SINGLET-OXYGEN OXIDATION OF THIOSALTS

by

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A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment
of the requirements for the degree of Master of Science

Department of Chemistry

Carleton University

Ottawa, Ontario

September 18, 2008

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ISBN: 978-0-494-44139-8

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ISBN: 978-0-494-44139-8

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ABSTRACT

The milling of sulfide ores forms thiosalts that are dissolved in effluent which is stored in holding ponds. The natural oxidation of these thiosalts generates significant acid concentrations that elicit toxic effects in aquatic life. The purpose of this research is to address the potential adverse effects of thiosalts in the mining effluents by singlet oxygen oxidation of thiosalts (SOOT). In the current research Zinc 2,3,9,10,16,17-(hexacarboxylate)-23,24-(dicarboximide) phthalocyanine sodium salt was synthesized, purified and characterized using electronic absorption spectroscopy and elemental analysis and used as the photosensitizer in the SOOT experiment. The monomer/dimer equilibrium of the photosensitizer in aqueous solution was investigated under various pH conditions and in the presence of surfactants. Cationic surfactants were found to be effective in promoting monomer formation in slightly acidic solutions at approximately the critical micelle concentration of surfactants. The quantum yield of singlet oxygen production in pH 11 solution remained approximately the same in the presence and absence of DTAB with $Q_s = 0.47$ and 0.50 , respectively. This suggested that the primary function of the surfactant in the SOOT process was to protect the photosensitizer from oxidation by hydrogen peroxide anion and not to prevent dimerization. SOOT experiments were carried out in the presence of DTAB at pH 11 to compare the photoactivity of the $\text{ZnPc}(\text{COONa})_4$ with the photosensitizer, the yield of sulfate at the end of 8 hours was determined to be 33% and 67% respectively. Therefore, it is evident that the photosensitizer is more efficient in converting thiosalts to sulfates at lower temperature when compared to $\text{ZnPc}(\text{COONa})_4$.

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge my gratitude to my research supervisor, Dr. Robert J. Crutchley. His dedication, guidance and knowledge made the work an extremely valuable learning experience.

I would like to thank Dr. Tito Scaiano and Michel Grenier from the University of Ottawa for their technical assistance required for running the experiments used to determine the quantum yields of singlet oxygen.

I would like to thank my parents, Commodore (Retired) Taimoor Sultan and Nasrin Temur for their strong support and encouragement in getting me this far. I would like to thank Yasir Sultan for all his help and guidance throughout my research project. I would like to thank my husband, Wahid Siddiqi who stood beside me and encouraged me constantly. Finally, I would also like to express my appreciation to Maliha Mohammed, Isa Mohammed, Hana Mohammed, Sameer Sultan, Maham Sultan, Zehra Sultan, Rashid Siddiqi, Anjum Siddiqi, Taranum Siddiqi, Fuwad Siddiqi and Ziad Siddiqi for their continued support.

This work is dedicated to my beloved grandmother, Razia Zia, for giving me the courage
and drive to complete my research

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LIST OF ABBREVIATIONS

FT-IR	Fourier Transform Infrared Spectroscopy
UV-vis	Ultraviolet-visible Spectroscopy
HCl	Hydrochloric Acid
PMD	Pyromellitic Dianhydride
DMF	Dimethyl Formamide
TCB	Tetracyanobenzene
BA	N-butylamine
TBAB or Bu ₄ NBr	Tetrabutylammonium Bromide
CTAB	CetylTrimethylAmmonium Bromide
DTAB	DodecylTrimethylAmmonium Bromide
DTAC	DodecylTrimethylAmmonium Chloride
SDS	Sodium Dodecyl Sulfate
SOOT	Singlet Oxygen Oxidation of Thiosalts
CMC	Critical Micelle Concentration
Q _s	Quantum Yield of Singlet Oxygen
The photosensitizer	Zinc 2,3,9,10,16,17-(hexacarboxylate)-23,24-(dicarboximide) phthalocyanine sodium salt

CHAPTER 1

1. INTRODUCTION

1.1 Singlet Oxygen Oxidation of Thiosalts (SOOT) Process

The milling of sulfide ores forms partially oxidized sulfur oxyanions such as $S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, etc., which are termed thiosalts. These thiosalts, along with other mining by-products are dissolved in the effluent. The natural oxidation of these thiosalts generates significant acid concentrations, thereby allowing minerals to dissolve in the water and be released where these harmful substances will elicit toxic effects in aquatic life [68].

The problem of thiosalts in mining effluent was the impetus of much research in the Natural Resources Canada (NRCan) laboratories beginning in 1976 and continues to the present day. During the period of 1976-1982, NRCan, in conjunction with university and industrial stakeholders, carried out a project to evaluate the chemistry, generation and treatment of thiosalts in mining effluent. These studies have been summarized in a paper published by Wasserlauf and Durtrizac in 1984 [18]. The first studies examined direct chemical oxidation of thiosalts by the addition of a chemical oxidant (O_3 , Cl_2 , H_2O_2 , ClO^- ... etc.) to mining effluent. While oxidation of thiosalts to sulfate was complete when using these methods, the cost of purchasing these industrial oxidants in bulk made these processes uneconomical. In this regard, catalytic processes or those that generate a

chemical oxidant in situ would seem to hold the greatest potential for an economically viable solution.

Chanda, O'Driscoll and Rempel proposed using a polymer bound copper complex to catalyze the oxidation of thiosalts by molecular oxygen [3]. According to the reaction:

However, a preliminary cost estimate yielded a cost of \$2.89/m³ of effluent [19]. This was regarded by the industry as too high (a treatment cost of \$0.30/m³ effluent is the target [4]).

Currently, thiosalts are oxidized in effluent holding ponds using thiobacilli. After the thiosalt levels have reached a threshold (<10 mg/L [29]) in the holding ponds, the pH of the effluent can be adjusted to natural levels and the effluent discharged into the water systems (rivers, lakes and oceans). In a 1985 study of the parameters for the operation of thiosalt oxidation ponds [16], the negative effects of lead, copper and low temperatures on thiosalt oxidation were evaluated. The presence of 2 mg/liter copper or lead reduced the rate of thiosalt oxidation by 55 and 30% respectively [16]. Dropping the temperature from 30 to 5 °C decreased the rate of thiosalt oxidation by a factor of 10 [16]. The study emphasized that when dealing with mining effluent at temperatures lower than 2 °C "...a supplementary method of thiosalt oxidation must be used" [16]. Thus, due to this hindrance mining productivity in the winter is restricted under *Metal Mining Effluent Regulations (MMER)* [30].

