of moles of A and B in the total volume of the system, $V_t$. Actual concentrations of reactants in the micelles are approximately $[A]/f_m = [A]_m$ and $[B]_m = [B]/f_m$,

Where $f_m$ is the volume fraction of micelles. Substitution of these concentration terms into eq.2 gives

$$K_{obs} = K_m[A][B]/f_m^2 \quad \text{.............. (3)}$$

Eq.3 reflects the fact that the observed rate is enhanced by inclusion of reactants into reaction volume $V_t f_m$. Rate enhancements is mainly a consequence of high reactant concentrations in the volume defined by surfactant aggregates [10].

Although more sophisticated treatments of kinetics in micelles are available, the simple concepts above are useful for a qualitative understanding of mediated electrochemical catalysis in surfactant media. Rate determining step (rds) in mediated electrolyses are nearly always bimolecular. The most effective enhancement mode is when the reaction occurs in a surfactant film on the electrode. In this, case, reactant preconcentration occurs in the film volume [10].

## 1.6 CONTROL OF ELECTROCHEMICAL REACTIONS IN MICROEMULSIONS.

In oil-in-water (o/w) microemulsions, the continuous liquid "phase" in the system is water, with surfactant-coated oil droplets. Water-in-oil (w/o) microemulsions, have continuous oil phases and surfactant-coated water droplets. In bicontinuous microemulsions, both oil and water are continuous in an intertwining network with surfactant at oil-water interfaces. Salts and cosurfactants such as alcohols are sometimes added [10]. High conductivities of bicontinuous and o/w microemulsions make them directly applicable to electrosynthesis [10].

Owlia et al. were the first to study the kinetics of an electrochemical catalytic reduction in w/o microemulsions [8]. They investigated reductions of several alkyl vicinal dibromides catalyzed by vitamin $B_{12}$. The rate-determining step (rds) in this reaction (Scheme I) is an inner sphere electron transfer between $B_{12}$ Co (I) and the alkyl dibromide (eq.5). This can occur by a radical mechanism (scheme I) or by a concerted E2 elimination.

SCHEME I

$$Co(II) + e \rightleftharpoons Co(I) \text{ at electrode} \quad (_4)$$

$$Co(I) + RX \xrightarrow{k_2} Co(II) + RX^{\bullet} + X^{-} \quad (rds) (_5)$$

$$RX^{\bullet} + Co(I) \rightarrow Co(II) + alkene + X^{-} \quad (6)$$
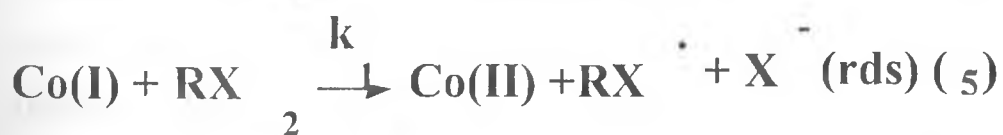
These two pathways are kinetically indistinguishable. Both give an alkene as the product [14].

In w/o microemulsion of Aerosol OT (AOT)/water/isoctane, the highly water soluble vitamin $B_{12a}$ resides entirely in water pools. Substrates ethylene dibromide (EDB), 1, 2-dibromobutane (DBB), and trans-1,2-dibromocyclohexane (t-DBCH) are present mainly in

the continuous isoctane phase. Thus, catalyst and substrate are partially separated in the two phases of the microemulsion [8, 14].

Iwunze et al. showed that quasireversible electrode reactions of several oil and water soluble redox couples in bicontinuous microemulsions of DDAB, oil, and water could be described by voltammetric theory developed for homogeneous solutions [7]. Cyclic voltammetry was used to study the electrochemistry of water soluble ferrocene and polycyclic aromatic hydrocarbons (PAHs) in microemulsions of DDAB/dedecane/water. Results were in good agreement with simulated voltammograms assuming that the bicontinuous medium was homogeneous [7]. This is because both water and oil are continuous [7, 14]. Each microemulsion phase behaves as a homogeneous medium. This is in sharp contrast to micelles, w/o, and o/w microemulsions, for which coupled diffusion and dynamic binding equilibria of reactants with surfactant aggregates must be considered for a full interpretation of voltammetric results [14].

Standard heterogenous rate constants ($K_o$) for the above species in DDAB microemulsions were similar to those found in isotropic solutions [7, 14]. Diffusion of solutes did not reflect the high bulk viscosities (19-38 CP) of the DDAB microemulsions. Hydrophilic ions diffused with rates characteristics of the water phase, nonpolar molecules diffused at rates similar to the self-diffusion of oil in the oil phase [14].

Preliminary work by Kamau and coworkers explored catalytic dehalogenation of trichloroacetic acid and alkyl vicinal dibromides in bicontinuous microemulsions of DDAB/dodecane/water [9]. Mediators used as catalysts were nickel (II) phthalocyaninetetrasulfonate ($Ni(II)PcTS^{4-}$) and copper (II) phthalocyaninetetrasulfonate ($Cu(II)PcTS^{4-}$). These catalysts are water soluble as is trichloroacetic acid (TCA), but the alkyl vicinal dihalides, 1,2-dibromobutane (DBB) and trans-1,2-dibromocyclohexane (t-DBCH) are expected to reside predominantly in the oil phase. The reactions are similar to that in scheme I, giving acetic acid from TCA and alkenes from the vicinal dibromides. Cyclic voltammetry (CV) and square wave voltammetry (SWV) showed much larger catalytic efficiencies at glassy carbon electrodes for DBB and t-DBCH in the

microemulsions than in homogeneous acetonitrile/water [9]. However, catalytic efficiency for TCA was larger in the homogeneous solution than in the microemulsion [9]. A tentative explanation of these data given involved rate enhancement in the microemulsion by coadsorption of catalysts, DDAB, and the nonpolar substrates, DBB and t-DBCH at the electrode, as found previously for a number of the bimolecular reactions in micellar solutions [14].

## 1.7 DDAB MICROEMULSIONS.

The double-chain surfactant, didodecyldimethylammonium bromide (DDAB), is only sparingly soluble in water and oil and therefore the oil-water interfacial area is directly related to the surfactant concentration [19]. The system being three-component, is not subject to the usual dilution and partitioning problems which beset multicomponent systems [20]. The DDAB microemulsions hold promise for electrocatalytic reduction of nonpolar substrates [21].

A fascinating series of microemulsions made from DDAB, oil, and water are bicontinous and conductive over significant regions of their phase diagram [7]. Cyclic voltammograms for ions in the water phase and nonpolar molecules in the oil phase of bicontinuous microemulsions of dodecane/water/DDAB have been found to be in good agreement with theory for electrochemistry in homogeneous media [7]. This is because both water and oil are continuous.

## 1.8 ELECTROCHEMICALLY CATALYSED REDUCTION OF ORGANOHALIDES.

In electrochemical catalysis, mediators shuttle electrons between electrodes and substrate molecules. In this way, the potential required to reduce or oxidize recalcitrant substrates is significantly lowered. When applied potential is controlled, current for

electrocatalysis of the mediator (catalyst) is amplified in the presence of substrate. In catalytic reduction, for example, the mediator is reduced at the electrode and transfers electrons to the substrate. This regenerates the oxidized form of the mediator, which is reduced again at the electrode. It is this cycling of mediator between oxidized and reduced form at potentials near its $E_O'$ that amplifies the cathodic current. Electrochemical catalysis has been used frequently as the basis for sensitive electroanalytical methods. The amount of current amplification, and the sensitivity of the method, depend on the rate of reaction between reduced mediator and substrate [23].

The application of homogeneous redox catalysis for the determination of electron-transfer rate constants has been developed by saveant and coworkers [23]. In case of a bromide (X = H), the mechanism for the catalytic reduction is given by eqs 7,8, and 9a while that for the vicinal dibromide (X = Br) is given by eqs 7,8,9b, and 10 [24]. In both cases a total of two electrons are transferred with both homogeneous electron-transfer reactions (eqs 8, and 9a or 10) resulting in the regeneration of the oxidized form of the catalyst near the electrode surface that is responsible for the observed catalytic current (Scheme II)

## Scheme II

$$A \rightleftharpoons A^{\cdot-} \quad (7)$$

$$A^{\cdot-} + RCHBrCH_2 \xrightarrow{k_2} A + RC^{\cdot}HCH_2X + Br^- \quad (8)$$

$$A^{\cdot-} + RC^{\cdot}HCH_2X \rightarrow A + RC^{-}HCH_2X \quad (9a)$$

$$RC^{\cdot}HCH_2X \rightarrow RCH=CH_2 + X^{\cdot} \quad (9b)$$

$$A^{\cdot-} + Br^{\cdot} \rightarrow A + Br^- \quad (10)$$
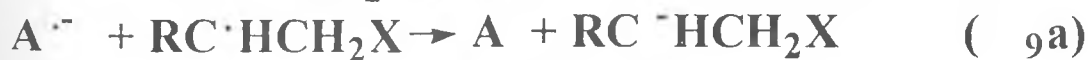
The pathway for electrochemically catalyzed reduction of aryl halides (Arx) has been studied in surfactant media [5, 14]. This is illustrated in scheme III below.

## SCHEME III

$$P + e \;\rightleftharpoons\; Q \qquad E^0 \;\; \textit{(at the electrode)} \;........(11)$$

$$ArX + Q \;\underset{k_2}{\overset{k_1}{\rightleftharpoons}}\; ArX^{\cdot -} + P ...............(12)$$

$$ArX^{\cdot -} \;\xrightarrow{k}\; Ar^{\cdot} + X^- \;.....................(13)$$

$$Ar^{\cdot} + Q \;\longrightarrow\; P + Ar^{\cdot -} \;\textit{(fast)} \;.............(14)$$

$$Ar^{\cdot -} + (H^+) \;\longrightarrow\; ArH \;\textit{(fast)} \;...................(15)$$
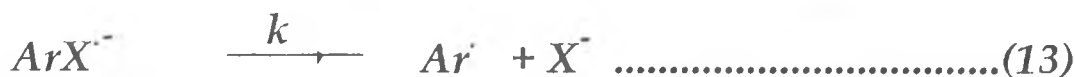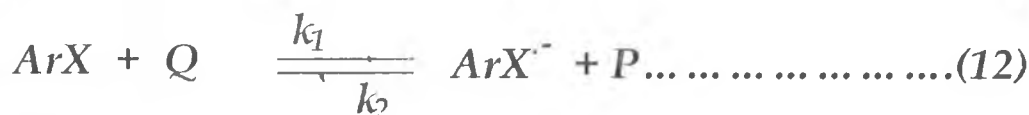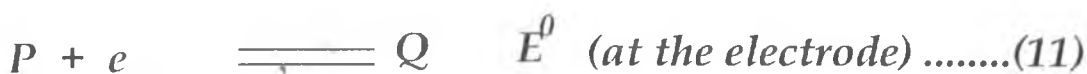
Mediator (catalyst) P is added to solution or immobilized on the electrode (eq.11) [5]. At potentials near $E^O$ P is reduced to its active form Q by accepting an electron from the electrode (eq.11) [14]. Q transfers an electron to acceptor ArX (eq.12) [5,14]. Equation 12 is the rate determining step (rds) in many aryl halide reductions, but cleavage of $ArX^{\cdot -}$ in eq. 13 is also important [5]. For alkyl halides, processes in eq. 12 and 13 usually occur as a single concerted step. A second electron transfer (ET) and protonation (eqs 14 and 15) yield RH [5, 14]

The resulting advantage is that ArX is reduced to ArH at the lower standard potential $E^O$ of the catalyst, rather than the more negative potential for direct, irreversible reduction of ArX at the electrode [5, 14]. Catalyst P is regenerated in the catalytic cycle (eqs 12 and 14), and gets reduced again at the electrode. As a result, the electrochemically measured peak current for reduction of P (eq. 11) is larger when RX is present [5, 14].

In summary, a major advantage of homogeneous redox catalysis lies in the possibility of performing electrolyses at a potential less negative than that of the direct electrochemical reduction. This amounts to decreasing the overpotential featuring the direct

electrochemical reaction. The existence of such redox catalytic processes has long been recognized for inorganic systems and more recently for organic systems [21].

Surfactant aggregates can be used to bind redox catalysts which are cycled at an electrode to their reactive forms. Taking reductions as an example, the electrochemically generated reduced form of an aggregate - bound catalyst can react with a nonpolar organic substrate bound to hydrophobic regions of the same surfactant aggregate. Such organized systems are potential models for dark biological redox processes at membranes. Other advantages include providing non-toxic, aqueous media for organic redox reactions of nonpolar substrates, and enhancing rates of reactions due to compartmentalization of reactants in the aggregates [6].

## 1.9 PHTHALOCYANINES IN ELECTROCHEMISTRY.

The first phthalocyanine was discovered by chance in 1928 during the course of the industrial production of phthalimide in the grangemouth works of Messrs. Scottish Dyes, Ltd., [25]. The process consists of passing ammonia into molten phthalic anhydride in iron vessels and it was found that during certain preparations traces of a dark blue substance were formed in the molten imide. This material was stable, crystalline, and contained iron which was not eliminated by treatment with concentrated sulphuric acid. As it appeared that the substance might prove of academic interest, its study was taken up in 1929 through the kindness of Professor J.F. Thorpe, F.R.S., and the research committee of the Dyestaffs Group of Imperial chemical Industries, Ltd. [25].

Robertson and coworkers have carried out complete X-ray structure determinations on some metal phthalocyanines [26]. The large organic molecule is tetradentate, with the four coordinating nitrogen atoms at the corners of a square. The planar structure does not vary greatly in dimension from metal to metal and is the same for all of the metallic ions, irrespective of whether they ordinarily form planar coordination compounds or tetrahedral ones. The stereochemistry of these compounds is determined by the ligand molecule [26]. The phthalocyanines have a coplanar structure and are capable of occupying four

coordination positions and neutralizing two charges of a metal ion. The stability of complexes of the chromophore has been demonstrated by preparing derivatives of more than twenty elements [26]. These include representatives of each group of the periodic table. Divalent metals displace hydrogen atoms to form a nonionic complex. Trivalent ions form compounds of the type (phthalocyanineMX) while tetravalent ions give (phthalocyanineMX$_2$) compounds.

Although many phthalocyanines have been synthesized, the copper derivative is the most important and sold commercially in the monastral Fast Blue, Heliogen Blue, and Vulcan Blue series. Copper phthalocyanine is more stable than the other compounds of this series and in this respect is classed among the most remarkable of organic compounds [27]. It resists the action of molten potash and of boiling hydrochloric acid. It dissolves in concentrated sulphuric acid and is precipitated unchanged and in almost quantitative amount by dilution with water. It is exceptionally resistant to heat and at about 580$^o$c it may be sublimed at low pressure in an atmosphere of nitrogen or carbon dioxide. The sublimate is beautifully crystalline and analytically pure. The substance also sublimes with some decomposition in air at atmospheric pressure [27]. As with the other members of metallophthalocyanine class, copper phthalocyanine is decomposed by nitric acid to give phthalimide in good yield, together with copper and ammonium nitrates. It also undergoes a similar decomposition when treated with dilute acid permanganate [27].

The electrochemistry of phthalocyanines has been systematically studied by Lever et al [28]. The redox centre is either the metal or the macrocyclic P system, and usually two successive oxidations and four reductions are observed for the latter. The ring reduction sequence is generally reversible, but the oxidation steps are often irreversible [28].

For main group metallophthalocyanines, the ring centred redox is the only process to occur. The separation between the first oxidation and reduction potentials corresponds to the energy difference of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital hence to the Q(0/0) absorption band at 670 nm and is about 1.56V [28]. Deviation from the mean value becomes large when the size of the metal

significantly exceeds the cavity of the phthalocyanine (PC) ring. The first reduction and oxidation potentials ($E^O$ vs. NHE) depend on the polarizing power of the metal ion (Ze/g) and are approximated by equation (16) and (17) [28].

first oxidation: $(Ze/g)(E^O - 1.410) = -0.012$ .....(16)

first reduction: $(Ze/g)(E^O + 0.145) = -0.012$ .......(17)

The second reduction occurs at a potential some 0.42V more negative but more scattered than the first. The third and fourth reduction waves appear around 1.7V and 2.0V respectively [28].

The metal redox intervenes the ring processes in some transition metal phthalocyanines. Fe and Co change their oxidation state from $M^{III}$ to $M^I$, and Mn and Cr change from $M^{III}$ to $M^{II}$ between the first ring redox steps, while $Ni^{II}$, $Cu^{II}$ and $Zn^{II}$ are unaffected [28].

The ring redox potentials for transition metal complexes are similar to those of the main group with the metal atom at the same oxidation state and of analogous size. The effect of PC peripheral substitution is small and usually less than 0.1V unless the substituent is charged [28].

Electrogenerated metallophthalocyanine intermediates can be used to catalyze the transformation of inert molecules, modifying the properties of an electrode surface by adsorbing or otherwise binding a coordination compound to it [29]. Many researchers have carried out studies on electrocatalyzed reactions with catalysts of various types [8,14,21,22,24]. Current studies have focused on the use of metallophthalocyanines and especially their sulphonated derivatives as mediators in electrochemical dehalogenation of toxic organohalides in surfactant media. Up-to-date, no comprehensive study on any one of the mediators has been carried out.

We felt that such an approach was necessary if any of these mediators was going to be of potential use as a catalyst for bulk dehalogenation of organohalide pollutants present in every corner of our globe. To our group, copper phthalocyanine was the mediator of choice due to its attractive properties of stability and resistance to extreme conditions and

as such is of potential use in almost any environment without deterioration in its performance. Another important point to note is that this compound can be decomposed completely at will by use of concentrated nitric acid.

We began by carrying out UV/VIS spectroscopic analysis of copper phthalocyanine tetrasulphonic acid tetrasodium salt CuPcTS in aqueous media. Copper phthalocyanine itself is insoluble in this media but the sulphonated derivative is highly soluble to give a blue solution. This was followed by extensive study on electrochemical behavior of this catalyst in aqueous media, isotropic acetonitrile/water media, and finally in bicontinuous DDAB microemulsion. In aqueous media, the voltammetric behavior of CuPcTS with change in pH was monitored. CuPcTS catalyzed reduction of p-chlorophenol in isotropic media and DDAB microemulsion was attempted. Later work involved bulk dehalogenation of 1,2-dibromobutane (DBB) in DDAB microemulsion. The reaction was monitored by means of UV/VIS spectroscopic method.

Due to unavailability of copper phthalocyanine in our local market, a preliminarily study was performed on possible synthetic methods in our laboratory. Some voltammetric study on the synthesized compound in DDAB microemulsion is reported.

Finally, we began studies on the possible correlation of voltammetric half-wave potentials to molecular and quantum mechanically calculated parameters in case of organohalide molecules. If the theoretical correlation prove to be effective, it would in future be easy to predict the best conditions for decomposition of a given organohalide pollutant.

## 1.10 SYNTHESIS OF COPPER PHTHALOCYANINE.

Literature on phthalocyanine synthesis is readily available [25, 27]. Phthalonitrile combines readily at high temperatures with metallic copper and many of its compounds to yield phthalocyanines [27]. The reaction with the metal begins at 190 $^O$C, and proceeds vigorously at 210 $^O$C with evolution of heat to give copper phthalocyanine in excellent yield as a bright blue compound with a purple lustre. The reagents are used up in the ratio

of 1 atom of metal to 4 molecules of phthalonitrile, in agreement with which the product gives analyses corresponding to $(C_8H_4N_2)_4Cu$. The tendency to form this compound is great and the readiness with which the various compounds of copper react appears to be determined by the ease with which they can supply the metal. Experiments [27] have shown that with the two

chlorides of copper:

(a) $4C_8H_4N_2 + Cu_2Cl_2$ ------------> $(C_8H_4N_2)_4Cu + CuCl_2$      (18)

(b) $4C_8H_4N_2 + CuCl_2$ --------> $(C_8H_4N_2)_3 Cu(C_8H_3N_2Cl) + HCl$   (19)

Reaction 18 occurs between 150-200 $^oC$, whereas reaction 19 occur above 200 $^oc$.

Phthalocyanine can also be formed using phthalic anhydride as the starting material other than phthalonitrile. In this case, urea is used as the nitrogen source [30]. In general, a phthalocyanine (PC) nucleus-forming organic compound, metal or metal compound forming centre atom in PC nucleus and optionally N source compound for PC with or without organic solvent are all that is required for metal phthalocyanine formation [31].

## 1.11 STATIONARY ELECTRODE VOLTAMMETRY AS AN ELECTRO-ANALYTICAL TECHNIQUE.

Stationary Electrode Voltammetry was adopted as an electroanalytical technique much later than polarography. The first theoretical considerations of the reversible process were published by Randles and Servcik in 1948 [32]. No significant use was made of this method until several years later when hanging mercury electrodes were applied to electroanalysis [32-35].

In stationary electrode voltammetry, as in polarography, the variation of current with the potential applied to the indicator (working) electrode is recorded but, contrary to polarography in which a step-shaped wave is obtained, the relationship gives a graph in the form of peaks [32]. During measurements the electrolytic cell should be protected from external shock, so that movement of the substances to the electrode surface and away from it occurs only as a result of diffusion forces [32]. The migration of ions to the

electrodes is practically eliminated as a result of introduction of a strong electrolyte into the sample solution at concentrations usually exceeding the concentration of the reacting substance by several orders of magnitude. If the substance present in the solution is reducible at the indicator electrode, then at a characteristic potential difference, reduction takes place and current flows in the circuit. At the same time, the equivalent amount of another substance is oxidized at the reference electrode material, itself, e.g. mercury in the case of a calomel electrode. Since the surface area of the indicator electrode is usually small, and that of the reference electrode is large, the current intensity in these conditions depends on the former. This small current has only a slight effect on the distribution of concentration of substances constituting the reference electrode. This is one of the major reasons why the potential of this electrode is constant during voltammetric measurements.

The substance formed at the electrode surface in the reduction process can be reoxidized when the direction of polarization is reversed. If the reaction is fast enough, the oxidation is observed at the same potential region as that of the formation of the reduction peak.

The initial potential is so chosen that the rate of the electrode process is negligibly small. In the cathodic part the reduction process starts at a potential close to the standard potential of the reducible substance present in the solution (provided that the electrode process is fast). A current peak is formed on the stationary electrode voltammetric curve at a potential less than that at which the plateau of the polarographic wave is reached. At this moment the concentration of the depolarizer at the electrode surface is not yet at zero level. Further negative polarization of the electrode results in a decrease of the current, due to the decrease in depolarizer concentration in the region of the electrode. In cases where the reduction takes place at moderately negative potentials, and where more negative potentials are necessary to decompose the supporting electrolyte, the decrease of current becomes appreciable, after passing the peak. Frequently the solution contains another species which is reduced at a more negative potential than the first species; moreover, the difference between the reduction potential of the second depolarizer and the

decomposition potential of the supporting electrolyte may not be very great. Only a moderate decrease in current is observed after the peak current in such cases.

The peak current, $i_p$ ($\mu A$), of fast electrode processes is described by the Randles - Servcik equation [32];

$$i_p = 2.72 \times 10^5 \, n^{3/2} \, D^{1/2} \, An^{1/2}C_O \text{ ------(20)}$$

It follows from equation (20) that the peak current depends on the following factors: concentration of the depolarizer in the bulk of the solution ($C_O$, moles/cm$^3$), diffusion coefficient of the substance being reduced or oxidized (D, cm$^2$/s), the area of the electrode surface (A, cm$^2$) and the number of electrons taking part in the elementary electrode process (n). Furthermore, the current increases with increasing polarization rate (n). This is understandable since the thickness of the diffusion layer decreases and the concentration gradients increases with increasing polarization rate. In polarography the limiting current is proportional to the concentration of the depolarizer in the bulk of the solution, but in case of stationary electrode voltammetry it is the peak current which is proportional to concentration. The linear dependence of the peak current on the concentration of the reacting substance makes this method useful in quantitative analysis.

The potential applied to the electrodes, which changes linearly with time, is often obtained by means, of a polarograph. The sweep rate is usually 0.1-0.8V/min. Most polarography experiments are designed for a potential sweep of 0.05V/min. This is the minimum rate that should be used in stationary electrode voltammetry [32]. Lower rates result in erroneous results, due to a considerable convection effect.

Although the lower limit of useful potential sweep can be obtained by use of a polarograph, special voltage generating devices are necessary for obtaining the upper limit. With such generators the potential sweep rate can be changed by hundreds of volts per second, and the voltage amplitude can be controlled at will, although in practice, it seldom exceeds 2V. Furthermore cyclic polarization of the indicator electrode is possible.

The stationary electrode voltammetric technique has been employed in studies of mechanisms of electrode processes. It is particularly useful in investigations of

mechanisms of oxidation and reduction of a number of organic substances. In this case, in contrast to polarography, the substance produced during cathodic reduction remains in the neighbourhood of the electrode surface and can be reoxidized when the direction of polarization is reversed. From the intensity of the recorded current and from the potentials at which the current are observed, information on reversibility or irreversibility of the system and on chemical reactions accompanying electrode processes can be obtained.

A factor limiting the application of this technique is the appreciable capacity current observed at high polarization rates. In cases when the high capacity current exists, however, stationary electrode voltammetry can be used in investigation of the structure of the double layer [35].

## 1.13 CYCLIC OR FAST LINEAR SWEEP VOLTAMMETRY.

Cyclic voltammetry involves the measurement of current -voltage curves under diffusion controlled mass transfer conditions at a stationary electrode, utilizing symmetrical triangular scan rates ranging from a few millivolts per second to hundreds of volts per second. The triangle returns at the same speed and permits the display of a complete polarogram with cathodic (reduction) and anodic (oxidation) wave forms one above the other. This technique yields information about reaction reversibility and also offers a very rapid means of analysis for suitable systems. The method is particularly valuable for the investigation of stepwise reactions, and in many cases direct investigation of reactive intermediates is possible. By varying the scan rate, systems exhibiting a wide range of rate constants can be studied, and transient species with half-lives of the order of milliseconds are readily detected. The method can be applied to stationary electrodes as well as to a single mercury drop, and to reactions for which stripping analysis is inapplicable due to highly irreversible electrode processes or the formation of solution soluble reaction products.

For a reduction reaction [36],

$$E_{peak} = E_{1/2} - 0.0285 \qquad \text{---------------------------(21)}$$

For an oxidation reaction the sign of the numerical term is reversed. On the reverse scan, the position of the peak depends on the switching potential. As this potential moves more negative, the position of the anodic peak becomes constant at 29.5/n mV anodic of the half-wave potential. With the switching potential more than 100/n mV cathodic of the reduction peak, the separation of the two peaks will be 59/n mV and independent of the rate of potential scan. This is a commonly used criterion of reversibility. Reversibility can also be ascertained by plotting ($E_{cath}$ - $E_{anod}$) as a function of the square root of scan rate, which should be a straight line if reversible [36].

To do qualitative analysis with cyclic voltammetry, one observes four characteristics of an electroactive substance: peak potential, wave slope, reversibility, and the effect of changing the supporting electrolyte. Another method used to determine whether an electrode reaction is reversible consists of preparing a plot of E versus log (($i_p$-i)/i). For a reversible electrode reaction, a straight line should result whose slope is 0.0592/n. Furthermore, $E_{1/2}$ for the cathodic reduction should coincide with $E_{1/2}$ in the anodic oxidation, after a correction is made for the iR drop across the electron solution interface. When the electrode reaction is irreversible, a straight line may still result but the slope of the log plot will differ from the theoretical line [36].

# 1.14 THEORETICAL CALCULATIONS;
# A: MOLECULAR MECHANICS.

Molecular mechanics calculations also known as force field calculations, are now of considerable importance in organic chemistry. These calculations have been used to investigate molecular conformations, thermodynamic properties, and vibrational spectra.

The method treats a molecule as a collection of particles held together by simple harmonic forces. These forces can be described by potential energy functions of structural features like bond lengths, bond angles and nonbonded interactions. The contribution of these potential energy functions is the force field. The energy, E, of the molecule in the force field arises from deviations from "ideal" structural features, and can be approximated by a sum of energy contributions.

$$E = E_{st} + E_b + E_w + E_{nb} + \ldots \qquad \text{-------------------------(22)}$$

E is sometimes called the "steric" energy. It is the difference in energy between the real molecule and a hypothetical molecule where all the structural values like bond lengths and bond angles are exactly at their ideal or "natural" values. $E_{st}$ is the energy of a bond being stretched or compressed from its natural bond length, $E_b$ is the energy of bending bond angles from their natural values, $E_w$ is the torsional energy due to twisting about bonds, and $E_{nb}$ is the energy of nonbonded interactions. If there are other intramolecular mechanisms affecting the energy, such as electrostatic (coulombic) repulsion or hydrogen bonding, these too may be added to the force field. Generally speaking, there are no strict rules concerning how many or what types of potential energy functions should be used and, because of this, many different molecular mechanics force fields have been developed.

## B: QUANTUM MECHANICS.

To understand the behavior of individual atoms and molecules, and of their electronic structure, we need to know how particles move in response to the forces acting on them using quantum mechanics.

## SEMI-EMPIRICAL MNDO-SCF STUDY OF THE MOLECULAR AND ELECTRONIC STRUCTURE OF ORGANOHALIDES.

To-date there are three main molecular orbital schemes for treatment of molecules. The Hückel approximation, the Semi-empirical methods and the Ab initio method. The Ab initio method gives the best results but requires very long computation time. The semi-empirical method gives better results than the Hückel approximation and is the one commonly used for big molecules (20 heavy atoms or more) though it requires slightly more computation time [48].

Stams, et al. have successfully obtained estimates of the stabilites of fluorine - containing cations using the Empirical and Ab Initio method [49]. Beland, et al. have reported a molecular orbital (CNDO/2) study of the chlorinated benzenes, DDT, and lindane [50]. CNDO/2 calculations of DDT, Lindane, and g-3,4,5,6-tetrachlorocyclohexene indicated that both the s and $\sigma$ LUMO's were equal and were linearly related with the reduction potentials for all chlorinated benzenes. The calculations indicated that the molecules picked up the electron in a s orbital to form the radical anion even when a p-system was available. The LUMO s is antibonding with the electron delocalized in the C-Cl bonds which undergo cleavage to the reduction products. The relative electron density for different C-Cl bonds was correlated with the product ratios when several products were formed [50].

# CHAPTER 2

## EXPERIMENTAL SECTION:

### 2.0  CHEMICALS AND SOLUTIONS

Copper phthalocyaninetetrasulphonic acid, tetrasodium salt (99 + %) was from Aldrich, Didodecyldimethylammonium bromide (DDAB, 99 + %) was from Eastman Kodak, and n-dodecane was ACS certified from Fisher Scientific. Acetonitrile was HPLC grade Baker Analyzed. Tetraethylammonium bromide, TEAB (BDH Chemicals Ltd. Poole England) was used as received. All other chemicals were reagent grade or better and used without further purification.

The composition of the bicontinuous microemulsion was 23% DDAB; 43% water; 34% n-dodecane (W/W/W) as described previously [9]. The isotropic solution was 1:1 acetonitrile/water (V/V) containing 0.1M tetraethylammonium bromide. For electrochemical experiments in purely aqueous media, the solution were buffered between pH 2.0 and pH 8.0 using laboratory grade buffer chemicals [37].

### 2.1  APPARATUS AND ANALYTICAL TECHNIQUES.

The electrochemical experiments in this investigation were conducted using a Princeton Applied Research, PAR model 174A polarograhpic analyzer or a PAR model 270 electrochemical instrument with software control. All voltammetric experiments were performed with a three-electrode cell with a platinum wire as the counter electrode. The readout device was a standard Houston Ominographic model 2000 X-Y recorder for the PAR model 174A instrument. The working electrode was a planar glassy carbon of geometric area 0.071 cm$^2$ (Le carbone) press fitted into a Teflon Collar. The electrical

contact was through a mercury pool and a copper wire. Except where noted, a PARC saturated calomel electrode (SCE) with vycor tip, separated from the sample compartment by a salt bridge filled with electrolyte usually 0.1M tetraethylammonium bromide in case of aqueous media and acetonitrile/water solution or a microemulsion-filled salt bridge in case of DDAB microemulsion media, was the reference.

Controlled potential Electrolyses were done in an undivided cell with a two electrode set up. About 0.5 x 0.5 x 4 cm carbon felt (WDF, Union carbide) cathode was used when the cell was a UV/VIS cuvette or about 0.5 x 3 x 5 cm carbon felt cathode when the cell was the voltammetric cell. A platinum wire connected to both the counter and reference terminals was the anode.

Electrolyzed solutions were analyzed by UV/VIS spectrophotometry. For solutions electrolyzed in the UV/VIS cuvette, a PERKIN ELMER Lambda 3 UV/VIS spectrophotometer was used. For solutions electrolyzed in the voltammetric cell, a PYE UNICUM model SP3 UV/VIS spectrophotometer was used. Un-electrolysed solutions were also analyzed with the latter instrument. Conductivity of DDAB microemulsion were obtained with a Philips Type PR 9501 conductivity meter. All experiments were done at ambient temperatures.

Prepurified grade nitrogen was used for deaeration of the solutions prior to electrochemical experiments. A stream of nitrogen was maintained during controlled potential electrolysis. Traces of oxygen were removed by bubbling the nitrogen through an acidified vanadous chloride solution.

Before entering the cell, the nitrogen was passed through an indifferent supporting electrolyte in case of aqueous and acetonitrile/water media or water in case of DDAB microemulsion. Deaeration times were 15 minutes or longer. Except where specified, laboratory deionized water was used in all solution preparations. Electrodes were polished with a slurry of aluminium oxide on a glass slide prior to each voltammetric scan, similar to procedures described previously [38].

## 2.2 LINEAR SWEEP AND CYCLIC VOLTAMMETRY.

For electrochemical experiments, 0.4 mM Copper phthalocyanine tetrasulphonic acid, tetrasodium ($Cu(II)PcTS^{4-}$) solutions were prepared as described previously [9]. In aqueous and acetonitrile/water media, this salt, $Cu(II)PcTS^{4-}$, was dissolved in a solution of 0.1 M tetraethylammonium bromide. An exception was when working in buffered aqueous media in that the voltammetric solution was prepared immediately before use by pipetting 5ml buffer solution into the voltammetric cell and then adding 5ml of a solution of 0.4 mM copper phthalocyanine tetrasulphonic acid, tetrasodium salt prepared as above. Thus, in this case, the overall concentration of CuPcTS was 0.2 mM. The buffer solution were prepared in distilled water following standard procedures described previously [37].

Buffer solutions were prepared as described in table I below and the desired specific solutions prepared as shown in table II. 5 mL of each of the buffer solutions was mixed with 5 mL of aqueous solution of 0.4 mM $Cu(II)PcTS^{4-}$ and the resulting solution thoroughly agitated and finaly subjected to voltammetric studies. Linear sweep voltammograms were recorded at different scan rates.

**Table I. Preparation of solutions of Different pH**

| Basic solution | Concentration of acid/base | Amount of acid/base added then diluted to 1 L | pH |
|---|---|---|---|
| I | 0.2 M oxalic acid | 25.213g oxalic acid | 1.09 |
|  | 0.2 M boric acid | 12.367g $H_3BO_3$ |  |
| II | 0.2 M $KH_2PO_4$ | 27.218g $KH_2PO_4$ |  |
|  | 0.2 M succinic acid | 23.618g oxalic acid | 3.05 |
|  | 0.2 M boric acid | 12.367g $H_3BO_3$ |  |
|  | 0.2 M $K_2SO_4$ | 34.853g $K_2SO_4$ |  |
| III | 0.2 M potassium succinate, 0.2 M dipotassium hydrogen phosphate | 23.618g $(CH_2COOH)_2$ | |
|  |  | 27.2178g $KH_2PO_4$ | 5.86 |
|  |  | 12.367g $H_3BO_3$, 200 mL | |
|  | 0.2 M boric acid | 2N KOH | |
| IV | 0.2M $KH_2PO_4$ | 27.618g $KH_2PO_4$ | |
|  | 0.05 M $K_2B_4O_7.8H_2O$ | 150 mL 2N KOH, 12367g | 9.27 |
|  | 0.05 M $K_2SO_4$ | $H_3BO_3$, 8.713g $K_2SO_4$ | |
| V | 0.2M $KH_2BO_3$ | 12.367g $KH_2BO_3$ | |
|  | 0.2 M $K_2CO_3$ | 100 mL 2N KOH | 11.48 |
|  |  | 27.643g $K_2CO_3$ | |

**Table II. Preparation of necessary pH buffers using base (I-V) from table I.**

mL of basic solution added

| pH | I | II | III | IV | V | Influence of dilution on $pH_{1/2}$ |
|---|---|---|---|---|---|---|
| 1.5 | 71.0 | 29.0 | | | | +0.20 |
| 2.0 | 45.0 | 55.0 | | | | +0.16 |
| 2.5 | 21.4 | 78.6 | | | | +0.09 |
| 3.0 | 2.0 | 98.0 | | | | +0.06 |
| 3.5 | | 90.0 | 10.0 | | | +0.02 |
| 4.0 | | 94.8 | 25.2 | | | +0.03 |
| 4.5 | | 55.0 | 45.0 | | | +0.05 |
| 5.0 | | 34.4 | 65.6 | | | +0.05 |
| 5.5 | | 14.0 | 86.0 | | | +0.08 |
| 6.0 | | | 93.6 | 6.4 | | +0.10 |
| 6.5 | | | 70.6 | 29.4 | | +0.11 |
| 7.0 | | | 51.8 | 48.2 | | +0.10 |
| 7.5 | | | 39.2 | 60.8 | | +0.10 |
| 8.0 | | | 30.2 | 69.8 | | +0.09 |
| 8.5 | | | 20.8 | 79.2 | | +0.04 |
| 9.0 | | | 8.8 | 91.2 | | -0.03 |
| 9.5 | | | | 91.6 | 8.4 | -0.06 |
| 10.0 | | | | 65.5 | 34.5 | -0.03 |
| 10.5 | | | | 33.6 | 66.4 | -0.01 |
| 11.0 | | | | 10.5 | 89.5 | -0.02 |
| 11.5 | | | | 0 | 100 | -0.13 |

Bicontinuous microemulsions of didodecyldimethylammonium bromide, DDAB/n-dodecane/water were prepared by weighing 21g of DDAB into a 250ml beaker and then adding 40ml of n-dodecane followed by 39ml of deionized water. A milky mixture was obtained with undissolved DDAB particles. A magnetic stirring rod was introduced into the above mixture and the beaker transferred onto a magnetic stirrer. After 30 minutes stirring, the mixture began to clear and after about 2 hours stirring, the resultant emulsion was clear without any suspended air bubbles. The electrical conductivity of this emulsion was in good agreement with reported values [9].

A standard procedure [38] was followed in the use of the Glassy carbon electrode (GCE). The GCE was polished before each voltammetric scan. After rinsing with water, the electrode was inserted in the test solution which had been purged with nitrogen for over 15 minutes; passage of nitrogen was continued for about 1 minute. The electrode was then equilibrated at the initial potential of the experiment, either -0.0 or -0.3V vs SCE, after which the potential scan was initiated.