Bacterial oxidation of thiosalts was clearly the most economical of all those studied and is presently used to treat effluents by the Brunswick Mining and Smelting Corp., Bathurst, N.B. during fall and summer. Annual operating costs were estimated [18] to be \$430,000 to treat 1250 ppm thiosalt effluent or \$0.135/m³ effluent.

In 1996, Haque and Dinardo [6] explored the possibility of removing thiosalts from effluent by halide mediated electro-oxidation. The reaction half-equations are [6]:

The preliminary operating cost estimate based on reagents (rock salt, etc.) and power consumption was \$0.45/m³ effluent [6]. Capital costs were not included in this estimate and so while the electro-oxidation method appeared promising, an even more economical alternative was desired.

Due to the discussion above, there has been an increased interest by government and academic researchers to remedy this situation so that mining restrictions may be minimized with little or no harm to aquatic species. Recent studies have shown that thiosalts in the holding ponds may be oxidized by singlet oxygen.

1.2 Singlet Oxygen

It is known that the ground electronic state ($^3\Sigma_g^-$) of molecular oxygen contains two unpaired electrons. The two electronic excited singlet states which arise from the same electron configuration but with different spin pairing (Figure 1) in the π -antibonding orbitals of the two electrons are $^1\Delta_g$ and $^1\Sigma_g^+$ states that lie 94 and 157 kJ mol $^{-1}$ respectively above the ground state [32]. The $^1\Sigma_g^+$ state is very short lived and rapidly relaxes to the lowest lying excited $^1\Delta_g$ state. The transition from $^1\Delta_g$ state to $^3\Sigma_g^-$ state is spin forbidden; therefore, $^1\Delta_g$ state of oxygen is a long lived specie (45 min [33]). Due to the meta-stability of $^1\Delta_g\text{O}_2$ and its excited state energy (0.98 V), it is used in many photobiological and photochemical reactions [34, 35].

State	Orbital Assignment
$^1\Sigma_g^+$
$^1\Delta_g$
$^3\Sigma_g^-$

Figure 1: Primitive representations of molecular oxygen lowest singlet and triplet states. [33]

Oxygen by itself (i.e., O_2) is not a very good oxidant as demonstrated by its calculated reduction potential of -0.137 V (using NHE standard) [57]. In contrast, singlet oxygen is a powerful oxidant [54], as shown by Saito et. al., [54] and Eriksen et. al., [56], where the emission energy of singlet oxygen is added to the reduction potential of O_2 to

determine the reduction potential of singlet oxygen. Hence, the reduction potential for singlet oxygen was calculated to be 0.84 V.

Singlet oxygen is an electrophilic molecule and has been shown to oxidize phenols as well as sulfides and thiosalts [7]. It is also been linked to the process responsible for killing cancer cells under photodynamic therapy [7]. Recently, Iliev et. al., [14] examined the photocatalyzed oxidation of sulfides and thiosulfate. They showed that it was possible to completely convert 4.2 mmol of Na₂S to sulfate over a period of approximately 3 hours when irradiating an aqueous reaction solution containing 1.7 μmol of Zinc tetracarboxylate phthalocyanine (pH of 9.2, temperature 25 °C) [14]. In addition, of the photosensitizer's studied (photo-semiconductor powders and Zinc tetracarboxylate phthalocyanine); only Zinc tetracarboxylate phthalocyanine photocatalyzed the oxidation of thiosulfate to sulfate [14].

There are many ways by which singlet oxygen can be produced [34], but it is most commonly produced by photosensitization. Ground state triplet oxygen (³O₂) can be photosensitized to an excited singlet state (¹O₂) by energy transfer from a photosensitizer (*Sens*) possessing a long lived triplet excited state (³*Sens*). The triplet excited state of the photosensitizer transfers its energy to the ground state of oxygen generating the oxygen excited state (¹O₂):

Superoxide can be formed from the oxidation of thiosulfate by singlet oxygen. In an aqueous solution, superoxide is not stable and forms peroxide ions according to the disproportionation reaction given below:

and thus leads to chemical oxidation of thiosulfates by peroxides [18]:

This research project evaluates the effectiveness of singlet oxygen oxidation of thiosalts (SOOT), by photosensitization in a basic medium at temperatures where biological oxidation is inefficient (<0 °C) [7]. It also keeps in mind the demand by industry to create a cheap and widely available methodology that ideally costs less than the biological system while being more effective year around.

1.3 Photosensitizers

Photosensitizers are organic or organometallic macromolecules that have the ability to absorb light forming a long lived triplet excited state [33]. These photosensitizers have the unique ability to photocatalyze chemical reactions which promotes their use in many different industries [21].

Phthalocyanines are a class of photosensitizers with a cage-type structure [10]. These photoactive systems are unique as they are stable, easy to use due to their strong

adsorption of light and easy to quantify due to their high color intensity. The first phthalocyanine was synthesized in 1907 by Braun and Tcherniac who heated o-cyanobenzamide at a high temperature [1]. The structure of this metal free, unsubstituted phthalocyanine was determined only a quarter of a century later by Linstead et. al. [2] and Robertson et. al. [13], while examining both metal-free and metallophthalocyanines [10].

A simplified Jablonski diagram for a photosensitizer is shown below in which a photosensitizer is excited to its triplet state. If oxygen ($^3\text{O}_2$) is in close proximity, energy transfer between the triplet states may occur resulting in the formation of singlet oxygen ($^1\text{O}_2$). The number of $^1\text{O}_2$ molecules generated for each photon absorbed by a photosensitizer is called the quantum yield of singlet oxygen formation (Q_s).

Figure 2: A simplified Jablonski diagram for the photosensitizer.

1.3.1 Energy Transfer Mechanisms

Forster transfer is described as the transfer of excitation energy from an excited donor molecule to a ground state acceptor molecule via long distance dipole-dipole interaction [45] that is capable of transferring excitation energy from donor to an acceptor over a separation distance as long as 100 Å [44].

According to Forster et. al. [45], the rate of energy transfer, k_{ET} , is given by:

$$k_{ET} = \frac{1}{\tau_d} \left(\frac{R_0}{r} \right)^6 \quad (10)$$

where r is the distance between the donor molecule (i.e., ZnPc) and the acceptor molecule (i.e., 3O_2), τ_d is the lifetime of the donor molecule in the absence of the acceptor and R_0 is the Forster distance [45].

The Dexter mechanism is another dynamic energy quenching mechanism occurring as a result of electron exchange. It is a short range mechanism, with the distance between donor and acceptor typically less than 10 Å [52] and requires that the orbitals of donor overlap with the orbitals of the acceptor since the electrons are exchanged. This is shown by the Dexter equation below, where the energy transfer is dependant upon the distance between the donor-acceptor (r_{DA}) and the orbital overlap (K). As seen from the equation 11, as the distance of the donor-acceptor gets larger, the rate of energy transfer is expected to decrease exponentially [52]. Therefore, it is evident that Dexter mechanism only hold true for molecules in close proximity.

According to the Dexter equation [69, 45], the rate of energy transfer (k_{ET}) is given by:

$$k_{ET} = \frac{2\pi}{h} K J e^{\left(\frac{-2r_{DA}}{L}\right)} \quad (11)$$

where K is the orbital overlap depending on the specific orientations of the donor molecule (i.e., ZnPc) and the acceptor molecule (i.e., 3O_2), L is the sum of van der Waals radii, J is the Dexter constant and r_{DA} is the donor-acceptor separation relative to their van der Waals radii [41].

1.4 Photobleaching

The photosensitizer may react with singlet oxygen or peroxide and lose its ability to absorb visible light. Thus, this decomposition reaction is commonly referred to as photobleaching. Photobleaching results in a reduction in the production of the singlet oxygen and hence the oxidation of thiosalts in the mining effluent. There are many modifications that can reduce the rate of photobleaching [11] some of which are discussed later (i.e., surfactants), but these modifications must not adversely affect the photosensitizer excited state properties. In order to catalyze the formation of singlet oxygen, a sensitizer in its triplet excited state should have a lifetime that permits bimolecular reaction (at least 1 μ s) and be energetically capable of energy transfer to the ground state of dioxygen to form singlet oxygen. Photosensitizers whose triplet excited

state is formed with a large quantum yield will also result in increased singlet oxygen production.

1.5 Dimerization

Figure 3: From ref 12, the visible absorption spectrum of solutions of (a) H₂Pc and (b) CuPc in chloroform as the solvent.

The characteristic solution visible absorption spectrum for H₂Pc and CuPc is given in Figure 3. In both cases there is a strong absorption between 670 nm and 690 nm, termed Q-band [12]. In addition there is a strong absorption band in the ultra-violet region between 320 nm and 370 nm [12], which has been designated the B-band (or Soret band). The former absorption is responsible for the characteristic intense blue-green

colour of the compound [12]. A typical value of the extinction coefficient of the intense Q-band is $2 \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}$ for mononuclear phthalocyanine complexes of high purity [12]. The weak absorption bands at about 600 nm are vibrational overtones of the Q-band.

It has been noted by many researchers [10, 21] that phthalocyanine complexes form aggregates (dimer, trimer, etc) in solution as shown in eqn. 12:

Phthalocyanines tend to aggregate because their planar geometry optimizes π - π interactions. Figure 4 is an experiment that illustrates how the monomer-dimer equilibrium in pH 10 aqueous solution is affected by the presence of Bu_4NBr . The intense Q-band seen above in Figure 3b is diagnostic of having mostly monomer species in solution. Comparing Figure 4b to Figure 3b, there is no significant difference observed in the spectra suggesting that the phthalocyanine in the presence of Bu_4NBr is mostly a monomer specie (i.e. equilibrium in eqn. 12 is mostly to the left). On the other hand, when Bu_4NBr is not present a new band appears at 620 nm in the absorption spectrum (Figure 4a) and the Q-band has lost so much intensity that it now appears as a shoulder. We associate the growth of the band at 620 nm as diagnostic of dimer formation which is to be avoided. Excitation of the dimer creates excimers (an excited dimer) whose photophysical properties of these excimers are not appropriate for photosensitization of singlet oxygen.

Figure 4: Electronic absorption spectrum of $\text{ZnPc}(\text{COONa})_4$ in the presence of Bu_4NBr (b), and the $\text{ZnPc}(\text{COONa})_4$ aggregate (a), both in aqueous solution, pH 10 borax buffer.

Research carried out by Brian MacLean (a former postdoctoral fellow in Dr. Crutchley's lab) indicated successful conversion of thiosalts to sulfates but only in the presence of Bu_4NBr which limited dimerization of the photosensitizer (see Figure 4b) [21]. Unfortunately, the high concentrations of Bu_4NBr that were required to reduce dimerization made the SOOT reaction expensive and uneconomical. An alternative to Bu_4NBr was surfactants.

1.6 Surfactants

Surfactants find their uses amongst a myriad of industries (e.g., soaps, oils, pharmaceuticals, etc). Recently, surfactants have become the subject of intense

investigation by researchers in the fields of chemical kinetics and biochemistry because of the unusual properties of the supramolecular form (micelle) of these materials [10].

A surfactant is a surface-active agent that, when present at low concentrations in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering the surface or interfacial free energies of those surfaces (or interfaces). The term interface indicates a boundary between any two immiscible phases, and the term surface indicates an interface where one phase is a gas, usually air [10].

The interfacial and solution behaviour of surfactants leads to the key surface-active properties of surfactants such as wetting/re-wetting, emulsification/demulsification, foaming, dispersing, defoaming, detergency and solubilising.

1.6.1 Structure of a Surfactant

The general structure of a surfactant consists of a structural group that has very little attraction for the solvent (lyophobic group), along with a group that has strong attraction for the solvent (lyophilic group). This is known as an amphipathic structure [15]. Surfactants are called amphiphiles because they possess 2 distinct regions with extreme differences in physicochemical properties. When a surfactant is dissolved in a solvent, the presence of lyophobic groups in the interior of the solvent causes a distortion of the solvent liquid structure, therefore increasing the free energy of the system [15]. In case of water being the solvent, the tail of the surfactant molecule (lyophobic group), is referred to as a hydrophobic group and the head (lyophilic group) as a hydrophilic group as illustrated below.

Figure 5: Schematic illustration of a surfactant molecule.

1.6.2 Types of Surfactants

Surfactants are classified according to their dissociation in water. They are divided in four groups, anionic surfactants, non-ionic surfactants, cationic surfactants and amphoteric surfactants.

Figure 6: Demonstration of charges on different types of surfactants.

Anionic surfactants are used in laundry and hand dishwashing detergents, household cleaners, and personal cleansing products. They ionize (are converted to charged particles) in solution, carry a negative charge, and have excellent cleaning properties. Alcohol sulphates, phosphate esters and sulphonated fatty acids are some examples of the anionic surfactants.