With the PAR 174A instrument, both linear sweep voltammetric (LSV) and Cyclic voltammetric (CV) techniques were used to study the behavior of CuPcTS in aqueous, acetonitrile/water and microemulsion media. For CuPcTS, a reducible species, the LSV i-E curves were recorded from a potential at which reduction does not occur towards more negative potentials. The potential was varied either between -0.0V to -1.5V vs SCE or between -0.3V to -1.8V vs SCE. Scan rate studies were performed. In general potential scan rates were varied from 5 mV/sec to 200 mV/sec. Current sensitivity were adjusted so as to have large and well defined reduction waves as well as have waves of interest within the Y-axis scale limit. Where reduction waves were not well formed, the current output was improved by adjusting the X-Y recorder to give a 1 V full scale current output instead of the commonly used 10V output.

Cyclic voltammograms in this work were recorded following the method of Chuang and Elving [39]. After the wave at most negative potential was located following the

forward scan, the direction of polarization was reversed and a voltammogram recorded going toward less negative potential.

For peak current measurements, a similar method to that by Polcyn and Shain [40] was followed for correcting charging (nonfaradaic) current contribution. For peaks at more negative potentials, the baseline was taken as the tangent to the descending branch of the preceding wave. For the first reduction wave, the baseline was taken as the tangent at the point where this wave begins to form.

For acetonitrile/water and microemulsion media, scan rate studies were performed in absence and in presence of added substrate with the PAR 270 potentiostat. The concentration of copper(II) phthalocyaninetetrasulphonate in both media was 0.4mM whereas that of p-chlorophenol substrate was 4mM (10 times that of the CuPcTS mediator). In recording of the voltammograms and treatment of data the PAR 270 potentiostat was software controlled.

## 2.3  CONTROLLED POTENTIAL ELECTROLYSIS.

Controlled potential electrolysis experiments were performed at two different potentials. Potentials were either controlled at -0.77V or -1.42V by a Princeton Applied Research (PAR model 174A) potentiostat. These potentials correspond to the two diffusion controlled peak potentials found for copper phthalocyanine tetrasulphonate vs SCE. Potentials were also controlled at -1.20V vs Ag/AgBr with a BAS 100 electrochemical instrument. With this technique, the mechanism for electrocatalytic reduction of 1,2-dibromobutane (DBB) mediated by CuPcTS was investigated. Unless otherwise noted, the initial concentration of CuPcTS in bicontinuous DDAB/n-dodecane/water microemulsion was $2.0 \times 10^{-6}$M. In most experiments the CuPcTS solution was electrolyzed in absence of added DBB. Generally electrolyses times were either 1 hr, 2hrs, or 4 hrs. Purified nitrogen was bubbled through the stirred solution prior to and during electrolysis.

UV/VIS spectra of the CuPcTS solution was recorded prior to electrolysis. After electrolysis, the nitrogen stream was stopped briefly and another UV/VIS spectra of the resultant solution was recorded on the same chart. 1,2-dibromobutane was then added ensuring that the solution was at least 10 times more concentrated in DBB relative to the initial concentration of CuPcTS. After equilibration of the solution with DBB for about 2 minutes while maintaining the nitrogen stream, another UV/VIS spectra was recorded on the same chart paper.

Two methods were followed, one in which electrolysis was performed in a Quartz cuvette placed in position inside a PERKIN ELMER UV/VIS spectrophotometer. The second setup involved a case in which electrolysis was performed inside the voltammetric cell and the reaction path followed by recording UV/VIS spectra with a PYE UNICUM SP3 spectrophotometer. In some experiments, electrolysis was performed in presence of DBB following the first method. For each experiment, a new piece of carbon felt cathode was cut, immersed in pure DDAB Emulsion and the emulsion left to drain out. This pre-treatment was found necessary in order to avoid carbon felt fibres getting suspended in solution and possible carry over contamination.

Electrolysis was accomplished by setting the initial potential of the PAR instrument at either -0.77V or -1.42V, depressing the initial potential button, and setting the current output to 10mA full scale output. The experiments were started by setting the selector switch to external cell and stopped by setting this switch to off position. The BAS 100 was software controlled.

## 2.4 UV/VIS SPECTROMETRIC MEASUREMENTS.

Preliminary studies indicated that CuPcTS could be subjected to UV-VIS spectrophotometric measurements at concentrations of the order of $10^{-6}$ M CuPcTS. CuPcTS gives an intense blue solution and normally absorbs in the ultraviolet and visible regions. Thus, all solution in these experiments were prepared in the neighbourhood of $10^{-6}$ M CuPcTS.

In aqueous media, the spectra were recorded between 800nm and 200nm using a PYE UNICUM model SP3 spectrophotometer. In DDAB microemulsion, a blank absorption relative to air was observed below 300nm. Thus during controlled potential electrolyses experiments in the UV/VIS cuvette, the Perkin Elmer instrument was set between 750nm and 290nm. Apart from this being a region which could be accessed with this instrument without any difficult, we were able to avoid switching on the UV lamb which might have affected reduced states of CuPcTS generated.

## 2.5 COPPER PHTHALOCYANINE SYNTHESIS.

A mixture of phthalic anhydride (5.0018g), cupric chloride (1.1001g), urea (6.5035g) and catalytic amount of ammonium molybdate (VI) (0.2072g) in nitrobenzene was refluxed (heating mantle, $210-211^0$C) in a 500ml round bottomed flask for seven hours. A dark blue mass was obtained. Since phthalocyanines have been known to be insoluble in virtually all the common organic solvents [25,27], the product was washed off soluble impurities with acetone. This was achieved by use of a soxhlet extraction system for about 12 hours (i.e. until the solvent becomes clear). The product so obtained was left to dry in air and then boiled in pyridine and filtered. The pyridine turned dark brown (filtrate) and a phthalocyanine residue (blue with purple lustre) was obtained. This product dissolved in boiling quinoline to a very low extent. The product dissolved in conc. sulphuric acid and precipitated as a blue solid on dilution with water.

Cupric chloride is reported to give a mixture of copper phthalocyanine and copper monochlorophthalocyanine, $C_{32} H_{15} N_8$ ClCu [27]. Thus, in order to form the chlorine free copper phthalocyanine, metallic copper was used as a source of copper instead of cupric chloride. A mixture of phthalic anhydride (40.00g), copper turnings (5.5469g), urea (17.0185g) and catalytic amount of ammonium molybdate (VI) (1.06g) in nitrobenzene were refluxed in a 500ml round bottomed flask for seven hours. A dark green product was obtained. The product was purified following a similar method to the one used above. This method was modified in that the pyridine step was omitted. The

product was left to dry completely in air and then dissolved in conc. sulphuric acid. The resultant solution was filtered to remove undissolved copper granules via a buchner funnel (note: no filter paper). On dilution of the filtrate with deionized water, a blue precipitate formed. This was filtered, washed with acetone and finally with water. The steps beginning with dissolution in conc. sulphuric acid were repeated several times (about 5 times).

The copper phthalocyanine synthesized above was left to dry in vacuum for a period of one week. This compound was dissolved in the bicontinuous DDAB/n-dodecane/water microemulsion to give a solution 0.4 mM in CuPc. Scan rate studies using the LSV technique were performed. Similar studies were done in presence of added p-chlorophenol (4 mM) and finally 100µl of DBB were added into the above mixture and scan obtained at 100mv/sec.

# 2.6 THEORETICAL CALCULATIONS
## A: QUANTUM MECHANICS:
## PRINCIPLE OF METHOD.

The study involved the use of Allinger's MM2 force field which is currently one of the most widely used. For successful use an initial set of three-dimensional atom coordinates of the molecule under investigation is required. This trial set is progressively modified during the calculations to minimize the steric energy. Of the various conformational isomers that may be possible for a given molecule the assumption is that the conformer of lowest steric energy represents the most favourable conformation of the isolated molecule.

It is important to appreciate that molecular mechanics is basically an empirical method and the final molecular model obtained relates to a hypothetical motionless state at absolute zero. However, it is possible to parameterize using experimental data steric energy to the heat of formation by addition of group enthalpy increments.

The method was applied to p-dichlorodiphenyltrichloroethane (DDT), the two known DDT metabolites, i.e., p-dichlorodiphenyldichloroethene (DDE) and p-dichlorodiphenyldichloroethane (DDD), and other possible reductive dechlorination products of DDT, i.e., 1,1-diphenylethane (DPE) and 1,1-diphenylethene (DPET). The method was also applied to other molecules taken to be models for recalcitrant substances. These were 1,2-dibromobutane (DBB), trichloroacetic acid (TCA) trans- 1,2-dibromocyclohexane (DBCH), O-dichlorobenzene (DCB) and 1,3-dibromobutane(1,3-DBB).

Strainless heat of formation (i.e. the heat of formation for an isomer of a compound which is strainless and exclusively in its minimum energy conformation) was also obtained for these molecules. The difference between this and the normal heat of formation gives the "inherent strain" of the compound. Other important features obtained with this method include dipole moment, moment of inertia and the final coordinates (optimum geometry). A correlation between the obtained heat of formation and half-wave reduction potentials for these compounds is presented here for the first time.

# B: QUANTUM MECHANICS:
## SEMI-EMPIRICAL MNDO-SCF STUDY OF THE MOLECULAR AND ELECTRONIC STRUCTURE OF ORGANOHALIDES.

In our study, we used a recent and more superior MNDO method to follow the reduction pathways of organohalide compounds. We report a preliminary study in that only the parent molecules were subjected to our method and the results obtained correlated with voltammetric reduction potentials.

## PRINCIPLE OF METHOD:

A general molecular orbital package, AMPAC, was used. AMPAC is a general purpose semi-empirical molecular orbital package for the study of chemical reactions. In AMPAC the semi-empirical Hamiltonians MNDO was used.

NOTE: How the program is handled is irrelevant to the chemistry.

A short description is obtained from the original references describing the theory on which the program is based. In our case, we used MNDO as in MOPAC package.

The reference is:

Dewar M.J.S; Thiel W. J. Am. Chem. Soc. 1977, **99** (4899)

Origin of MOPAC reference is

QCPE 1984, No. 455 (MOPAC).

For MM2

Theory: Allinger, N.L. J.Am. Chem. Soc. 1977, **99** (8127)

Program: Allinger, N.L:Yuh, Y.H. QCPE 1981 No. 13 395.

All the field parameters were taken by analogy from previous parameters (MM2 references above). MM2 geometry optimized coordinates were used as Cartesian input for MNDO without optimization.

# CHAPTER 3

## RESULTS AND DISCUSSION:

## 3.1 UV/VIS SPECTROSCOPIC ANALYSIS FOR COPPER PHTHALOCYANINE TETRASULPHONIC ACID TETRASODIUM SALT (CuPcTS).

The unsulphonated form of copper phthalocyanine (CuPc) has characteristic absorption spectra consisting of four main intense $\pi$-$\pi^*$ bands in the UV-VIS region [41]. Similar absorption bands were obtained for copper phthalocyanine tetrasulphonate, CuPcTS (Fig. 1). For metal free phthalocyanine ($H_2Pc$) and metal phthalocyanines (M(II)Pc), the assignment of these main bands to $\pi$-$\pi^*$ transitions has been confirmed by molecular orbital (MO) calculations and magnetic circular dichroism (MCD) studies [42]. Q band (710-650nm), $^a1u$ $(\pi)$ - $^eg(\pi^*)$, an intense band ($\varepsilon$, $10^5$), which splits into two in metal-free $H_2Pc$ spectra, and is usually accompanied by one or two vibrational bands ($\varepsilon$, $10^4$) on the blue side; B(360-330nm), $^a2u(\pi)$ - $^eg$ $(\pi^*)$, the soret band ($\varepsilon$, $10^4$), broadened presumably by overlapping of NP(s) - $^eg(\pi^*)$ PC; N(270nm), $^a2u(\pi^*)$ - $^eg(\pi^*)$ ($\varepsilon$, $10^5$); ($\lambda_{max}$, 240nm), $^a1u(\pi)$ - $^eg(\pi^*)$ ($\varepsilon$, $10^5$).

**Figure 1** UV/VIS Spectra of 2.0µM CuPcTS in aqueous solution no electrolyte.
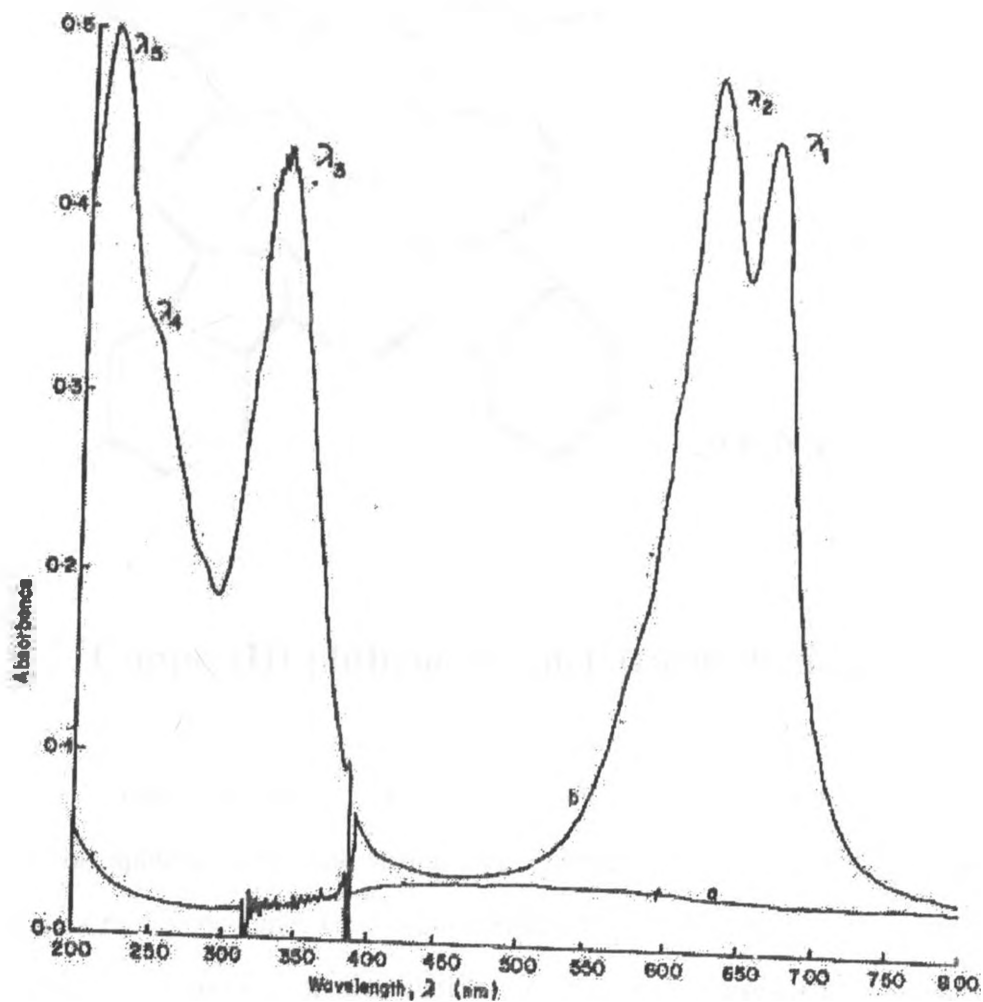
## 3.2 SPECTROSCOPIC STUDIES OF CuPcTS IN WATER.

Copper phthalocyanitetrasulphonate is generally available as the tetrasodium salt whose structure is given by figure 2 [43].
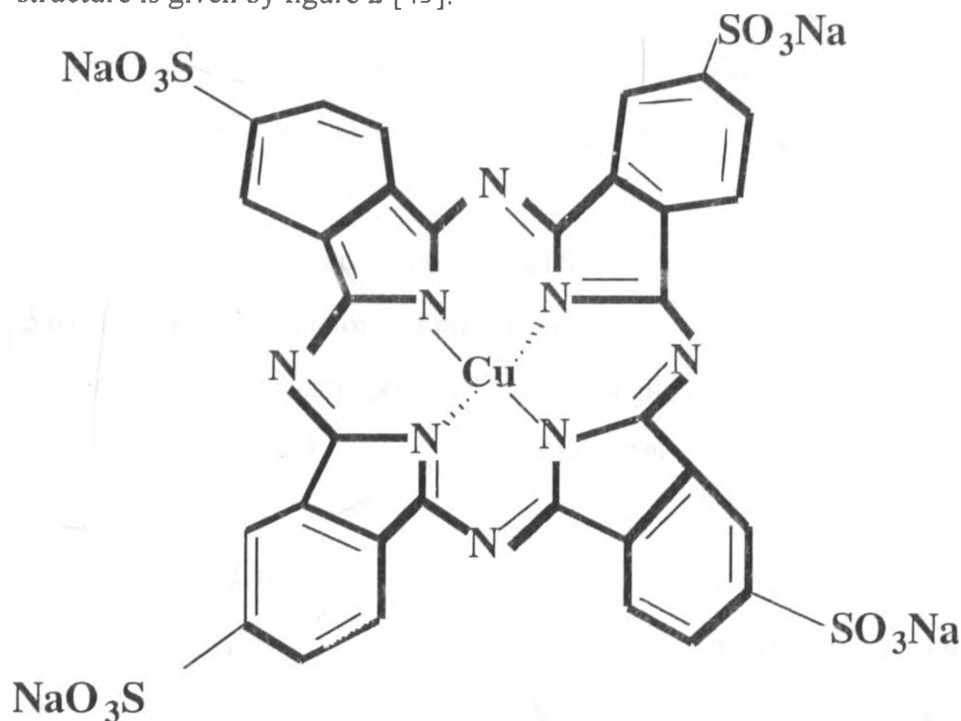


# Figure 2. Copper(II) phthalocyaninetetrasulphonate

Bragrove and Gruen found that the tetrasodium salt of copper phthalocyanine-4,4',4'',4'''- tetrasulphonic acid had strong aggregating tendency in water. At low concentrations a monomer-dimer equilibrium exists [44]. The same workers found that both the enthalpy and entropy of dissociation are increased in presence of compounds which enhance the structure of water. Conversely, both of these parameters are decreased by structure-breaking compounds [45].

In the present study in aqueous solutions (no electrolyte), we were able to observe all the four main bands. At concentrations of $2 \times 10^{-6}$M CuPcTS in water, a dimer band occurred in the visible region with $\lambda$maxima at 665nm ($\varepsilon$= 4.92 $\times 10^4 \pm$ 695) and $\lambda$625nm ($\varepsilon$= 5.23$\times 10^4 \pm$ 290). Where $\varepsilon$ is the molar absorptivity in $M^{-1}$ $cm^{-1}$. The same solution gave other bands at $\lambda$332nm ($\varepsilon$ = 4.83$\times 10^4 \pm$ 210), a broad peak, $\lambda$245nm ($\varepsilon$ = 3.65 $\times$

$10^4 \pm 240$), a shoulder peak, and $\lambda 215\text{nm}$ ($\varepsilon= 5.38 \times 10^4 \pm 320$) (tables 1-5). Except for a shift in wavelengths of maximum absorption at the lower wavelengths, added sulphonic acid groups do not cause a significant change in the absorption spectra of copper phthalocyanine (CuPc). There was no significant decrease of absorbance at all the four wavelengths of maximum absorption with days (table 1).