Nonionic surfactants are low sudsing and are typically use in laundry and automatic dishwasher detergents and rinse aids. Because they do not ionize in solution and thus have no electrical charge, they are resistant to water hardness and clean well on most soils. Alkyl phenol ethoxylates, fatty amine ethoxylates and sorbitan esters are some examples of nonionic surfactants.

Cationic surfactants are used in fabric softeners and in fabric-softening laundry detergents. Other cationics are the disinfecting/sanitizing ingredient in some household cleaners. They ionize in solution and have a positive charge. Imidazolinium salts, cetyltrimethylammonium bromide and dodecyltrimethylammonium chloride are some examples of cationic surfactants.

Amphoteric surfactants are used in personal cleansing and household cleaning products for their mildness, sudsing and stability. They have the ability to be anionic (negatively charged at low pH conditions), cationic (positively charged at high pH conditions) or nonionic (no charge at neutral pH ~7) in solution. Betains and Imidazolines are some examples of amphoteric surfactants.

1.6.3 Critical Micelle Concentration (CMC)

A fundamental property of surfactants is that they tend to form aggregates in solution, called micelles. The concentration at which micelles start to form is called the Critical Micelle Concentration, or CMC. The exact structure of micelles formed and some details of the process of micellization are issues that are still debated [15]. For our purpose, it is sufficient to indicate that in a non-aqueous solvent the hydrophobic tails tend to orient themselves towards the outside, and the hydrophilic heads form the interior of the micelle, hence ensuring that the surfactant is soluble in that solvent (Figure 7A). On the other hand, having water as the solvent, the hydrophilic heads orient themselves in the opposite direction, i.e., towards the outside, and the hydrophobic tails form the interior of the micelle. This orientation is responsible for the formation of a reverse micelle (Figure 7B).

Furthermore, if a negatively charged complex is introduced in an aqueous solvent, both micelle orientations (Figure 7A and 7B) will be seen with a single surfactant specie. Firstly, a layer of surfactant molecules will orient themselves to interact with the anionic compound (such as Figure 7A) after which another coordinating layer of surfactant molecules will orient themselves around the first layer of the surfactant in a manner similar to Figure 7B to form a soluble micelle in water (Figure 7C).

Figure 7: Illustration of a spherical micelle in A) non-aqueous solvent, B) aqueous solvent, C) aqueous solution containing a negatively charged complex and cationic surfactant molecules.

1.7 Temperature Dependence

Studies by Dr. MacLean showed that $\text{ZnPc}(\text{COONa})_4$ photocatalyzed the oxidation of $\text{S}_2\text{O}_3^{2-}$ to SO_4^{2-} at several temperatures and the data is summarized in Figure 8. His results showed that the oxidation of thiosulfate ions to produce sulfate, while slower, was still significant at lower temperatures. Dr. MacLean noticed an approximately two-fold drop in the production of sulfate with decreasing temperature from 14.2 to 0 °C. Nevertheless, the sulfate produced after 12 hours at 0 °C corresponded to almost 24% conversion of thiosulfate to sulfate ion, thus giving a preliminary indication that this approach was better than the ones used by industry (i.e., thiobacilli). The sulfate production levelled off at longer times. This behaviour was attributed to photobleaching of the photosensitizer by singlet oxygen generated during the reaction. As

the photosensitizer is degraded with time, less is available to convert the remaining thiosulfate.

Figure 8: Temperature dependent SOOT experiment using $\text{ZnPc}(\text{COONa})_4$ as a photosensitizer. Conditions: $\text{S}_2\text{O}_3^{2-}$ 1000 ppm, $\text{ZnPc}(\text{COONa})_4$ 5.7 μM , Bu_4NBr 0.12M, pH = 10.0 borax buffer, irradiation intensity 120 klux.

1.8 Proposed Research

This current research will evaluate the effectiveness of a photosensitizer system to convert thiosalts to sulfates in the presence of conditions that are typically seen at a mining effluent holding pond.

Firstly, an octacarboxylate phthalocyanine complex will be synthesized (see below) and fully characterized via spectrophotometry and elemental analysis.

zinc octacarboxy phthalocyanine

Octasubstituted phthalocyanines are symmetrical compounds that contain two substituents in each benzo ring. These systems are less soluble in polar solvents due to the decrease in polarity based on the symmetrical nature of these compounds [1]; however, they can be solubilized by the generation of their corresponding salts. Also, these complexes have higher repulsion with each other in solution thus minimizing the effect of dimerization. The nature of the monomer/dimer equilibrium will be explored under various pH conditions. SOOT studies will be performed at an environmentally relevant pH and at different temperatures to mimic summer and winter conditions of the holding ponds.

Surfactants will be used to keep the photosensitizer in its monomeric form during the SOOT experiments. The optimum concentration of surfactant will be evaluated for the SOOT experiments using spectrophotometry. As an alternative to the uneconomical tetrabutylammonium bromide (i.e., high concentration of 0.12 M), surfactants such as cetyltrimethylammonium bromide $C_{19}H_{42}N.Br$ (CTAB, cationic surfactant), sodium dodecyl sulfate $C_{12}H_{26}O_4S.Na$ (SDS, anionic surfactant), Triton X-100 $(C_2H_4O)_n C_{14}H_{22}O$ (non-ionic surfactant), Tween 20 (non-ionic surfactant), dodecyltrimethylammonium bromide $C_{15}H_{34}N.Br$ (DTAB, cationic surfactant) and dodecyltrimethylammonium chloride $C_{15}H_{34}N.Cl$ (DTAC, cationic surfactant) will be evaluated in the SOOT process.

Figure 9: Structure of different surfactants, used to evaluate the SOOT process.

The effectiveness of the photosensitizer system (i.e., with and without cationic surfactants; at different pH conditions) will be evaluated by quantum yield experiments. The orientation of the cationic surfactant around the photosensitizer can be seen in Figure 7C. Studies will be carried out at the University of Ottawa to determine the singlet oxygen generated by the quenching of the triplet (excited) state of the photosensitizer. The ground state photosensitizer ($Sens_0$) will be irradiated with visible light generating excited singlet state ($Sens_1$). $Sens_1$ can relax back to an excited state T_1 , generating singlet oxygen. All measurements of quantum yield of singlet oxygen formation (Q_s) will be scaled to a reference substance (Methylene Blue in aqueous medium, $Q_s = 0.52$ [33]).

CHAPTER 2

2. EXPERIMENTAL

2.1 Physical Measurements

Electronic spectra were acquired on a CARY 5 UV-vis near IR spectrophotometer, using quartz cells with path lengths of 0.2, 1 and 5 cm. Infrared spectroscopy was performed using a BOMEM Michelson 120 FT-IR spectrophotometer on KBr discs (KBr was dried at 102 °C). Elemental analysis was performed by the Canadian Micro Analytical Service Ltd.

2.2 Solvents and Reagents

Distilled Acetone, ethanol (anhydrous, Commercial Alcohols), methanol (spectrograde, Caledon), ethylene glycol (Aldrich), conc. HCl (Anachemia), Phosphate buffer solutions 0.05 M for pH 4, pH 6, pH 7, pH 9, pH 10 and pH 11 (VWR), 1,2,4,5-Tetracyanobenzene (TCB) (97%, Aldrich), anhydrous zinc acetate (99.9%, Aldrich), sodium chloride (NaCl) (98%, reagent grade, Aldrich), hydrochloric acid and sodium hydroxide (NaOH) (Anachemia).

Tetrabutylammonium bromide (Bu_4NBr) (Aldrich), $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (Anachemia) $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (Anachemia), sodium tetraphenyl borate (99%, Lancaster), Cetyltrimethylammonium bromide (CTAB) (Aldrich), sodium dodecyl sulfate (SDS)

(Fluka), Tween 20 (Aldrich), Triton X-100 (Aldrich), dodecyltrimethylammonium bromide (DTAB) (Aldrich) and dodecyltrimethylammonium chloride (DTAC) (Aldrich).

2.3 SOOT Instrumentation

The experimental setup to carry out the SOOT process employed a Techne constant temperature bath equipped with a circulator and a TE-10D temperature regulator. The bath was cooled with copper coils that were in turn cooled by a Neslab LT-50 low temperature refrigerated circulating bath set at -35 °C. An Agrosun Gold metal halide lamp was (Hydrofarm, MH1000W) was mounted in a ballast fixture with a reflector. This lamp was chosen due to its similarity to the visible light spectrum of the sun. Light intensity was measured to be 166 klux using an International Light radiometer/photometer (model IL 1400-A). The detector had UV and IR cut-offs at 435 nm and 705 nm, respectively. The samples were saturated with air by constant bubbling. Tests to determine the concentration of dissolved oxygen in solution were conducted with a Cole-Parmer 5949 oxygen meter. The concentration of the dissolved oxygen in the bubbled solution was determined to be 14.2 ppm. An ISFET pH meter (model IQ-125) was used to monitor the pH of the solutions. A schematic diagram of the SOOT instrumentation is shown below.

Figure 10: Experimental setup to carry out the SOOT process.

2.4 Test Solutions for the SOOT Experiment

Test solutions for the SOOT experiment were made up of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (1000 ppm), Zinc 2,3,9,10,16,17-(hexacarboxylate)-23,24-(dicarboximide) phthalocyanine sodium salt ($5.7 \mu\text{M}$) with either Bu_4NBr (0.12 M), CTAB (1 mM), DTAB (16 mM) or DTAC (16 mM) in pH 11 water-alkaline solution (final volume 300 ml). Solutions were placed in 500 ml cylindrical beakers (Berzelius), giving a solution depth of approximately 7 cm. The solutions were bubbled with air throughout the experiment. Previous studies demonstrated that there were no other oxidation products of thiosulfate other than SO_4^{2-} . On this basis, the amount of SO_4^{2-} generated was determined gravimetrically by precipitation of its barium salt.

CTA^+ and DTA^+ ions co-precipitate with BaSO_4 and had to be separated from the SO_4^{2-} ions prior to the addition of BaCl_2 solution. This was achieved by the addition of 10 ml of 0.03 M sodium tetraphenyl borate which precipitated the CTA^+ or DTA^+ ions as a BPh^- salt. After filtration, the pH of the filtrate was lowered from pH 11 to pH 4 by adding 0.1 M HCl dropwise, monitored by a pH meter, to avoid the production of BaCO_3 . 15 ml of 0.5 M BaCl_2 solution was then added precipitating BaSO_4 . The solution was allowed to stand in the dark overnight before filtration. The BaSO_4 precipitate was collected on an ultrafine glass frit filters (4-5.5 μm porosity), dried for 12 hours (120 °C) and weighed to a constant mass.

2.4.1 Sample Calculation for the Percentage Conversion of Thiosulfate to Sulfate
in the SOOT Experiment Carried Out in the Presence of DTAB at 22°C.

Table 1: Illustration of the Weight in Grams of Barium Sulfate in the SOOT Experiment Carried Out for 8 hours in the Presence of DTAB.

Trial 1: Weight of BaSO ₄ (g)	0.551
Trial 2: Weight of BaSO ₄ (g)	0.530
Trial 3: Weight of BaSO ₄ (g)	0.481
Average Weight of BaSO ₄ (g)	0.521

$$1. \quad \frac{\text{Weight of BaSO}_4 \text{ (g)}}{\text{Molecular weight of BaSO}_4 \text{ (g/mol)}} = \text{Moles of BaSO}_4 \text{ (mol)} = \text{Moles of SO}_4^{2-} \text{ (mol)}$$

$$2. \quad \frac{\text{Moles of sulfate (mol)}}{2 \times \text{moles of Na}_2\text{S}_2\text{O}_3 \text{ (mol)}} \times 100 = \% \text{ Na}_2\text{S}_2\text{O}_3 \text{ converted to SO}_4^{2-}$$

$$1. \quad \frac{0.521 \text{ g}}{233 \text{ g/mol}} = 0.00223 \text{ mol of SO}_4^{2-}$$

$$2. \quad \frac{0.00223 \text{ mol}}{2 \times 1.21 \times 10^{-3} \text{ mol}} \times 100 = 92.6 \% \text{ of SO}_4^{2-}$$

2.5 Singlet Oxygen Quantum Yield Determination

Singlet oxygen quantum yield measurements were conducted in the labs of Dr. Tito Scaiano (University of Ottawa). A Nd:YAG laser was used to irradiate an aqueous solution of the photosensitizer. This formed the triplet excited state (3Sens) of the photosensitizer which then transferred its energy to triplet oxygen (3O_2) causing the formation of singlet oxygen (1O_2). A Hamamatsu NIR PMT Module, Model H10330-75 was used to detect singlet oxygen emission [20] and the output was amplified and converted to a voltage pulse using a high speed current preamplifier (model SR445). A multichannel scaler (model SR430) connected to a personal computer was used for the time resolved single photon counting. A schematic diagram of the instrument is shown below.