Table 1: Absorbance of Cu(II)PcTS at the first band ($\lambda 665\text{nm}$), in aqueous media (no electrolyte), as a function of time (days).

| Time(days) | Concentration $\mu M$ | Wavelength $\lambda_{max}$, nm | Absorbance A | $10^{-4}$Molar absorptivity, $M^{-1}cm^{-1}$ |
|---|---|---|---|---|
| 0 | 2.16 | 665 | 0.434 | 5.02 |
| 2 | 2.16 | 665 | 0.424 | 4.90 |
| 4 | 2.16 | 665 | 0.422 | 4.88 |
| 11 | 2.16 | 665 | 0.417 | 4.87 |
| X±SD | | 665 ±b 0.00 | 0.424 ± 0.007 | 4.92 ± 0.0695 |

Table 2: Absorbance of Cu(II)PcTS, aqueous media (no electrolyte), at the second band ($\lambda 625\text{nm}$), as a function of time in days .

| Time (days) | Concentration $\mu M$ | Wavelength $\lambda_{max}$, nm | Absorbance A | $10^{-4}$Molar absorptivity, $M^{-1} cm^{-1}$ |
|---|---|---|---|---|
| 0 | 2.16 | 625 | 0.45 | 5.2 |
| 1 | 2.16 | 627 | 0.454 | 5.25 |
| 4 | 2.16 | 627 | 0.455 | 5.26 |
| 11 | 2.16 | 625 | 0.451 | 5.21 |
| X±SD | | 626 ± 1.2 | 0.453 ± 0.0023 | 5.23 ± 0.029 |

Table 3: Absorbance (aqueous Cu(II)PcTS, no electrolyte) at the third band ($\lambda$ 332nm), as a function of time in days.

| Time (days) | Concentration $\mu M$ | Wavelength $\lambda_{max}$,nm | Absorbance A | $10^{-4}$Molar-absorptivity, $M^{-1}$ $cm^{-1}$ |
|---|---|---|---|---|
| 0 | 2.16 | 332 | 0.418 | 4.83 |
| 1 | 2.1 | 335 | 0.418 | 4.83 |
| 4 | 2.16 | 335 | 0.416 | 4.81 |
| 11 | 2.16 | 333 | 0.420 | 4.86 |
| X±SD | | $333.8 \pm 1.5$ | $0.418 \pm 0.002$ | $4.83 \pm 0.021$ |

Table 4: Absorbance (aqueous Cu(II)PcTS, no electrolyte) at the fourth band ($\lambda$245nm, shoulder peak) as a function of time in days.

| Time (days) | Concentration $mM$ | Wavelength $\lambda_{max}$,nm | Absorbance A | $10^{-4}$Molar absorptivity, $M^{-1}$ $cm^{-1}$ |
|---|---|---|---|---|
| 0 | 2.16 | 245 | 0.314 | 3.63 |
| 1 | 2.16 | 247 | 0.318 | 3.68 |
| 4 | 2.16 | 249 | 0.314 | 3.63 |
| 11 | 2.16 | 245 | 0.315 | 3.64 |
| X±SD | | 246.5 | $0.315 \pm 0.002$ | $3.65 \pm 0.024$ |

Table 5:  Absorbance (aqueous Cu(II)PcTS, no electrolyte) at the fourth band $(\lambda_{215nm,})$ as a function of time in days.

| Time (days) | Concentration $\mu M$ | Wavelength $\lambda_{max}$, nm | Absorbance A | $10^{-4}$Molar absorptivity $M^{-1}cm^{-1}$ |
|---|---|---|---|---|
| 0 | 2.16 | 215 | 0.462 | 5.34 |
| 1 | 2.16 | 217 | 0.468 | 5.4 |
| 4 | 2.16 | 216 | 0.466 | 5.35 |
| 11 | 2.16 | 215 | 0.468 | 5.38 |
| X±SD | | $215.8 \pm 1.0$ | $0.466 \pm 0.0028$ | $5.38 \pm 0.032$ |

*where,  SD= Standard deviation and X = Mean*

The results shows that CuPcTS remains stable in solution for at least 10 days, hence, solutions of this complex  can be studied over a long period of time without deterioration. This is in line with known stability properties of copper phthalocyanine tetrasulphonate [27].
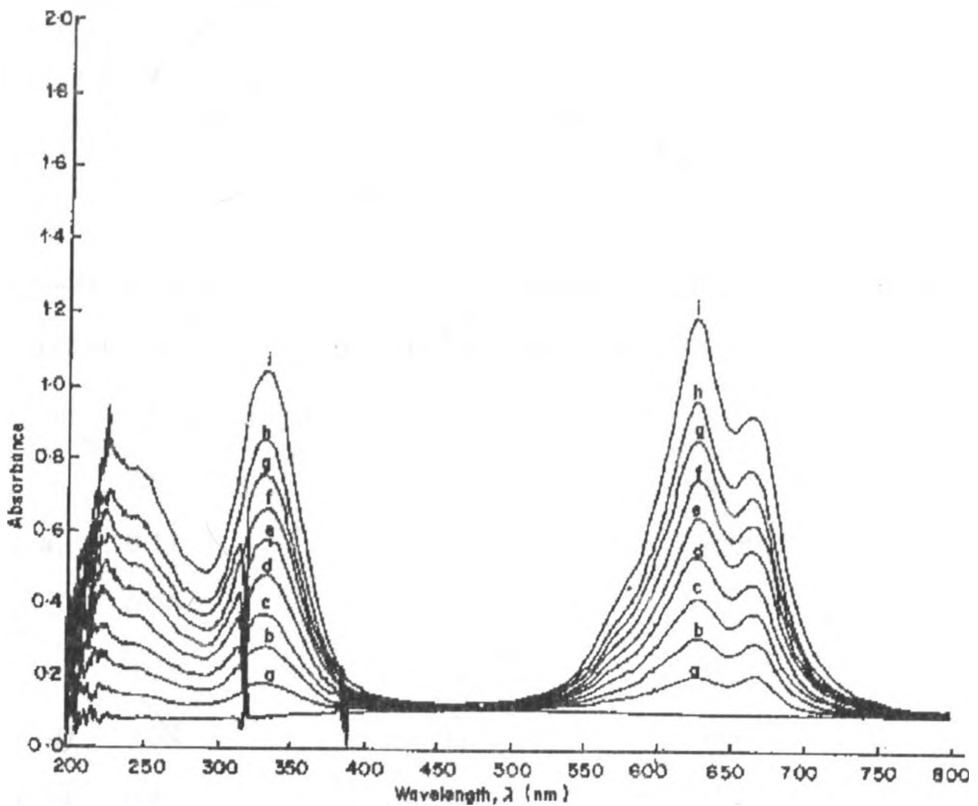
The effect of change in the concentrations of CuPcTS in aqueous media is depicted in figure 3 and Table 6. A plot of absorbance versus concentration gives the characteristic expected curve (figure 4).

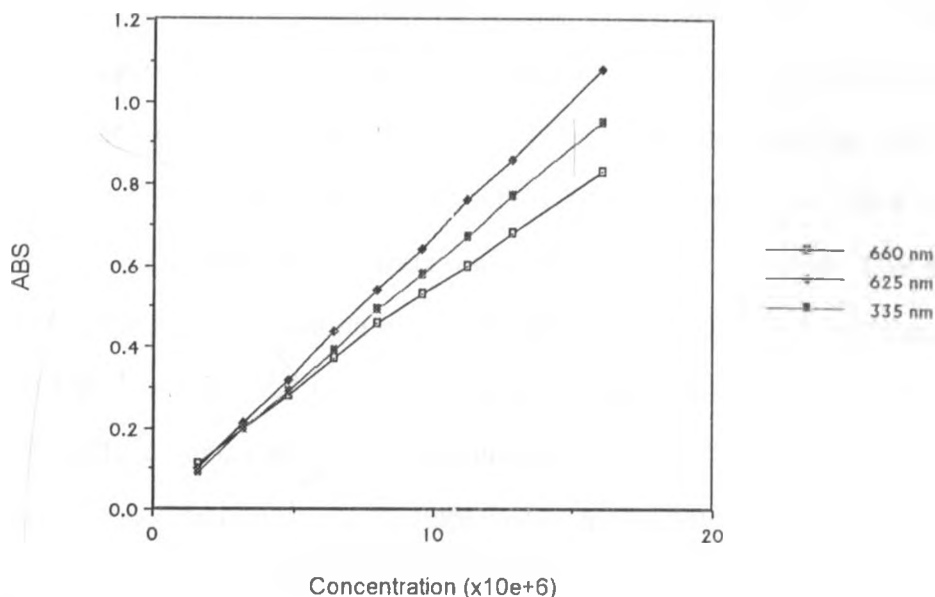## Figure 4: Absorbance vs concentration for aq. CuPcTS



Table 6. Concentration studies of Cu(II)PcTS (aqueous) for peaks A ($\lambda_{max}$ 660), B( $\lambda_{max}$ 625nm) and C( $\lambda_{max}$ 335) for CuPcTS/water system.

Concentration     Absorbance, A

| µM | A | B | C |
|---|---|---|---|
| 1.6 (curve a) | 0.11 | 0.102 | 0.09 |
| 3.2 (curve b) | 0.20 | 0.21 | 0.20 |
| 4.8 (curve c) | 0.28 | 0.32 | 0.29 |
| 6.0 (curve d) | 0.37 | 0.44 | 0.39 |
| 8.0 (curve e) | 0.46 | 0.54 | 0.49 |
| 9.6 (curve f) | 0.53 | 0.64 | 0.58 |
| 11.2 (curve g) | 0.60 | 0.76 | 0.67 |
| 12.8 (curve h) | 0.68 | 0.86 | 0.77 |
| 16.0 (curve i) | 0.83 | 1.08 | 0.95 |

According to the plots, the absorbance at each of the five wavelengths of maximum absorption was found to vary linearly with a change in concentration particularly the B-band at $\lambda$335nm. In case of metal free phthalocyanine tetrasulphonate, the dimer band has

been attributed to aggregation of the phthalocyanine sulphonate in solution [46]. The curves for absorbance vs concentration for the 660nm and 625nm wavelengths diverge away from each other with increase in concentration, with 625nm (dimer peak) showing a relative higher increase in absorbance with increased concentration due to extent of aggregation. The absorption peak at 660nm is due to monomer of CuPcTS, and in water it decrease with increase in concentration relative to the dimer peak. This is in line with expected patterns of aggregation with increased concentration [46]. At concentrations of $10^{-2}$ M litre$^{-1}$ of the metal free phthalocyanine tetrasulphonate, a mixture of dimers and predominantly tetramers are well documented [46].

Thus, at concentrations normally employed in voltammetric studies (generally 0.4mM in the case of CuPcTS), CuPcTS is expected to be predominantly dimerized in aqueous media with a possibility of the presence of higher aggregates [46 b].

Since our main interest was to use CuPcTS as a mediator (catalyst) for electro-reduction of recalcitrant substances such as organohalides, we felt that there was need to study the effect of added salt on CuPcTS in solution. In our case, tetraethylammonium bromide (TEAB) was used as the supporting electrolyte salt in aqueous media.

At a concentration of $8 \times 10^{-7}$ M and in presence of added TEAB (0.1M), only three main UV/VIS peaks (bands) were observed at 665nm, 635nm, and 340nm for CuPcTS. Over a period of 6 days, the absorbance at these wavelengths were 0.069 ±0.0013, 0.102 ± 0.0013 and 0.081 ± 0.0058 respectively. From these results, added salt appears to decrease the number of observed peaks to only those close to the visible region. From figure 4 the absorbance at 665nm would be expected to be slightly higher than that at 635nm at a concentration of $8 \times 10^{-7}$M. This is due to the fact that in purely aqueous media, CuPcTS shows a relatively higher absorbance for the higher wavelength at 660nm as compared to that at the lower wavelength (625nm) at concentrations below $2 \times 10^{-6}$M. But in case of added TEAB, the band at 665nm is merely a shoulder whereas that at 635nm is a well formed broad band. This suggests that presence of electrolyte fovours the predominant species to be the dimer. Such a high extent of aggregation at the low

concentrations used in recording the UV/VIS spectra could imply that CuPcTS is possibly completely aggregated at concentrations of 0.4mM in presence of added TEAB. If this is the case then, only two main bands could be expected at these concentrations. This compares well with the two observed diffusion controlled electro-reduction waves in the case of CuPcTS [9]. For CuPc, the first band at wavelength 670nm has been attributed to the first reduction potential [29], i.e. the energy difference between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).

## 3.3 UV/VIS SPECTROSCOPIC STUDIES OF CuPcTS IN MICROEMULSION.

Since we were also interested in the voltammetric studies of CuPcTS in microemulsion we felt it was necessary to have an idea of its extent of aggregation in this media. The results obtained shows a lower extent of aggregation in microemulsion as compared to aqueous media (figure 5). According to figure 5 the aggregation of CuPcTS in microemulsion is negligible, since the expected dimer peak at 605nm remained relatively constant with increase in concentration. Moreover, in microemulsion the peaks were well resolved compared to broad peaks encountered in aqueous solutions. Thus microemulsion media appears to inhibit aggregation of CuPcTS. Such a low extent of aggregation could be due to compartmentalization of CuPcTS (catalyst) in the microemulsion media [46b].
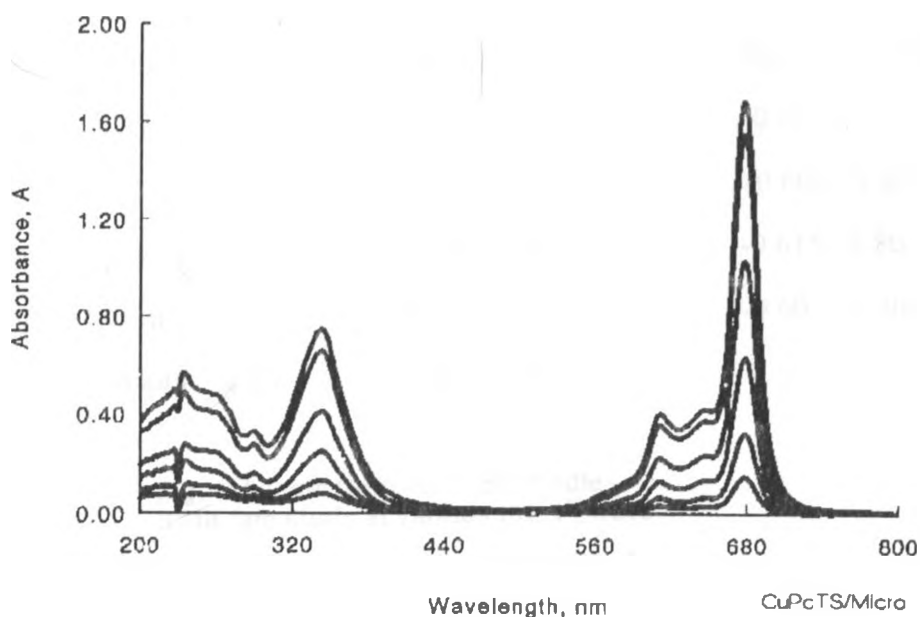
## 3.4 VOLTAMMETRY OF COPPER PHTHALOCYANINE TETRASULPHONATE (CuPcTS) IN BUFFERED AQUEOUS MEDIA.

Electroreduction of metal phthalocyanine generally gives two observable diffusion controlled single electron transfer waves. The effectiveness of these catalysts as mediators for electrochemical reduction has been found to be pH dependent [47]. Metal phthalocyanine tetrasulphonate, (MPcTS), mediators have four negative charges and are soluble in water. They reside in the water phase or associated with DDAB head groups in the microemulsion [10]. Although control of acidity in DDAB dispersions has been found to be necessary in order to maintain good rates of catalytic dehalogenation [14], no work has so far been reported on the voltammetric behavior of CuPcTS with pH. Thus, we present a preliminary account of such work.

In aqueous media, there was a general improvement in peak current with a decrease in pH. Two very distinct waves at potentials positive of -1.0V vs SCE were observed. Between pH 3.0 and pH 6.0, a third wave appeared at potentials negative of the first two.

Table 8. Variation of peak current with square root of scan rate for the second peak (first wave) at a concentration of 0.2 mM CuPcTS in 0.05M aqueous TEAB electrolyte.

| Scan rate $(mV/s)^{1/2}$ | pH 2.0 | | pH 3.0 | | pH 4.0 | |
|---|---|---|---|---|---|---|
| | $E_{pc}(V)$ | $i_{pc}(\mu A)$ | $E_{pc}(V)$ | $i_{pc}(\mu A)$ | $E_{pc}(V)$ | $i_{pc}(\mu A)$ |
| 3.16 | -0.471 | 0.561 | -0.57 | 0.90 | -0.60 | 1.16 |
| 4.47 | -0.461 | 1.00 | -0.58 | 1.70 | -0.601 | 1.80 |
| 7.07 | -0.461 | 1.40 | -0.58 | 3.60 | -0.615 | 3.80 |
| 10.00 | -0.46 | 2.80 | -0.58 | 4.70 | -0.60 | 5.40 |
| 14.14 | -0.445 | 4.20 | -0.58 | 7.10 | - | - |



Fig. 6: 0.2mM CuPcTS in aq. media
Scan rate study at variuos pH, 1$^{st}$ wave

Current in uA

Square root of Scan rate (mV/sec)^(1/2)
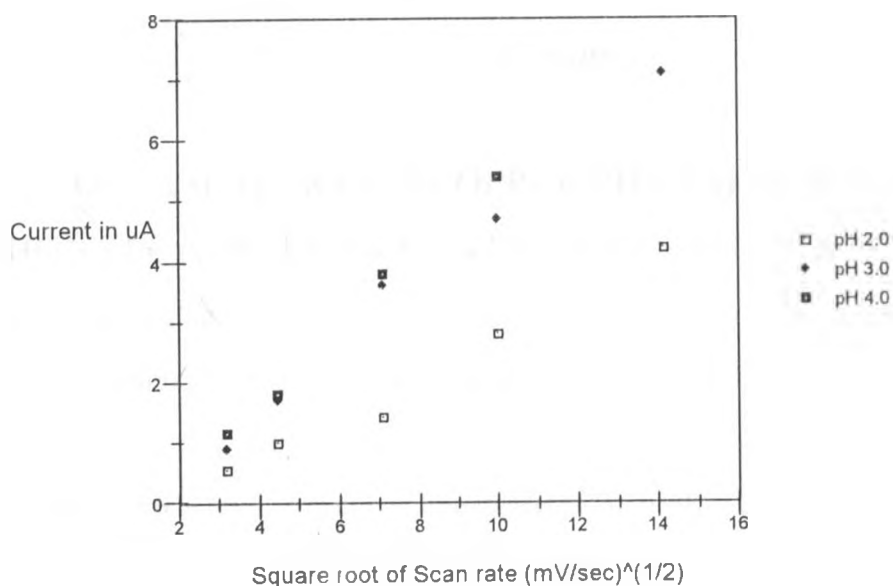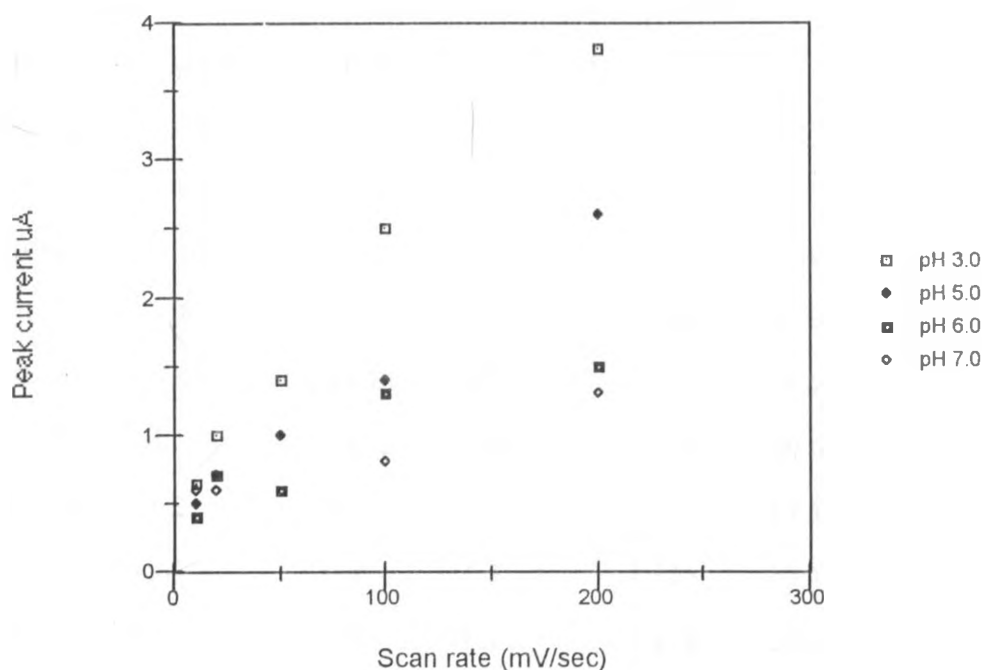
pH 2.0
pH 3.0
pH 4.0

**Fig.7 : 0.2mM CuPcTs in aq. media**
Scan rate study at various pH, 1$^{st}$ prewave



## 3.5 VOLTAMMETRY OF COPPER PHTHALOCYANINE TETRASULPHONATE (CuPcTS) IN WATER/ACETONITRILE SOLUTION.

At scan rate of 50mV/sec, three distinct reduction waves were observed using tetraethylammonium bromide as the electrolyte and saturated calomel electrode (SCE) as the reference electrode (figure 8). The first reduction peak occurred at about -0.70V vs SCE. This peak has a reverse cyclic voltammetric (CV) peak at about -0.60V. The peak at the middle appeared to be split at peak potentials around -0.97V and -1.09V. Both of these peaks were reversible and the reverse peaks occurred at about -1.02V and -0.92V respectively. The peak at the most negative potential occurred at about -1.42V vs SCE. At the above scan rate, this peak had a corresponding reverse CV peak at -1 28V vs SCE In acetonitrile/water solution (1:1 v/v), CuPcTS exhibits three well defined reversible waves (figure 9a and table 9a), using tetrabutylammonium tetrafluoroborate as the electrolyte and Ag/AgBr as the reference electrode .