Figure 11: The experimental setup at University of Ottawa, for singlet oxygen quantum yield and lifetime measurements. Band width: ± 20 MHz, time: 25 μ s, wavelength: 650 nm, phosphorescence of singlet oxygen: 1270 nm.

2.6 Test Solutions for Determining the Quantum Yield of Singlet Oxygen

2.6.1 Determining the Quantum Yield in the Absence of Surfactant

The following concentrations of photosensitizer were used: 3.3×10^{-5} M, 1.6×10^{-5} M, 8.2×10^{-5} M and 4.1×10^{-5} M. Each sample was diluted in a pH 9, pH 10 and pH 11 water-alkaline solution (final volume 50 ml). The pH of each solution was determined using a pH meter before running the samples. The calibration standard used was Methylene Blue in pH 7 aqueous solution. UV-vis spectra of the samples were taken before and after laser irradiation to ensure that no photo-degradation had taken place.

2.6.2 Determining the Quantum Yield in the Presence of Surfactant

The following concentrations of photosensitizer were used: 1.4×10^{-4} M, 1.1×10^{-4} M, 7.2×10^{-5} M and 3.6×10^{-5} M. 16 mM of DTAB was added in each sample. Each sample was diluted in a pH 11 water-alkaline solution (final volume 50 ml). The pH of each solution was determined using a pH meter before running the samples. The calibration standard used was Methylene Blue in pH 11 water-alkaline solution. UV-vis spectra of the samples were taken before and after laser irradiation to ensure that no photo-degradation had taken place.

2.7 Attempted Synthesis of the Photosensitizer

The synthesis of pure phthalocyanines can be extremely difficult and attempts to prepare pure $\text{ZnPc}(\text{COOH})_8$ by following the procedures outlined by V. Iliev et. al., [21]

and N.A. Kuznetsova et. al., [36] was unsuccessful. In Section 2.7 these synthetic attempts are described in detail together with additional purification procedures. The purity of ZnPc purity was evaluated by the extinction coefficient of the Q band which for pure metal phthalocyanines should be ca. $2 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$ [37].

2.7.1 V. Iliev and A. Mihaylova's Protocol

The Zinc carboxy tetraimide phthalocyanine compound was synthesized following the procedures outlined by V. Iliev and A. Mihaylova [21]. 3.93 g of pyromellitic dianhydride (PMD), 19.8 g of urea, 4.50 g of zinc acetate and 0.04 g of ammonium molybdate were refluxed at 240 °C for 3 hours in a flask immersed in silicon oil forming the Zinc tetraimide phthalocyanine compound. The mixture was cooled and washed with water and acetone after which it was air dried. The dried product was stirred with 500 ml of 6 M hydrochloride acid for 12 hours at room temperature. The acid was removed by filtration and the solid product was washed with hot water until a neutral pH was reached. The crude sample [1.08 g, extinction coefficient (635 nm) in DMF: $800 \text{ M}^{-1}\text{cm}^{-1}$, $\text{Zn}(\text{C}_{40}\text{H}_{12}\text{N}_{12}\text{O}_8)$] was hydrolyzed using 2 M sodium hydroxide and 80 g of sodium chloride and stirred for 5 hours at 90 °C forming the carboxy phthalocyanine compound. The sample was filtered, after which it was acidified with 2 M hydrochloride acid and washed with water up to pH 7. The solid product was heated three times for 30 minutes at 90 °C with 100 ml of a dimethylformamide (DMF) - water solution (5:1 v/v). The weight of the dry carboxy sample was measured at 0.64 g. A UV-vis spectrum was obtained for the phthalocyanine complex, and the extinction coefficient (681 nm) was determined to be $1000 \text{ M}^{-1}\text{cm}^{-1}$ in distilled water [$\text{Zn}(\text{C}_{40}\text{H}_{15}\text{N}_9\text{O}_{14})$].

2.7.2 N.A Kuznetsova et al.'s Protocol

The Zinc carboxy tetraimide phthalocyanine compound was synthesized following the protocols outlined by N.A. Kuznetsova et. al., [36]. 23.5 g of pyromellitic dianhydride (PMD), 63.6 g of urea, 9.72 g of zinc acetate, 46 g of sodium sulphate, 25 ml of 1-bromonaphthalene and 0.5 g of ammonium molybdate were refluxed at 235 °C for 4 hours, forming the Zinc tetraimide phthalocyanine compound. The cooled reaction mixture was filtered and the precipitate was washed with benzene, followed by an acid/base (HCl/NH₄OH) precipitation for purification of the tetraimide compound (16.7 g). The tetraimide sample [5 g, extinction coefficient (632 nm) in DMF: 1500 M⁻¹cm⁻¹, Zn(C₄₀H₁₂N₁₂O₈)] was hydrolyzed using 21.6 g of potassium hydroxide (KOH) and 127 ml of triethylene glycol and stirred for 2 hours at 135 °C in an argon flow. The carboxy phthalocyanine solution was cooled, acidified with 2 M hydrochloric acid (HCl) and filtered. The precipitate was washed with 2 M HCl and water until a neutral pH (7) was reached. The weight of the dry carboxy phthalocyanine sample was measured at 0.5 g. A UV-vis spectrum was obtained for the phthalocyanine complex, and the extinction coefficient (684 nm) was determined to be 7300 M⁻¹cm⁻¹ in distilled water [Zn(C₄₀H₁₅N₉O₁₄)]. The carboxy phthalocyanine was converted into its sodium salt by using a 1% NaOH solution. The weight of the dry phthalocyanine salt sample was measured at 0.4 g. A UV-vis spectrum was obtained for the phthalocyanine complex, and the extinction coefficient (691 nm) was determined to be 11,000 M⁻¹cm⁻¹ in distilled water [Zn(C₄₀H₈N₈O₁₆Na₈)].

2.7.3 Soxhlet Extraction Purification

The crude Zinc carboxy tetraimide phthalocyanine compound was synthesized following the process outlined in section 2.7.2. The reaction mixture was filtered and the precipitate was washed with benzene, followed by an acid/base (HCl/NH₄OH) precipitation for purification of the tetraimide compound by removing the unreacted reagents like urea and PMD from the reaction mass. Soxhlet extraction was utilized as a means to further purify the tetraimide substance. The tetraimide complex [11.0 g, extinction coefficient in DMF: 1500 M⁻¹cm⁻¹, Zn(C₄₀H₁₂N₁₂O₈)] was placed inside a thimble, made from thick filter paper, located in the main chamber of the soxhlet extractor. The tetraimide complex was dissolved in DMF and collected in the distillation flask. After 10 hours the tetraimide compound was recovered from the distillation flask (5.4 g). The UV-vis spectrum for the tetraimide phthalocyanine compound showed an extinction coefficient (639 nm) of 10,000 M⁻¹cm⁻¹, Zn(C₄₀H₁₂N₁₂O₈). 5 g of the sample was further hydrolyzed and converted to the sodium salt (via 1% NaOH solution using the procedure outlined in section 2.7.2). The extinction coefficient (691 nm) of the final salt product was calculated in water at 21,000 M⁻¹cm⁻¹ [Zn(C₄₀H₈N₈O₁₆Na₈)].

2.7.4 Flash Chromatography Purification

The crude Zinc carboxy tetraimide phthalocyanine compound was synthesized following the process outlined in section 2.7.2. The reaction mixture was filtered and the precipitate was washed with benzene, followed by an acid/base (HCl/NH₄OH) precipitation for purification of the tetraimide compound by removing the unreacted reagents like urea and PMD from the reaction mass. To further purify the tetraimide

compound, a slurry of silica gel (70 g) in DMF (150 ml) was poured into a column. 1 g of the tetraimide phthalocyanine complex [extinction coefficient (632 nm) in DMF: $1500 \text{ M}^{-1}\text{cm}^{-1}$, $\text{Zn}(\text{C}_{40}\text{H}_{12}\text{N}_{12}\text{O}_8)$] was dissolved in 45 ml DMF and poured down the column to create a darkly colored band. Air pressure was applied to aid in the elution of the sample through the column at a steady rate (sample started to elute after 5.5 hours). After the complex had eluted, the solution was solvent stripped to dryness, after which it was left to dry overnight. The weight of the dry sample was measured at 0.4 g. The UV-vis of the dry sample gave an extinction coefficient (639 nm) of $18,000 \text{ M}^{-1}\text{cm}^{-1}$ in DMF [$\text{Zn}(\text{C}_{40}\text{H}_{12}\text{N}_{12}\text{O}_8)$]. 0.4 g of the tetraimide sample was further hydrolyzed and converted to the sodium salt by following the process outlined in section 2.7.2. The extinction coefficient (691 nm) of the final salt product was calculated in water at $32,000 \text{ M}^{-1}\text{cm}^{-1}$ [$\text{Zn}(\text{C}_{40}\text{H}_8\text{N}_8\text{O}_{16}\text{Na}_8)$].

2.7.5 Modifications to Kuznetsova et al.'s Protocol

10.0 g of PMD, 4.0 g of anhydrous zinc acetate, 26.0 g of urea, 0.2 g of ammonium molybdate and 10 ml of 1-bromonaphthalene were stirred in a round bottom flask (250 ml) and refluxed at 190°C for 4 hours, after which it was cooled to room temperature. The crude tetraimide sample was dissolved in DMF and refluxed for an additional 30 minutes. The solution was filtered to remove any solid impurities and solvent stripped to dryness. The dry tetraimide product was boiled in 2 M HCl (50 ml) solution and filtered. This cycle was repeated six times or until the yellow colour completely disappeared from the filtrate. The dry tetraimide weighed 8.42 g. The UV-vis spectrum for the tetraimide phthalocyanine compound gave an extinction coefficient (638

nm) in DMF of $27,000 \text{ M}^{-1}\text{cm}^{-1}$ [$\text{Zn}(\text{C}_{40}\text{H}_{12}\text{N}_{12}\text{O}_8)$]. For further purification, 0.5 g of the sample was dissolved in 25 ml of DMF and eluted through a silica column as previously discussed in section 2.7.4. The eluted sample was filtered, dried, weighed (0.2 g) and the extinction coefficient (636 nm) in DMF was measured at $45,000 \text{ M}^{-1}\text{cm}^{-1}$ [$\text{Zn}(\text{C}_{40}\text{H}_{12}\text{N}_{12}\text{O}_8)$].

0.1 g of the purified tetraimide compound (by flash chromatography) was added to a solution of 10.0 g NaCl in 50 ml NaOH to hydrolyze. The solution was stirred for 1.5 hours at 80°C . After cooling, the carboxy phthalocyanine complex was neutralized with dilute HCl (2 M) and filtered. The weight of the dry sample was measured at 0.07 g. UV-vis in water gave an extinction coefficient (689 nm) of $117,000 \text{ M}^{-1}\text{cm}^{-1}$ [$\text{Zn}(\text{C}_{40}\text{H}_{15}\text{N}_9\text{O}_{14})$].

0.07 g of the carboxy phthalocyanine compound was suspended in 100 ml of distilled water. 1% NaOH w/w was added to the suspension (sample in water) to convert the sample to its sodium salt. The salt was filtered and solvent stripped to dryness. The pure sample was washed with acetone and dried. The weight of the dry sample was measured at 0.05 g. UV-vis for the phthalocyanine compound gave an extinction coefficient (695 nm) in water of $119,000 \text{ M}^{-1}\text{cm}^{-1}$. The elemental analysis of the purified phthalocyanine complex is shown in Table 2.

Table 2: Comparison of the Calculated and Found Elemental Analysis (C, H and N) for Kuznetsova's ZnPc(COONa)₈ Product [Zn(C₄₀H₈N₈O₁₆Na₈), FW= 1105.84 g/mol].

Element	Calculated (%)	Found (%)
Carbon (C)	43.45	39.78
Hydrogen (H)	0.73	1.20
Nitrogen (N)	10.13	10.20

2.8 Synthesis of Zinc 2,3,9,10,16,17-(Hexacarboxylate)-23,24-(Dicarboximide)

Phthalocyanine Sodium Salt

The Zinc carboxy tetraimide phthalocyanine compound was synthesized following the protocols outlined by D.R. Boston and J.C. Bailer [38], where the tetraimide was hydrolyzed with 18 M KOH for 9 hours at 100 °C. These harsh conditions for hydrolysis led to the decomposition of ZnPc. To get a higher yield of ZnPc and to minimize decomposition, milder hydrolysis conditions were followed as described below.