Table 9a. Reduction of CuPcTS in acetonitrile-water(1:1) solution.

| Scan rate | Peak 1 | | Peak 2 | | Peak 3 | |
|---|---|---|---|---|---|---|
| mVs$^{-1}$ | -E(V) | Current (mA) | -E(V) | Current (mA) | -E(V) | Current (mA) |
| 5 | 0.586 | 2.36 | 0.884 | 2.24 | 1.126 | 5.23 |
| 25 | 0.566 | 5.47 | 0.886 | 1.38 | 1.13 | 8.27 |
| 50 | 0.582 | 7.51 | 0.888 | 3.25 | 1.12 | 11.36 |
| 100 | 0.588 | 6.30 | 0.834 | 1.80 | 1.064 | 6.90 |
| 200 | 0.598 | 9.40 | 0.840 | 2.79 | 1.08 | 9.40 |
| 300 | 0.588 | 14.1 | 0.872 | 7.60 | 1.126 | 10.4 |
| 500 | 0.566 | 31.2 | 0.888 | 9.20 | 1.126 | 17.3 |
| 1000 | 0.602 | 30.1 | 0.894 | 21.5 | 1.128 | 33.1 |
| 2000 | 0.600 | 54.0 | 0.90 | 18.3 | 1.138 | 28.4 |

Figure 8: Cyclic voltammogram of 0.4mM CuPcTS in acetonitrile/water (1/1 v/v)

Fig. 9(a): CuPcTS in water/acetonitrile



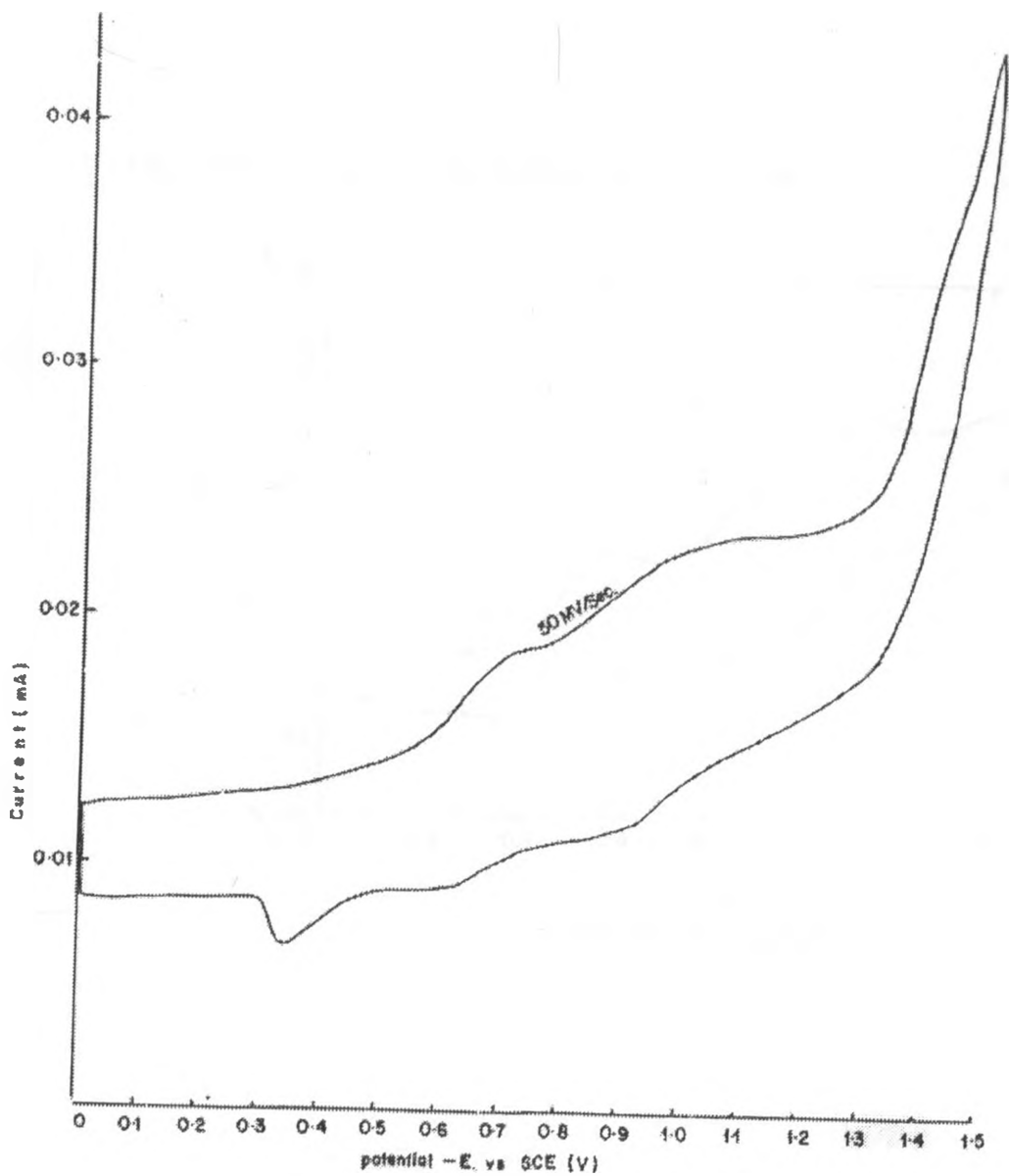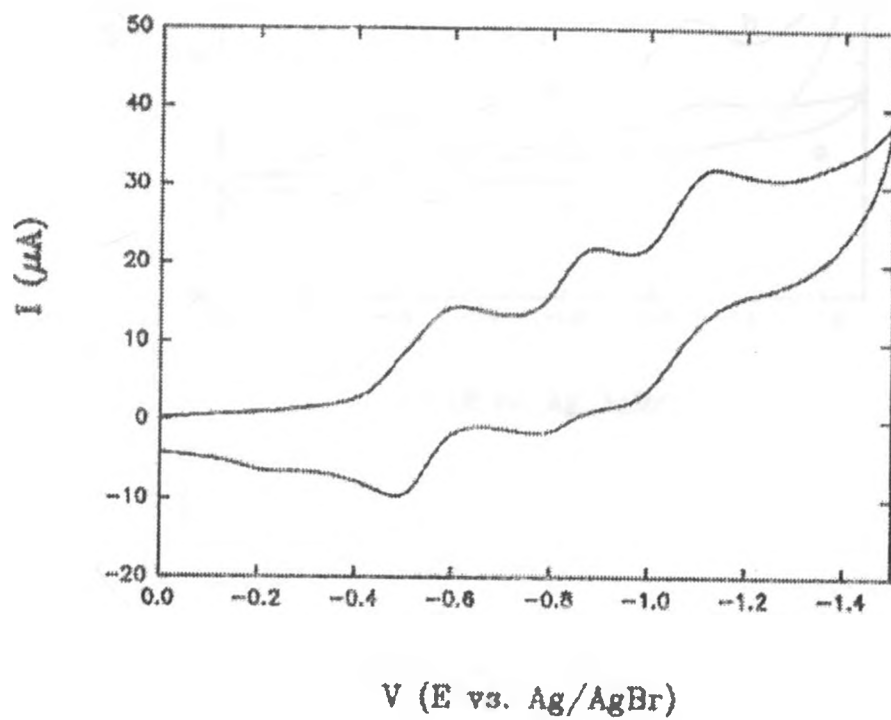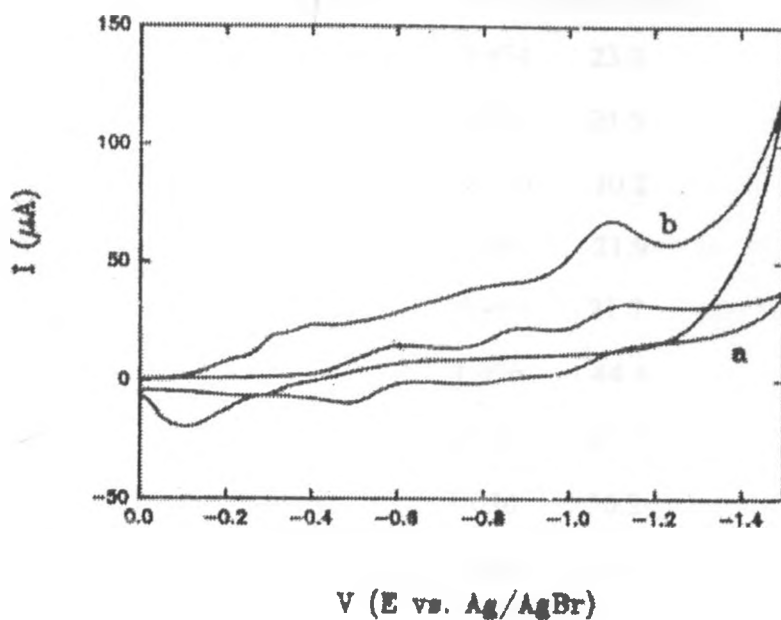V (E vs. Ag/AgBr)

Fig. 9(b): CuPcTS Catalysed reduction of p-Chlorophenol in water/acetonitrile



On addition of p-Chlorophenol (substrate), the third wave at -1.10V vs Ag/AgBr showed a marked increase in peak current (figure 9b; a= catalyst, b= catalyst + substrate). This is due to regeneration of the oxidized form [24] of the CuPcTS near the surface of the electrode in presence of added substrate.

Table 9b. Reduction of CuPcTS in presence of p-chlorophenol in acetonitrile-water (1:1) solution.

| Scan rate mVs$^{-1}$ | Peak 1 -E(V) | Current(mA) | Peak 2 -E(V) | Current(mA) | Peak 3 -E(V) | current(mA) |
|---|---|---|---|---|---|---|
| 5 | | | | | 0.974 | 23.2 |
| 25 | 0.394 | 7.4 | | | 1.006 | 21.5 |
| 50 | 0.406 | 9.1 | | | 0.986 | 30.2 |
| 100 | 0.554 | 19.3 | | | 0.984 | 21.9 |
| 200 | 0.554 | 21.5 | | | 0.934 | 21.7 |
| 300 | 0.402 | 23.2 | | | 1.096 | 44.4 |
| 500 | 0.566 | 46.1 | | | 0.990 | 47.7 |
| 1000 | 0.580 | 61.4 | | | 1.030 | 56.2 |
| 2000 | 0.588 | 73.6 | | | 1.046 | 72.5 |

In case of CuPcTS, the following reactions are expected to occur at the two diffusion controlled waves [9].

$$CuPcTS^{4-} + e \rightleftharpoons CuPcTS^{5-} \quad \text{(wave 1)} \quad (23)$$

$$CuPcTS^{5-} + e \rightleftharpoons CuPcTS^{6-} \quad \text{(wave 2)} \quad (24)$$

The increase in current at this first diffusion controlled wave, in presence of substrate, may be attributed to regeneration of CuPcTS$^{4-}$ which undergoes a one electron reduction to give CuPcTS$^{5-}$. The effect of added substrate at the first diffusion controlled peak potential was monitored in both isotropic acetonitrile/water media and bicontinuous DDAB microemulsion. The "catalytic efficiency" of a mediated reaction is the ratio of catalytic peak or plateau current ($i_c$) to the peak current ($i_d$) for mediator in the absence of substrate [10].

In the Presence of added substrate, p-chlorophenol, the second wave is not well defined and in most cases is not observed (table 9b). The "catalytic efficiency" was greater than 1.3 in the range of scan rates employed in this work. In pure acetonitrile solution, P-chlorophenol gave two irreversible reduction waves centred around -0.7V and -2.1V vs Ag/AgBr, respectively (Figure 10). During the electrocatalytic reduction it is the second reduction wave of the catalyst that increases, suggesting that in the presence of catalyst, p-chlorophenol is reduced at around -1.10V vs Ag/AgBr. Thus a lowering of overpotential of about 1.0V is obtained for reduction of p-chlorophenol. The catalytic efficiency decreased with increase in scan rate as expected for homogeneous catalysis [21]. The highest catalytic efficiency obtained was 3 at a scan rate of 100 mV/sec.

The increase in the first wave for the catalyst in the presence of the substrate can be attributed to reduction of both the catalyst and the substrate . This is because the first reduction wave of p-chlorophenol occurs at around -0.7V vs Ag/AgBr, which may be overlapped with the first reduction wave of CuPcTS.

Within the scan rates considered, the anodic waves decreased in the presence of substrate, particularly at low scan rates. However, with the increase in scan rates, greater than 500 mV/sec the anodic (oxidation) peaks increased in size, as expected [46c].

## Fig. 10: CV of 4.5 mM p-Chlorophenol
### in pure acetonitrile/0.1M TBAF



Potenial vs Ag/AgBr
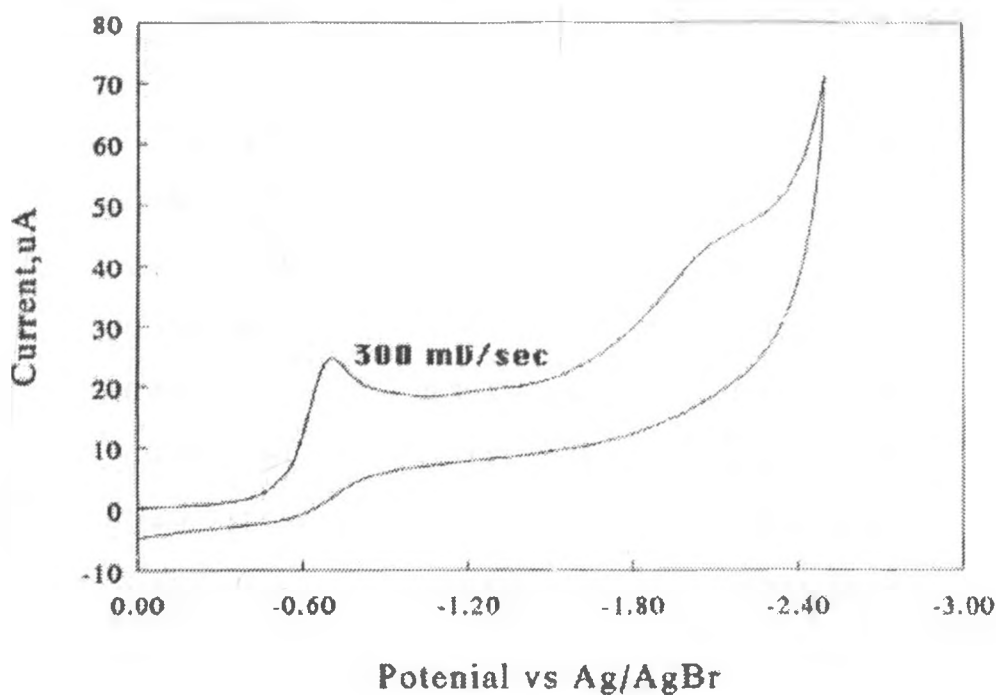
At various scan rates , the cathodic peak catalytic efficiency $i_c/i_d$ varied from 1.36 to 3.0. Thus, some catalytic reduction of p-chlorophenol in isotropic media is obtained with CuPcTS as the mediator.

Other researchers have reported better rate enhancement for nonpolar substrates in bicontinuous DDAB microemulsions as compared to isotropic water/acetonitrile media [9, 10]. The converse was found to be true for polar substrates such as trichloroacetic acid [9, 10]. In view of these facts, we decided to study similar media effects for p-chlorophenol substrate. Thus, the results obtained are given in tables 10(a) and (b). No catalytic reduction of p-Chlorophenol by CuPcTS in the DDAB microemulsion media was obtained. Presence of p-Chlorophenol appears to inhibit electron transfer to glassy carbon cathode possibly due to this substrate modifying the DDAB microemulsion microstructure.

Table 10(a). Reduction of CuPcTS in microemulsion.

| Scan rate | Peak 1 | | Peak 2 | | Peak 3 | |
|---|---|---|---|---|---|---|
| mV s⁻¹ | -E(V) | Current(mA) | -E(V) | Current(mA) | -E(V) | Current(mA) |
| 5 | 0.446 | 0.84 | | | 1.162 | 0.34 |
| 25 | 0.504 | 1.62 | | | 1.144 | 0.41 |
| 50 | 0.508 | 2.77 | | | 1.262 | 0.88 |
| 100 | 0.486 | 2.28 | | | 1.23 | 1.18 |
| 200 | 0.488 | 5.09 | | | 1.27 | 2.33 |
| 300 | 0.456 | 6.05 | | | 1.272 | 2.62 |
| 400 | 0.456 | 6.32 | 0.804 | 0.54 | 1.34 | 5.77 |
| 500 | 0.458 | 7.61 | 0.814 | 0.41 | 1.342 | 5.79 |
| 1000 | 0.466 | 11.0 | | | 1.336 | 8.40 |
| 2000 | 0.332 | 18.0 | 0.984 | 3.70 | 1.334 | 17.60 |
| 6000 | 0.362 | 38.1 | | | 1.406 | 38.10 |

Table 10(b). Reduction of CuPcTS in the presence of p-chlorophenol in microemulsion.

| Scan rate | Peak 1 | | Peak 2 | | Peak 3 | |
|---|---|---|---|---|---|---|
| mVs⁻¹ | -E(V) | Current(mA) | -E(V) | Current(mA) | -E(V) | current(mA) |
| 5 | 0.382 | 0.79 | | | 0.994 | 0.28 |
| 25 | 0.394 | 0.77 | | | 1.162 | 1.01 |
| 50 | 0.458 | 1.27 | | | 1.176 | 1.30 |
| 300 | 0.474 | 5.27 | 0.814 | 2.77 | 1.240 | 2.28 |
| 400 | 0.504 | 8.30 | 0.804 | 4.00 | 1.254 | 4.00 |
| 500 | 0.492 | 6.80 | 0.854 | 3.70 | 1.26 | 3.40 |
| 1000 | 0.508 | 11.4 | 0.868 | 4.50 | 1.28 | 12.3 |
| 2000 | 0.484 | 24.4 | 0.998 | 32.30 | 1.41 | - |
| 5000 | 0.544 | 36.1 | 0.860 | 11.50 | 1.408 | 27.5 |
| 6000 | 0.508 | 54.7 | 0.804 | 29.30 | 1.044 | 24.9 |

These results show that p-Chlorophenol is better reduced in isotropic water/acetonitrile media than in bicontinuous DDAB microemulsion. A possible explanation for the observed results is that in microemulsion reaction occurs in an adsorbed film of DDAB surfactant on the surface of the electrode [9]. If the substrate is not taken into the thin film on the surface of the electrode, then little or no reaction may be observed. This could be the case for p-chlorophenol. However, in acetonitrile/water system no such film formation is required and therefore p-chlorophenol is catalytically reduced by CuPcTS in this media.

In DDAB microemulsion, high rate enhancement have been found for 1,2-dibromobutane (DBB) reduction in presence of metal phthalocyanine tetrasulphonate mediators [9]. Thus, this substrate was used as a model for bulk electrolysis in n-dodecane/DDAB/water microemulsion with CuPcTS mediator (catalyst). Since species that are polarographically electroactive are known to be UV/VIS active [37], UV/VIS spectroscopic technique was used to monitor the mechanism for electrocatalytic reduction of DBB in DDAB microemulsion with copper phthalocyaninetetrasulphonate (CuPcTS$^{4-}$) as the catalyst. In case of CuPcTS, the above observation has been found to be true [43].

Controlled potential electrolysis was performed on a two or three electrode set up with carbon felt as the working electrode, platinum wire as the anode, and the Ag/AgBr or SCE as the reference. Carbon felt working electrodes have been used in bulk electrocatalytic reduction of toxic substrates with success [5]. The media used in this work is attractive due to the high conductivity of DDAB microemulsion. Our n-dodecane/DDAB/water microemulsion had conductivity of the order of $1.73 \times 10^{-3} \pm 1.00 \times 10^{-5}$ $\Omega^{-1}$ cm$^{-1}$ . Other workers have found similar values for these type of microemulsions [7].

For electrolysis, the potentials were controlled at -0.77V vs SCE for the first diffusion controlled reduction and -1.42V vs SCE for the second diffusion controlled reduction (figure 11) or -1.20V vs Ag/AgBr. Typical results for the former are tabulated in tables 11 and 12, and representative UV/VIS spectra depicted in figures 12 and 13a.

Table 11: Effect of electrolysis at -0.77V on the UV/VIS spectra of $CuPcTS^{4-}$ in DDAB microemulsion.

| Solution | 1st Band $\lambda_{max}$ | A | 2nd Band $\lambda_{max}$ | A | 3rd Band $\lambda_{max}$ | A | 4th Band $\lambda_{max}$ | A | 5th Band $\lambda_{max}$ | A |
|---|---|---|---|---|---|---|---|---|---|---|
| 2.0 mM CuPcTS | 672 | 0.755 | 640 | 0.125 | 605 | 0.165 | 337 | 0.295 | 248 | 0.17 |
| [a]After 4 hr Electrolysis | 672 | 0.595 | 640 | 0.160 | 605 | 0.160 | 337 | 0.23 | 245 | 0.385 |
| [b]After add. of 20 mM DBB | 672 | 0.605 | 640 | 0.125 | 605 | 0.125 | 335 | 0.255 | - | - |

[a] After 4 hour electrolysis of $CuPcTS^{4-}$/microemulsion solution.

[b] After addition of substrate, dibromobutane, to the electrolyzed solution.

Table 12: Effect of electrolysis at -1.42V on the UV/VIS spectra of CuPcTS in DDAB microemulsion.

| Solution | 1st Band $\lambda_{max}$ | A | 2nd Band $\lambda_{max}$ | A | 3rd Band $\lambda_{max}$ | A | 4th Band $\lambda_{max}$ | A | 5th Band $\lambda_{max}$ | A |
|---|---|---|---|---|---|---|---|---|---|---|
| 2mM CuPcTS | 675 | 0.75 | 645 | 0.15 | 607 | 0.15 | 340 | 0.29 | 253 | 0.13 |
| [a]After 4 hr. Elect. | 675 | 0.41 | 645 | 0.08 | 607 | 0.08 | 340 | 0.13 | 253 | 1.01 |
| [b]After add. 20m DBB | 675 | 0.41 | 645 | 0.08 | 607 | 0.08 | 340 | 0.15 | 245 | 1.01 |
| [c]Before ele. presence of DBB | 675 | 0.75 | 645 | 0.16 | 607 | 0.16 | 340 | 0.30 | 246 | 1.14 |

[a]After electrolysis for 4 hours. [b]After addition of dibromobutane (DBB). [c]Before electrolysis in the presence of DBB.
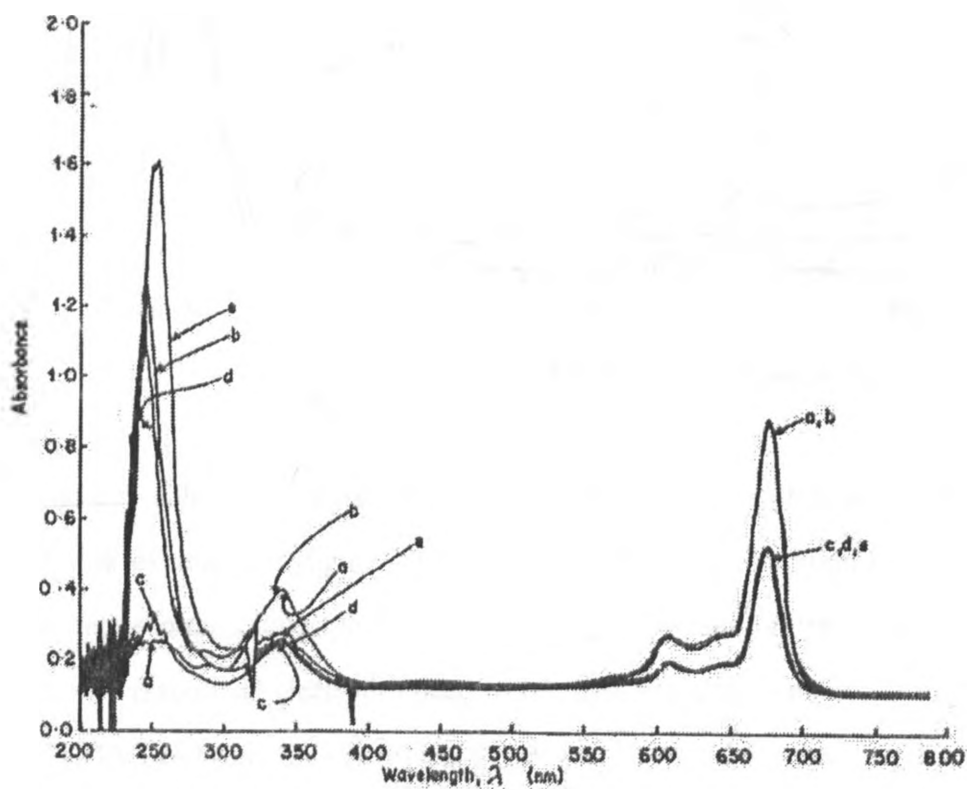
## FIGURE 11: Linear Sweep voltammogram of 0.4mM CuPcTS in Acetonitrile/water (1/1 v/v)
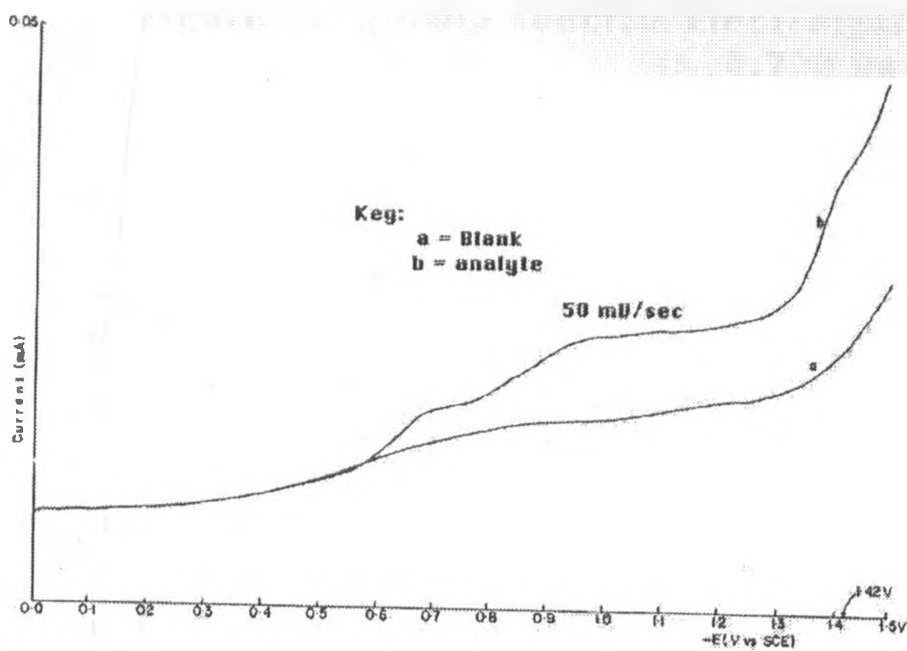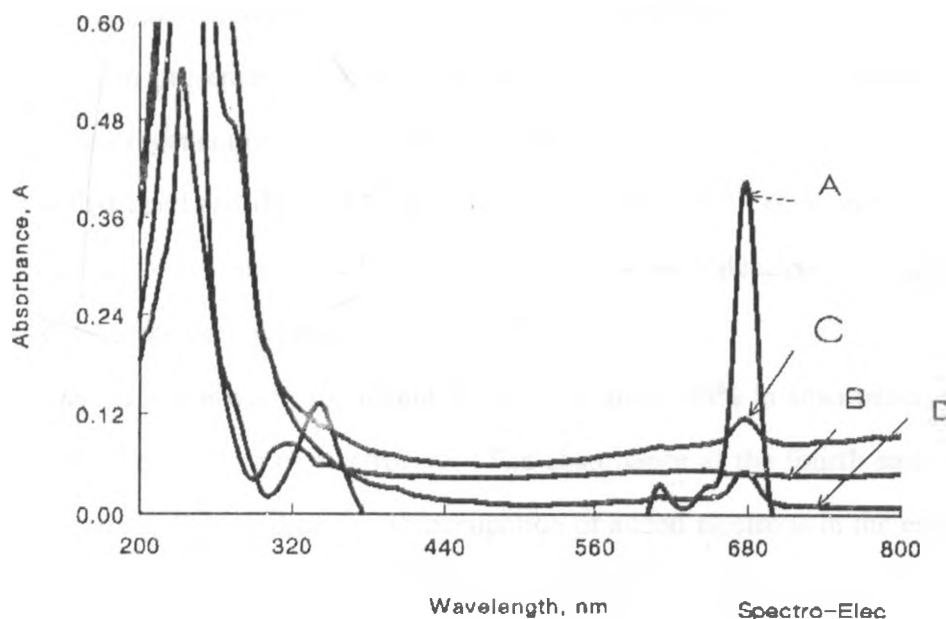
# Figure 12: UV/VIS Spectra-Electrolysis at -0.77V vs SCE
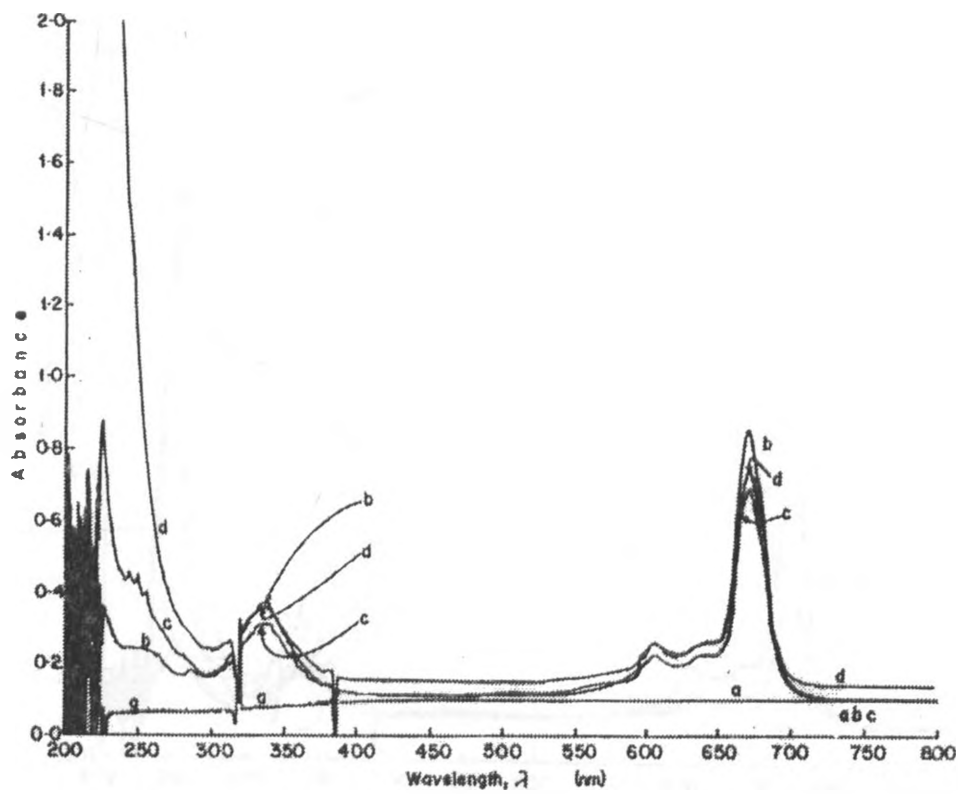
Figure 13a: UV/VIS Spectra-Electrolysis at -1.42V vs SCE

Figure 13b: UV/VIS Spectra-electrolysis at -1.20V vs Ag/AgBr

According to table12, there is little increase in absorbance, following addition of substrate. Latter experiments (figure 13b) indicate adequate equilibration time is required for reaction between the catalyst and substrate to occur. In addition the counter electrode like copper wire (sacrificial electrode) need to be used in order to minimize oxidation of bromide of DDAB to bromine, which give a yellow colour to electrolysis products. When copper wire is used as the counter electrode the resulting electrolysis products were colourless (figure 13b).

Figure 13b shows the effect of complete reduction of CuPcTS at the second reduction wave and the influence of addition of substrate. The electrolysis was   performed with a three electrode setup. A BAS 100 electrochemical Analyzer was used for potential control and a Perkin Elmer Lambda 6 UV/VIS Spectroscopic instrument with software control was used for recording the spectra. Potential was controlled at -1.20V vs Ag/AgBr with a copper wire counter electrode in a salt bridge connected to the electrolytic solution via a vycor tip, and a carbon felt cathode connected to the external circuit via a Ag wire.

76

Spectra A is for the CuPcTS before electrolysis, spectra B is for CuPcTS after electrolysis for 18 hours, spectra C is after addition of 1,2-dibromobutane (substrate) to the electrolyzed solution, and spectra D is after allowing the mixture in C to stand for three hours with continued supply of nitrogen (i.e. an inert atmosphere). The peak at 680 nm starts to grow in presence of added substrate. Thus it is clear that presence of added substrate causes regeneration of the CuPcTS catalyst .

Only the first band and the fourth band were well formed in DDAB microemulsion (fig. 12 and 13a). Thus, these bands were used to try and deduce the mechanism of electrocatalytic reduction of DBB by CuPcTS catalyst .

From table 12, there was a significant decrease of about 45% in absorbance at the first band $\lambda_{675nm}$ after 4 hours of electrolysis. The absorbance at the fourth band decreased by 55%. This decrease could be due to occupation of added electrons in the excited states of $CuPcTS^{4-}$. At -1.42V, addition of 1,2-dibromobutane (DBB) is expected to cause a regeneration of the oxidized form ($CuPcTS^{4-}$) of the CuPcTS mediator [9]. For CuPc the band at 665nm (675 nm in table 12 for CuPcTS) has been assigned to correspond to the first electron transfer [43]. Table 11 shows that addition of the first electron causes this band to decrease in absorbance. This is in line with the above earlier reports. The fact that addition of DBB after electrolysis at -1.42V only cause a slight increase in absorbance at this wavelength (figure 13b) suggests that during electrocatalytic reduction of DBB by the $CuPcTS^{6-}$ state, $CuPcTS^{6-}$ may not be reoxidized back to the $CuPcTS^{4-}$ state significantly.

On electrolysis at the second wave (i.e., - 1.42V), reduction of $CuPcTS^{4-}$ to the $CuPcTS^{6-}$ state resulted on a decrease in absorbance at the fourth band, 340nm (table 12). Addition of substrate 1,2-dibromobutane, resulted in a significant increase ( 23.1%) in absorbance at this wavelength. These results show that there is some reaction between the reduced $CuPcTS^{6-}$ state and DBB. A qualitative observation noted during the course of this work indicated that electrolysis at -1.42V caused the blue $CuPcTS^{4-}$ in microemulsion

to fade in colour. The blue colour started intensifying on addition of DBB. No such colour changes were observed when the potential was controlled at -0.77V.

The above results are in agreement with suggested catalytic reduction mechanism of organohalides    [24] as shown in Scheme IV.

Therefore, a tentative mechanism for electrocatalytic reduction of 1,2-dibromobutane in bicontinuous; n-dodecane/DDAB/water microemulsion by $CuPcTS^{4-}$ is given in scheme IV below.

## SCHEME IV

$$CuPcTS^{4-} + e \rightleftharpoons CuPcTS^{5-} \qquad 24)$$

$$CuPcTS^{5-} + e \rightleftharpoons CuPcTS^{6-} \qquad (25)$$

$$CuPcTS^{6-} \quad + \quad CH_3CH_2CHCH_2Br$$
$$| \, k \qquad\qquad\qquad\qquad\qquad | \atop Br$$

$$CuPcTS^{5-} + CH_3CH_2\overset{\cdot}{C}HCH_2Br + Br \quad (26)$$

$$CH_3CH_2CH = CH_2 + Br^{\cdot} \qquad (27)$$

$$CuPcTS^{6-} + Br \longrightarrow CuPcTS^{5-} + Br^{-} \quad (28)$$
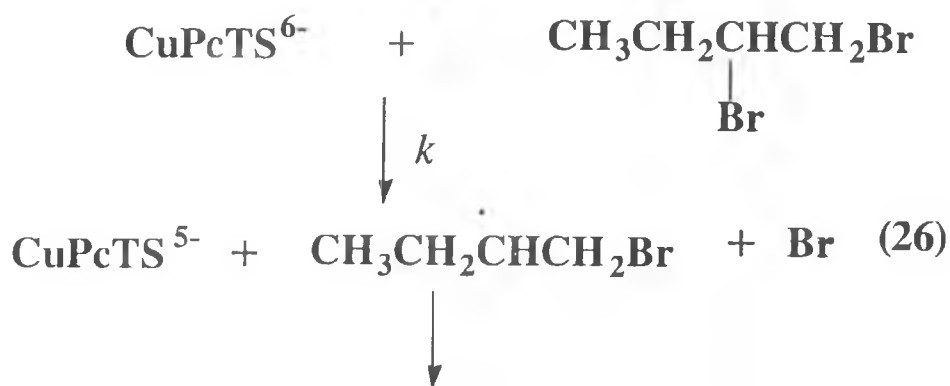
It is this regeneration of $CuPcTS^{5-}$ near the electrode (eq. 26 and 28) surface that is responsible for the observed catalytic current [9].

We felt that it would be a good idea to compare the voltammetric behavior of copper phthalocyanine (CuPc) with its sulphonated derivative, CuPcTS. This compound, CuPc, was not readily available in our local market and we decided to start with some

preliminarily work on its laboratory synthesis. Below we give some linear sweep voltammetric results obtained with our synthesized material.

## 3.6 VOLTAMMETRY OF LABOLATORY SYNTHESIZED COPPER(II) PHTHALOCYANINE IN DDAB MICROEMULSION.

Robertson and Co-workers have carried out complete X-ray structure determinations on some metal phthalocyanines [26]. The planar structure does not vary greatly in dimension from metal to metal and is the same for all of the metallic ions, irrespective of whether they ordinarily form planar coordination compounds or tetrahedral ones. Thus, the structure of copper phthalocyanine is as shown below (figure 14):



## Figure 14. Copper(II) phthalocyanine
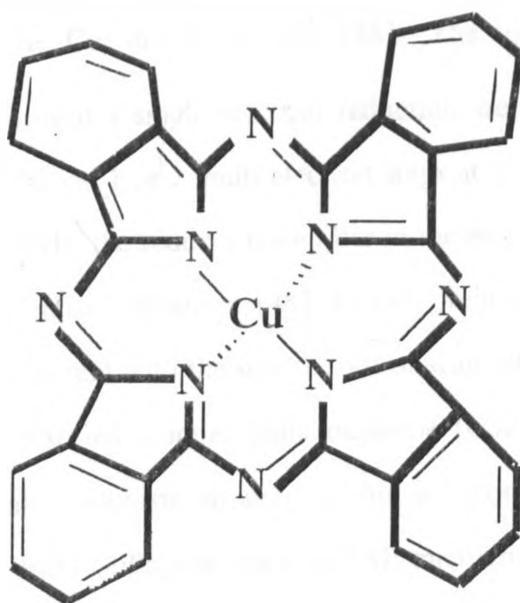
Even though the use of metal phthalocyanine as mediators in electrocatalytic reduction, has been extensively studied [5, 10, 22, 47, 48], the use of copper phthalocyanine (CuPc) for this purpose has received less attention. Much more attention has been on the use of the tetrasulphonated derivative of copper phthalocyanine in mediated electrochemical reduction reactions [9, 10, 49].

Neutral mediators cobalt and iron phthalocyanine (CoPc and FePc) have been found to reduce alkyl vicinal dihalides in DDAB microemulsion [10]. These complexes adsorb on carbon electrodes [10]. Zinc phthalocyanine (ZnPc) has been used effectively as a mediator for bulk dehalogenation of polychlorinated biphenyls (PCBs) [10]. Lieber and Lewis have given a brief account on electrocatalytic reduction of aqueous solutions of $CO_2(g)$ to $CO(g)$ mediated by cobalt phthalocyanine (CoPc) [48]. These workers found that the ease of reduction of the CoPc complex allows the $CO_2$ transformation to proceed at a much lower overpotential, yet with faster rates, than in previous catalytic systems for CO production.

Beck, F. et. al. studied the polarographic behavior of phthalocyanine with various central atoms (Fe, Co, Ni, Cu) in 85% $H_2SO_4$ [48]. The complexes of phthalocyanine with Co, Ni, and Cu showed a single electron reduction step in a solution from which oxygen had been removed and 1 or 2 multi-electron steps at more negative potentials (Vs. SCE). In the case of Cu(II), the reduction step lies in the negative region. This step was found to involve a 2 electron transition [48]. In our preliminary work with CuPc, we report variation of peak current with the square root of scan rate.

As synthesized and purified, copper phthalocyanine (CuPc) was blue in colour. It dissolved in DDAB microemulsion to give a blue solution. Figure 15 gives typical voltammograms of a 0.4mM CuPc solution in DDAB microemulsion at various scan rates. The results are summarized in table 13.

Figure 15: Linear Sweep voltammograms of Synthetic Copper Phthalocyanine in Microemulsion
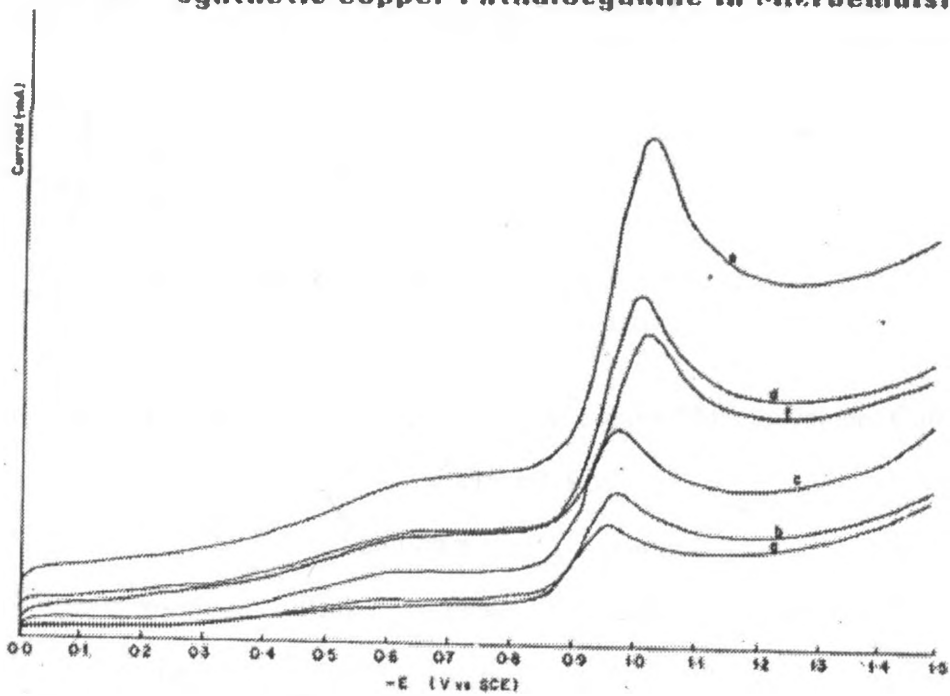
**Fig. 16: 0.4 mM CuPc in microemulsion**
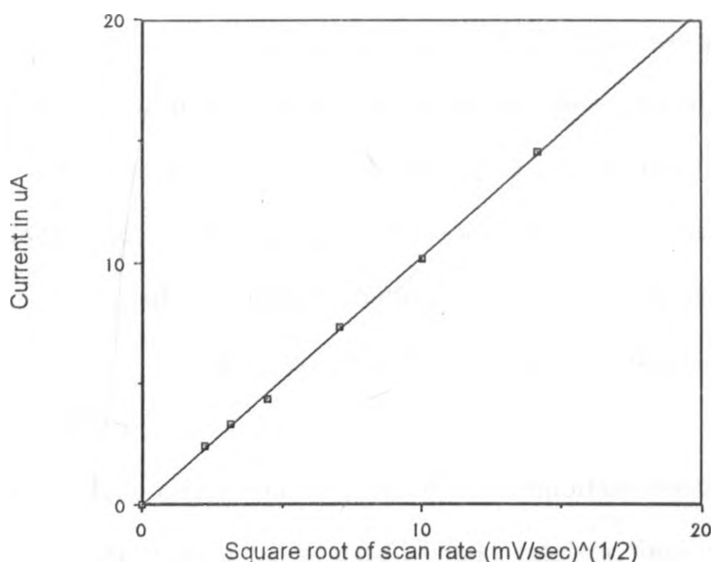**Scan rate studies**

Table 13 Linear sweep voltammetry of synthetic copper Phthalocyanine (CuPc) in DDAB
microemulsion.

| Scan rate, $v$ (mv/sec) | Sq. root of Scan rate, $v^{1/2}$ (mv/sec)$^{1/2}$ | Solution a | | solution b | | solution c | |
|---|---|---|---|---|---|---|---|
| | | Peak potential, -E vs SCE | Peak current, mA | Peak potential, -E vs SCE | Peak current, mA | Peak potential, -E vs SCE | Peak current mA |
| 200 | 14.14 | 1.02 | 14.51 | 1.03 | 13.63 | 1.04 | 18.24 |
| 100 | 10.00 | 1.02 | 10.16 | 1.01 | 8.78 | 1.04 | 12.20 |
| 50 | 7.07 | 1.01 | 7.29 | 1.00 | 7.45 | 1.01 | 9.25 |
| 20 | 4.47 | 0.97 | 4.31 | 0.98 | 4.78 | 0.99 | 6.00 |
| 10 | 3.16 | 0.98 | 3.29 | 0.96 | 3.53 | 0.98 | 4.39 |
| 5 | 2.24 | 0.96 | 2.43 | 0.97 | 2.31 | 0.97 | 2.43 |

solution a: *0.4 mM CuPc,*  solution b: *0.4 mM CuPc + 4.0 mM p-Chlorophenol,*

solution c: *0.4 mM CuPc + 4mM p-chlorophenol + 0.8 mM DBB*

In case of CuPc mediator alone a plot of peak current as a function of the square root of
scan rate gives a straight line characteristic for diffusion controlled processes (Fig. 16).

From table 13, addition of p-chlorophenol does not cause any improvement in observed peak current. There was a slight general decrease in peak current on addition of p-chlorophenol and this could be attributed to breakdown of microemulsion structure. Addition of 1,2-dibromobutane (DBB) resulted in a marked increase in peak current. This reflects the ease of mediated reductive dehalogenation of vicinal dihalides by phthalocyanines. Thus, copper phthalocyanine can be used to mediate electrocatalytic dibromination of 1,2-dibromobutane but not electrocatalytic dechlorination of p-chlorophenol in didodecyldimethylammonium bromide DDAB/n-dodecane/water microemulsion.

The catalytic effect obtained for DBB is important because the water insoluble copper phthalocyanine (CuPc) can be used to make catalytic films on electrodes as was found for cobalt and iron phathalocyanine (CoPc and FePc) [22]. Direct reduction of DBB occurs at about -1.82V vs SCE [9]. Table 14 points that this substrate could be reduced at about -1.00V vs SCE in presence of CuPc mediator. Thus, CuPc lowers the overpotential for reduction of DBB by about 0.82V.

A plot of E (V vs SCE) against $\log((i_p-i)/i)$ gives a straight line whose slope gives the characteristic value of n(number of electrons transferred) as 1 (Fig. 17).

Table 14: Variation of current with potential near the peak at a scan rate of 100mV/sec.

| Potential V vs SCE | Current i (mA) | Peak current ip (mA) | log((ip-i)/i) |
|---|---|---|---|
| -0.93 | 2.84 | 14.51 | 0.614 |
| -0.94 | 3.77 | 14.51 | 0.455 |
| -0.95 | 4.83 | 14.51 | 0.302 |
| -0.96 | 5.62 | 14.51 | 0.199 |
| -0.97 | 7.07 | 14.51 | 0.022 |
| -0.98 | 8.09 | 14.51 | -0.100 |

fig. 17 0.4 mM CuPc in Microemulsion
Var. of current with potential near peak
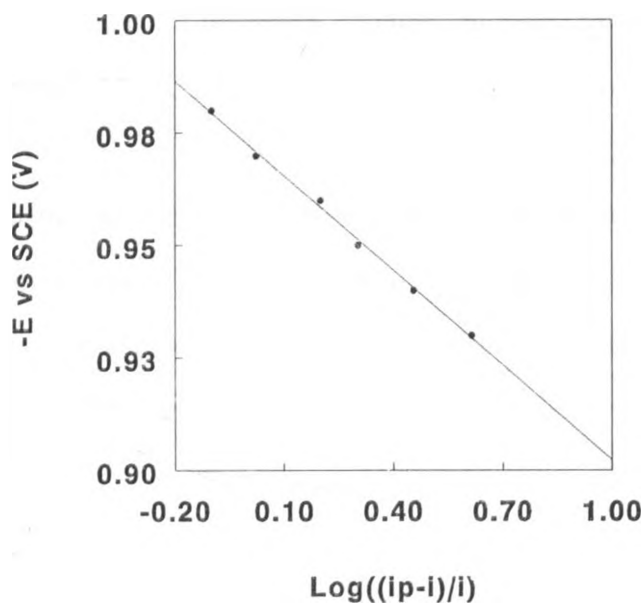


The linear E vs $\log((i_p-i)/i)$ plot (Fig. 17) over the rising portion of the voltammogram indicate that charge transfer for CuPc in DDAB microemulsion is reversible.

Table 15: The peak current function $ip/v^{1/2}$ for CuPc in DDAB microemulsion.

| Scan rate, (mv/sec) | Square root of scan rate ,$v^{1/2}$ | Peak current ip (mA) | $ip/v^{1/2}$ |
|---|---|---|---|
| 200 | 14.14 | 14.15 | 1.03 |
| 100 | 10.00 | 10.16 | 1.02 |
| 50 | 7.07 | 7.29 | 1.03 |
| 20 | 4.47 | 4.31 | 0.96 |
| 10 | 3.16 | 3.29 | 1.04 |
| 5 | 2.24 | 2.43 | 1.08 |

As expected for reversible systems, the peak current function $ip/v^{1/2}$ is independent of scan rate (table 15 ). The fact that we obtained a value of n slightly less than 1 (n = 0.85) implies that CuPc in DDAB microemulsion is not a completely reversible system.

Finally, as synthetic copper phthalocyanine portrayed some appreciable catalytic dehalogenation of vicinal dihalides, copper phthalocyanine is a potential candidate for the development of catalytic electrodes of surfactant intercalated clay films for electrochemical catalysis. This is possible due to the inherent insolubility of copper pthalocyanine in water.

## 3.7  THEORETICAL CALCULATIONS.

DDAB microemulsion media was observed to absorb in the UV region of the UV/VIS spectra. This could be due to scattering of light by DDAB microemulsion. Since the stability of the two reduced states of copper phthalocyanine tetrasulphonate (i.e. $CuPcTS^{6-}$ and $CuPcTS^{5-}$) in known UV/VIS solvent might be questionable, a novel approach might be to obtain the molecular energy level diagrams for the ground state of $CuPcTS^{4-}$ and its two reduced states ( $CuPcTS^{6-}$ and $CuPcTS^{5-}$). This could possibly be achieved by making use of the more recent semiemperical MNDO and AMI methods.

In our work, we had a chance to attempt the above approach on recalcitrant organohalides. The work involved correlation of molecular and quantum mechanically calculated parameters with observed reduction potentials and half-wave potentials for various substrates. Allingers MM2 molecular mechanical program was used for geometry optimization. Finally eigenvectors and bond orders were obtained by use of the semi empirical MNDO method. Heats of formation and lowest unoccupied molecular orbital energy results from these calculations are reported in this work. We were not able to have a similar treatment on the ground state of copper phthalocyaninetetrasulphonate together with its two reduced states due to the fact that our geometry optimizing program, Allingers MM2, did not have parameters for metallic elements such as copper atoms. Such a treatment has been given for unsulphonated copper phthalocyanine (CuPc) [42].

## TABLE 16: **MM2 CALCULATION RESULTS**

| Compound | Steric Energy, KCAL | Dipole Moment (Debye) | Heat of Formation, KCAL | Strainless Heat of Formation, KCAL | Energy from Planar SCF Calculation |
|---|---|---|---|---|---|
| DDT | 61.7295 | 1.280 | 43.90 | -20.34 | -1410.92 |
| 1,1-DPE | -1.5406 | 0.347 | 33.83 | 29.85 | -1410.94 |
| 1,3-DBB | 70.2265 | 2.86 | 42.10 | -25.10 | |
| 1,2-DBCH | 50.8111 | 2.741 | 19.35 | -26.94 | |
| TCA | 63.7156 | 2.759 | -63.72 | -128.28 | |
| DCB | -0.2004 | 2.673 | -4.20 | -4.14 | -705.46 |
| DDD | 21.2851 | 2.436 | 12.75 | -11.19 | -1410.77 |
| DDE | 40.0792 | 0.095 | 164.18 | 118.66 | |
| 1,2-DBB | 78.2837 | 1.279 | 50.16 | -25.10 | -1706.38 |
| 1,1-DPET | 22.2398 | 0.000 | 92.78 | 59.60 | |

**KEY**:  DDT:  P-Dichlorodiphenyltrichloroethane

1,1-DPE:  1,1- Diphenylethane

1,3-DBB:  1,3- Dibromobutane

1,2-DBCH: 1,2- Dibromocyclohexane

TCA:  Trichloroacetic acid

DCB:  1,2-dichlorobenzene

DDD:  p-Dichlorodiphenyldichloroethane

DDE:  p-Dichlorodiphenyldichloroethene

1,2-DBB:  1,2-Dibromobutane

1,1-DPET: 1,1-Diphenylethene

TABLE 17: **MOPAC OUTPUT**

| CPD | Heat of formation (KCAL/mol) | Dipole Moment (Debye) | Ionization Potential (EV) | HOMO (Energy, EV) | LUMO (Energy, EV) | Electronic Energy (EV) |
|---|---|---|---|---|---|---|
| DDT | 38.87 | 1.07 | 9.82209 | -9.82209 | -1.36814 | -21145.88 |
| DDE | 79.66 | 0.72 | 9.16961 | -9.16961 | -1.46952 | -18399.55 |
| DDD | 28.27 | 1.74 | 9.76588 | -9.76588 | -0.60472 | -18998.25 |
| 1,1-DPE | 47.93 | 0.10 | 9.24214 | -9.24214 | 0.23881 | -11983.48 |
| 1,1-DPET | 116.56 | 0.31 | 8.29609 | 180.240 | -0.28783 | -11271.66 |
| DCB | 9.62 | 2.71 | 9.86057 | -9.86057 | -0.47913 | -5548.55 |
| TCA | -83.03 | 2.23 | 12.24682 | -12.24682 | -1.92250 | -5941.97 |
| 1,2-DBB | 119.97 | 1.89 | 9.09660 | -9.09660 | -1.96392 | -4504.01 |
| 1,2-DBCH | 341.78 | 5.08 | 6.7356 | -6.76356 | -3.54664 | -6483.84 |

Table 18: Correlation of Voltammetric $E_{1/2}$ with Theoretically obtained Heat of formation and Lowest Unoccupied Molecular Orbital for Organohalides.

| Compound | $E_{1/2}$ V vs SCE | MM2, $H_f$ | MNDO, $H_f$ | LUMO |
|---|---|---|---|---|
| 1,2-DBCH | -1.87 | 19.35 | 341.78 | -3.55 |
| 1,2-DBB | -1.80 | 50.16 | 119.97 | -1.96 |
| TCA | -1.67 | -63.72 | -83.03 | -1.92 |
| DDT | -1.37 | 43.90 | 38.87 | -1.39 |

Table 19: Theoretically predicted $E_{1/2}$ by MM2 and MNDO methods.

| COMPOUND | $E_{1/2}$ from MM2 | $E_{1/2}$ from MNDO | $E_{1/2}$ from LUMO |
|---|---|---|---|
| DDT | -1.58 | -1.36 | -1.37 |
| 1,1-DPE | -1.74 | -1.50 | **** |
| 1,3-DBB | -1.60 | **** | **** |
| 1,2-DBCH | -2.14 | -1.84 | **** |
| TCA | **** | -1.72 | -1.68 |
| DCB | **** | -0.272 | **** |
| DDD | -2.48 | -1.11 | **** |
| DDE | **** | -1.71 | -1.45 |
| 1,2-DBB | -1.50 | -1.78 | -1.69 |
| 1,1-DPET | ***** | -1.78 | ***** |

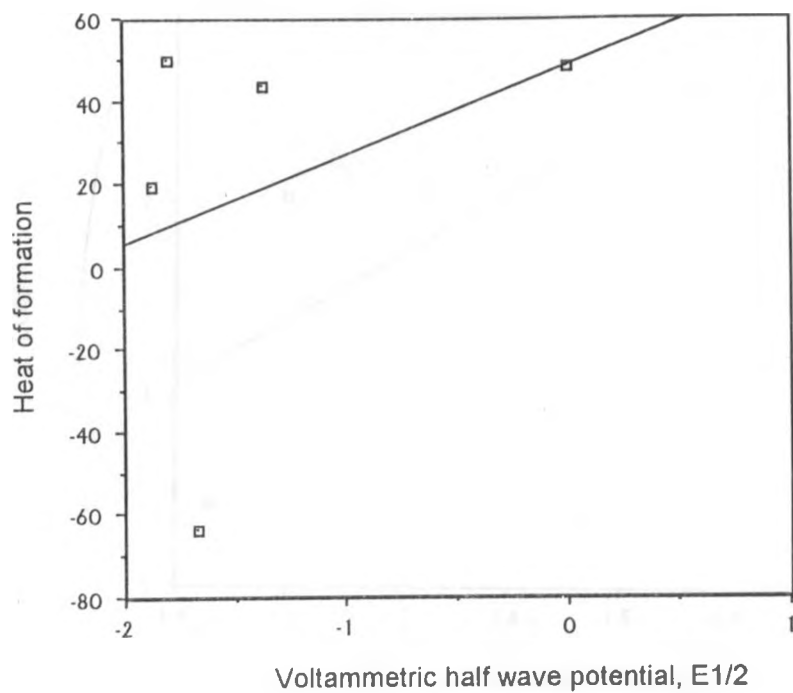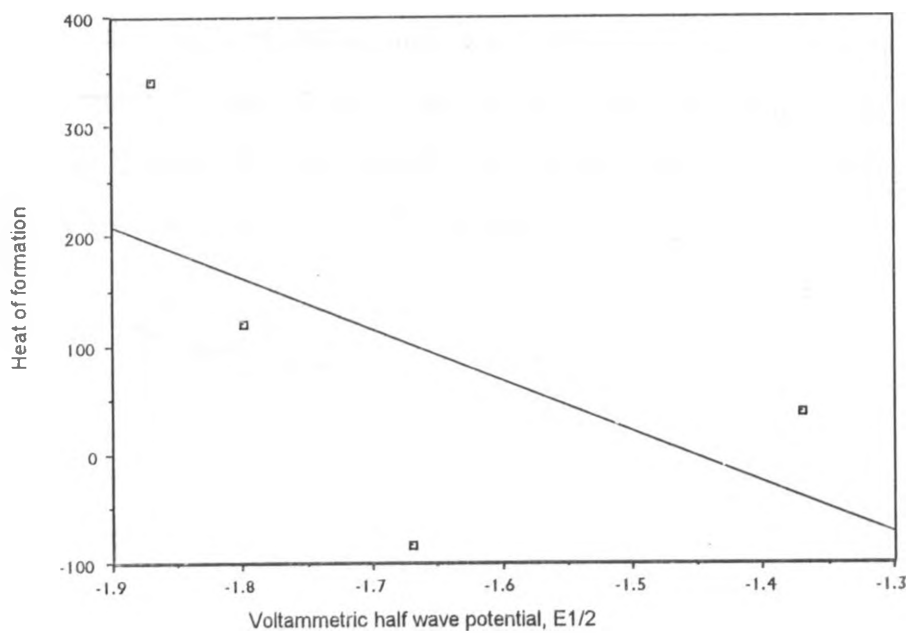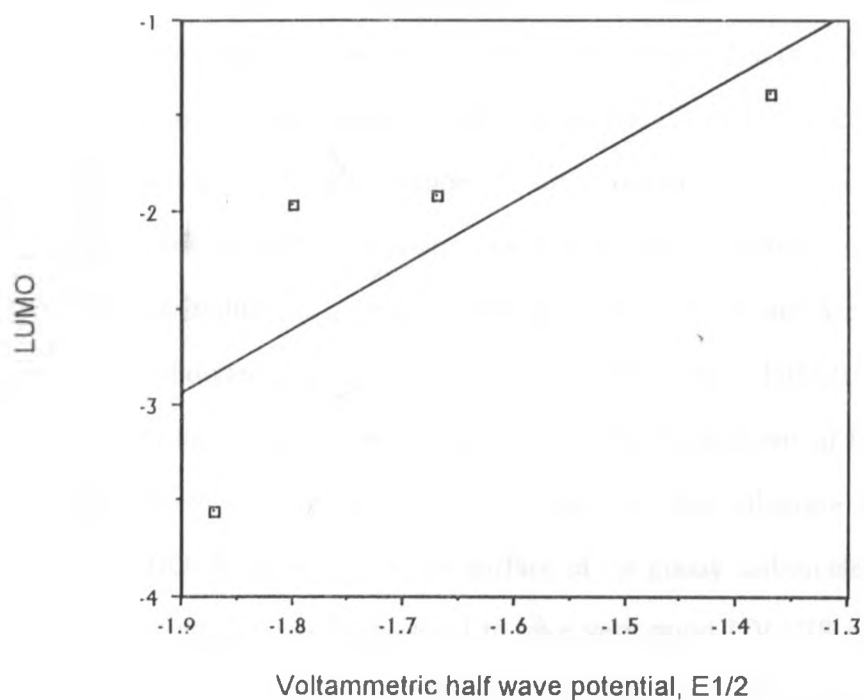**Fig. 18a: Theoretical calc. results; MM2, Heat of formation**



**Fig. 18(b): Theoretical Calc. results; MNDO method, heat of formation**

## Fig. 18(c): Theoretical Calc. results;
## Lowest unoccupied Molecular orbital



Voltammetric half wave potential, E1/2

Better linearity was obtained for both MNDO methods as compared to MM2 heat of formation. Thus the MNDO LUMO and Heat of formation methods can be used to predict theoretically the expected redox half wave potential of a given organohalide. On comparing tables 19 and 18 it is obvious that the MNDO methods predicts more acceptable $E_{1/2}$ values for the organohalides whereas the MM2 method generally gives significantly lower $E_{1/2}$ values (i.e. more negative values).

## SUMMARY AND CONCLUSIONS:

The main conclusions that emerge from the results obtained in our work are as follows: Copper phthalocyanine tetrasulphonic acid tetrasodium (CuPcTS) is a useful catalyst for reductive electrochemical dehalogenation of toxic organohalide pollutants. High rate enhancements by copper phthalocyanine tetrasulphonic acid, tetrasodium have been found for electrochemical reduction of p-chlorophenol in isotropic water acetonitrile media as compared to didodecyldimethyl ammonium bromide DDAB/n-dodecane/water microemulsion media. This was attributed to possible breakdown of the microemulsion structure on addition of this substrate and failure of this substrate to enter into the adsorbed film of DDAB surfactant on the surface of the glassy carbon electrode.

Copper phthalocyanine has been found to give very good UV/VIS spectra in aqueous media and also good VIS spectra in DDAB microemulsion. Other fascinating results were its inherent stability in solution as was found with the UV/VIS spectroscopic technique. On the basis of these findings, the UV/VIS spectroscopic technique was used to monitor the mechanism of electrocatalytic reduction of 1,2-dibromobutane in DDAB microemulsion mediated by copper phthalocyanine tetrasulphonic acid, tetrasodium at carbon felt cathodes. The results suggests that during the reductive debromination of 1,2-dibromobutane, the active form of copper phthalocyanine, $CuPcTS^{6-}$ is reoxidized back to the $CuPcTS^{5-}$ state and not the $CuPcTS^{4-}$ (ground state). Thus, the combination of two quite different techniques, electrochemistry and spectroscopy, has proved to be an effective approach for mechanistic studies involving mediated dehalogenation reactions in surfactant microstructures.

The copper phthalocyanine synthetic approach appears promising. First, the actual reaction (synthesis) occurs in a single batch. Secondly, the purification is not a problem as the impurities are either soluble in water or in organic solvents whereas copper phthalocyanine is water insoluble and almost virtually insoluble in common organic solvents. The solubility of copper phthalocyanine in DDAB/n-dodecane/water

microemulsion is a very important property since this compound needs not be derivatised (such as sulphonation) in order for its redox applications to be studied. In this report, the laboratory synthesized copper phthalocyanine gave a very well defined reversible cathodic peak at about -1.0V vs SCE at a glassy carbon electrode. This peak was found to correspond to a single electron transfer. An attempt to use copper phthalocyanine for mediated dechlorination of p-chlorophenol proved futile. Such mediated reactions were possible for vicinal dihalides such as 1,2-dibromobutane. In this case, copper phthalocyanine was found to lower the overpotential for reduction of 1,2-dibromobutane by about 0.82V compared to 0.40V for copper phthalocyanine tetrasulphonic acid, tetrasodium.

Although the ultimate goal of theoreticians is to make experiments obsolete, we have found the two approach inseparable in case of mediated reductive dehalogenation of recalcitrant substances. We have obtained some preliminary results on the use of molecular and quantum mechanically calculated parameters to predict the voltammetric behavior of halogenated compounds and some possible metabolites. We have presented a brief account of such an approach and voltammetric $E_{1/2}$ have been found to have a linear relationship with MM2 (molecular mechanics) heats of formation and MOPAC (quantum mechanics) heats of formation and lowest unoccupied molecular orbital (LUMO). From these results, voltammetric $E_{1/2}$ for various halogenated compounds and some metabolites have been suggested.

Preliminary studies involving pH control for aqueous CuPcTS indicated possible decrease in the overpotential for CuPcTS mediated dehalogenation of organohalides at low pH.

# RECOMMENDATIONS:

To-date, only very few toxic recalcitrant substances have been subjected to mediated electrocatalytic reductions. Since such a study has proved to be effective for copper phthalocyanine tetrasulphonic acid, tetrasodium mediated dehalogenation of toxic p-chlorophenol in isotropic water/acetonitrile media and 1,2-dibromobutane in didodecyldimethylammonium bromide DDAB/n-dodecane/water microemulsion, more halogenated substrates need to be studied.

Since theoretical methods avail data faster than experimental methods, a novel approach suggested for mediated electrocatalytic reduction of organohalides involves obtaining the quantum mechanics parameters for the mediator (catalyst) and that for substrates, correlate them with experimentally obtained $E_{1/2}$ for known standard molecules, and then be able to predict the voltammetric $E_{1/2}$ for the other halogenated substrates from the relationship obtained.

As pH was found to cause a marked change in the voltammetric behavior of copper phthalocyanine tetrasulphonic acid, tetrasodium, all experiments with this catalyst should be carried out in buffered media. For the first diffusion controlled wave, pH 4.0 was found to be the most ideal. For the second diffusion controlled wave, studies need to be carried out in order to obtain the optimum pH.

Finally, as synthetic copper phthalocyanine portrayed some appreciable catalytic dehalogenation of vicinal dihalides, copper phthalocyanine is a potential candidate for the development of catalytic electrodes of surfactant intercalated clay films for electrochemical catalysis. This is possible due to the inherent insolubility of copper phthalocyanine in water.

# REFERENCES:

1. Horne, R.A., 1978. The chemistry of our environment, John Willey and sons, Inc., Toronto.

2. Wade, C.G., 1976. Contemporary chemistry, Macmillan Publishing Co., Inc., New York.

3. Haque, R., and Freed, V.H. 1975. Environmental dynamics of pesticides, New York.

4. Jones, M.M., 1978. Chemistry, man and society, Saunders College, Philadelphia.

5. Rusling, J.F., 1991. Controlling Electrochemical catalysis with surfactant microstructures, Acc. Chem. Res. 24, 75-81.

6. Dryhurst, G. and Niki, K., 1988. Redox chemistry and interfacial behavior of biological molecules, plenum publishing corporation.

7. Iwunze, M.O., Sucheta, A., and Rusling, J.F., 1990. Bicontinuous microemulsions as media for Electrochemical studies, Anal. Chem., 62, 644-649.

8. Owlia, A., Wang, Z., and Rusling, J.F. 1989. Electrochemistry and Electrocatalysis with Vitamin B12 in an AOT water-in-oil microemulsion, J.Am. chem. Soc., 111, 5091-5098.

9. Kamau, G.N., Hu, N., and Rusling, J.F. 1992. Rate Enhancement and Control in Electrochemical catalysis using a bicontinuous microemulsion. Langmuir, 8, 1042-1044.

10. Rusling, J.F., and Bobbitt, J.M. Results unpublished, dynamics of mediated electrochemical synthesis in microemulsions, Department of Chemistry, Box U-60, University of Connecticut, Storrs, CT 06269-3060.

11. Cairns, T., and Siegmund E.G., 1981, PCBs, regulatory and analytical problems, Anal. Chem. 53, 1183A-1193A.

12. Kunitake, T. and Shinkai, S., 1990, Catalysis by micelles, membranes and other aqueous aggregates as models of enzyme action, Advances in physical organic chemistry, vol. 17, 435-487.

13. Bunton, C.A. Nome, F., Quina, F.H., and Romsted, L.S., 1991, Ion binding and reactivity at charged aqueous interfaces, Acc. Chem. Res., 24(12), 357-364.

14.     Rusling J.F., Critical review for bard, Department of Chemistry (U-60), University of Connecticut, Storrs (1992).

15.     Proske, G.E.O., 1952, New technique for polarography of water-insoluble compounds Anal. Chem., 24, 1834-1837.

16.     McIntire, G.L., 1990, Micelles in analytical chemistry, Critical Review Anal. Chem. 21, 257-278.

17.     Van Galen, D.A., Maida, M. 1988, Irreversible self-assembly of monomolecular layers of a cobalt(II) hexadecyltetrapyridylporphyrin amphiphile at gold electrodes and its catalysis of oxygen reduction, Anal. Chem. 60, 1549-1553.

18.     Zhang, X., Bard, A.J., 1989, In-trough cyclic voltammetric studies of Langmuir-Blodgett monolayers of a surfactant derivative of $Ru(bpy)_3^{2+}$ at an indium-tin oxide electrode, J. Am. Chem. Soc. 111, 8098-8105.

19.     Chen. V., Evans, D.F., Unpublished results, Co-Ion specificity in ionic microemulsions, Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55 455.

20.     Chen. S.J., Evans, D.F., and Ninham, B.W. 1984, properties and structure of three component ionic microemulsion J. Phys. Chem., 88, 1631-1634.

21.     Adrieux C.P., Blocman, C. Dumus-Bouchiat, J.M., M'Halla, F., and Savéant, J.M., 1980, Homogeneous redox catalysis of electrochemical reactions (Part V. cyclic voltammetry), J. electroanal. Chemistry, 113, 19-40

22.     Hu, N. and Rusling, J.F., Surfactant-Intercalated Clay films for electrochemical catalysis.  Reduction of trichloroacetic acid.  Department of Chemistry, Box U-6-, University of Connecticut, Storrs, Connecticut 06269-3060.

23.     Andrieux, C.P., Gelis, L., Savéant, J-M., 1990, Outer-sphere inner-sphere processes in organic chemistry reactions of trifluoromethyl bromide with electrochemically generated aromatic anion radicals and sulfur dioxide anion radicals, J.Am. Chem. Soc. 112, 786.

24. Huang, Y. and Wayner, D.D.M., 1993, Selective catalytic debromination by $C_{60}$ mono-di-, and trianion, J. Am. chem. Soc., 115 (1), 367-368.

25. Linstead, R.P., 1934. Phthalocyanines Part I. A new type of synthetic colouring matters, Journal of the Chemical Society, 1016-1017.

26. Bailer, J.C. and Busch, D.H., (1956), The chemistry of the coordination compounds. Reinhold publishing corporation, New York.

27. Dent C.E., and Linstead R.P. (1934) Phthalocyanines part IV. Copper phthalocyanines. Journal of the chemical society, 1027-1031.

28. Wilkinson, G., Gillard, R.D., and McCleverty, J., 1987, Comprehensive coordination chemistry. The synthesis, Reactions, properties and applications of coordination compounds, vol. 2, Pergamon press, Oxford.

29. Wilkinson, G., Gillard, R.D., and M. Cleverty, J. 1987, Comprehensive coordination chemistry. Theory and background, vol. 1, Pergamon press, 475-477.

30. Chemical abstract vol. 48. 13235e (1954).

31. Chemical abstracts vol. 79, 1973. 106140s.

32. Galus, Z., 1976, Fundamental of electrochemical analysis, polish scientific publishers, Warsaw.

33. Ross, J.W., DeMars, R.d. and Shain, I. 1956, Analytical applications of the hanging mercury drop electrode, Anal., Chem. 12, 1768-1771.

34. Frankenthal, R.P. and Shain, I. 1956, Diffusion currents at spherical electrodes, J. Am. Chem. Soc., 78, 2969-2973

35. (a) Loveland, J.W., and Elving, P.J., 1952, Application of the cathode-ray oscilloscope to polarographic phenomena(I. Differential capacity of the electrode double layer), J. Phys. Chem., 56, 250-255.

(b) Loveland, J.W., and Elving, P.J., 1952, Application of the cathode-ray oscilloscope to polarographic phenomena(III. Potentials of adsorption-desorption capacity peaks and surface charge density relationships exhibited by alcohols at aqueous saline solution-mercury interfaces), J. Phys. Chem., 56, 935-945.

36.     Willard, H.H., Merritt, L.I., Dean, J.A., Settle, F.A., 1986, Instrumental methods of analysis, CBS Publishers Distributors, New Delhi.

37.     Nurnburg H.W., 1974,   Electroanalytical Chemistry ,Vol.10, Interscience, London.

38.     Kamau, G.N., Willis, W.S., and Rusling, J.f., 1985, Electrochemical and electron spectroscopic studies of highly polished glassy carbon electrodes, Anal. Chem., 57, 545-551.

39.     Chuang. L. and Elving P.J. 1965, Effect of direction of polarization on current-potential curves at stationary electrodes, Anal. Chem. 37 (12), 1506-1509.

40.     Polcyn D.S., and Shain I., 1966, Multistep charge transfers in stationary electrode polarography, Anal, Chem., 38 (3).

41.     Lever, A.B.P., 1965, The phthalocyanines, Adv. Inorg. Chem. Radiochem., 7, 27-105, and references therein.

42.     Berkovitch-Yellin, Z. and Ellis,   D.E., 1981 Electronic structure of free-base and transition-metal tetraazaporphyrins, J. Am., Chem. Soc., 103, 6066-6073 and references therein.

43.     Wilkinson. G., Gillard, R.D., and McCleverty, J., (1987), Comprehensive inorganic chemistry volumes 5, page 944, Pergamon press, Oxford.

44.     Bragrove, R.J., Gruen, L.C. 1972, The aggregation of the tetrasodium salt of copper phthalocyanine-4',4'',4'''-tetrasulphonic acid, Aust. J. Chem. 25 (12), 2553-2558.

45.     Bragrove, R.J., Gruen, L.C., 1973, Thermodynamics of the dimerization of copper phthalocyanine-4',4'',4'''-tetrasulphonic acid, Aust., J. Chem. 26(1) 225-228 (Eng.)

46.     Gore, T.S., Joshi, B.S., Sunthankar, S.V. and Tilar, B.D., 1962, Recent progress in the chemistry of Natural and synthetic colouring matters and Related fields, Academic Press, London.

46b     Kamau, G.N., et. al., Influence of Organic solvent and Microassembly on electron transition of Copperphthalocyaninetetrasulphonate, Submitted, J . phthalocyanine

46c       Bard, A.J., Faulkner, L.R., 1980,  Electrochemical Methods, Wily and Sons, New York

47.       Kapusta, S. and Hockermann, N., carbon dioxide reduction at metal phthalocyanine catalyzed carbon electrode.   Department of Chemistry, Rice University, Houston, Texas 77251.

48        P.W. ATKINS, Physical chemistry, oxford university press, Oxford (1990)

49        Stams, D.A.; Thomas, T.D.;, MacLaren D.C.;, Ji, D.; and Morton, T.H., 1990, Empirical and Ab Initio Estimates of the stability of fluorine containing cations, J.Am. Chem. Soc.,112, 1427-1434

50 Beland, Frederick A.; Farwell S.O.; Callis, Patrick R.; Geer, Richard D., 1977, Reduction pathways of organohalogen compounds. (Part III.A molecular orbital (CNDO/2) study of the chlorinated benzenes, DDT, and Lindane), J. Electroanal. Chem. Interfacial electrochem., 78(1) 145-59 (Eng.).