1.78 g of TCB, 0.85 g of anhydrous zinc acetate and 40 ml of ethylene glycol were stirred and refluxed at 198 °C for 5 hours (the solution started to show signs of colour change at 160 °C and became dark green at 175 °C), after which it was cooled at room temperature. 100 ml of distilled water was added to the suspension and stirred for an additional 15 minutes. The mixture was filtered using a Buchner funnel (40-60 µm porosity), and the residue was washed with acetone (50 ml). This washing was repeated twice. The crude tetraimide sample was air dried overnight the weight was measured at 3.01 g.

The crude solid was crushed and placed in a beaker. A solution of 35 ml of water and 65 ml of acetone was prepared and added to the beaker containing the sample. The suspension was stirred at room temperature for 0.5 hours, after which it was filtered using a Buchner funnel (40-60 μm porosity) and the dry weight determined as 2.98 g. FT-IR spectrum of the crude sample was obtained in KBr and two distinctive peaks were observed (OH-stretch and the C=O stretch at 3740 cm^{-1} and 1772 cm^{-1} respectively). This purification procedure was repeated until the yellow colour completely disappeared from the filtrate (approximately five washings). The final weight of the sample was recorded as 2.81 g.

After air drying, the tetraimide complex was placed in a beaker containing 100 ml of 0.01 M HCl. The solution was stirred at room temperature for 15 minutes, and then filtered through a glass frit (10-15 μm porosity). The precipitate was washed with acetone; air dried and weighed (2.75 g). This procedure was repeated twice (or repeated until the filtrate became colourless). Final weight of the purified tetraimide sample was determined to be 2.63 g. UV-vis absorption spectrum [extinction coefficient (639 nm) was calculated in DMF to be $122,000\text{ M}^{-1}\text{cm}^{-1}$, $\text{Zn}(\text{C}_{40}\text{H}_{12}\text{N}_{12}\text{O}_8) \cdot 8\text{H}_2\text{O}$] and IR spectrum (OH-stretch and the C=O stretch at 3439 cm^{-1} and 1702 cm^{-1} respectively) were obtained for the dried pure sample.

1 g of the purified Zinc octa-4,5-carboxyphthalocyanine tetraimide was added to a solution of 200 ml of 2M NaOH and 80 g of NaCl, which was stirred for 3.5 hours at 70°C . The hot mixture was diluted with 100 ml of water and allowed to cool. The cold solution was filtered through a glass frit (10-15 μm porosity) and acidified with 262 ml of HCl (1.0 M; $\sim\text{pH } 2$) and left to sit for ~ 12 hours. The precipitate was filtered using a

Buchner funnel (10-15 μm porosity) and washed with 50 ml of 0.1 M HCl and ~100 ml of distilled water, until the filtrate was neutral as monitored by pH measurements (approximately six times). The weight of the wet sample was measured at 725 mg. This sample was vacuum dried and had a dry weight of 610 mg. UV-vis spectrum in distilled water for the Zinc 2,3,9,10,16,17-(hexacarboxylate)-23,24-(dicarboximide) phthalocyanine gave an extinction coefficient (689 nm) of $181,000 \text{ M}^{-1}\text{cm}^{-1}$ $[\text{Zn}(\text{C}_{40}\text{H}_{15}\text{N}_9\text{O}_{14}) \cdot 8\text{H}_2\text{O}]$.

0.5 g of Zinc 2,3,9,10,16,17-(hexacarboxylate)-23,24-(dicarboximide) phthalocyanine was suspended in 100 ml of distilled water. 10 ml of 1% NaOH (w/w) was added to the suspension, which was allowed to sit for 2 hours. The solution was filtered through a glass frit (4-5.5 μm porosity) and solvent stripped to dryness. The dry sample was washed with acetone and air dried (weight = 0.45 g, percentage yield = 17%). UV-vis for Zinc 2,3,9,10,16,17-(hexacarboxylate)-23,24-(dicarboximide) phthalocyanine sodium salt, hereafter called the photosensitizer, gave an extinction coefficient (696 nm) of $191,000 \text{ M}^{-1}\text{cm}^{-1}$ in water $[\text{Zn}(\text{C}_{40}\text{H}_9\text{N}_9\text{O}_{14})\text{Na}_6 \cdot 8\text{H}_2\text{O}]$. Elemental analysis is given in Table 3.

Table 3: Calculated and Found Elemental Analysis (C, H and N) for Zinc 2,3,9,10,16,17-(Hexacarboxylate)-23,24-(Dicarboximide) Phthalocyanine. $[\text{Zn}(\text{C}_{40}\text{H}_{15}\text{N}_9\text{O}_{14}) \cdot 8\text{H}_2\text{O}]$, FW= 1055.11 g/mol].

Element	Calculated (%)	Found (%)
Carbon (C)	45.53	45.15
Hydrogen (H)	2.96	2.11
Nitrogen (N)	11.95	11.76

Note: The molecular weight for the $\text{Zn}(\text{C}_{40}\text{H}_{15}\text{N}_9\text{O}_{14}) \cdot 8\text{H}_2\text{O}$ compound was calculated as 1055.11 g/mol and all concentrations of the Zinc 2,3,9,10,16,17-(hexacarboxylate)-23,24-(dicarboximide) phthalocyanine solutions were calculated based on this molecular weight.

CHAPTER 3

3. SYNTHESIS AND PROPERTIES OF THE PHOTSENSITIZER

3.1 Synthesis of the Photosensitizer, Zinc 2,3,9,10,16,17-(hexacarboxylate)-23,24-(dicarboximide) phthalocyanine sodium salt

The first synthetic procedure followed was that of V. Iliev and A. Mihaylova [21] who claimed to have synthesized the octacarboxy tetraimide zinc phthalocyanine by reacting pyromellitic anhydride with zinc acetate and ammonium molybdate in the presence of excess urea. The carboxy product of this reaction was very impure as judged by its electronic absorption spectrum which showed a Q-band extinction coefficient (681 nm) of only $1000 \text{ M}^{-1}\text{cm}^{-1}$ in distilled water [$\text{Zn}(\text{C}_{40}\text{H}_{15}\text{N}_9\text{O}_{14})$], and it was concluded that this method was inefficient to produce a pure phthalocyanine compound.

The second synthetic procedure followed was that of Kuznetsova et. al. [36]. Kuznetsova et. al., reacted pyromellitic dianhydride, excess urea, zinc acetate, sodium sulphate, 1-bromonaphthalene and ammonium molybdate to form the tetraimide compound. Sodium sulfate was used to absorb excess water from the reaction mixture. 1-bromonaphthalene solvent was used to create a partially homogenous reaction mixture (i.e. dissolve some of the pyromellitic acid, zinc salt and ammonia). Attempts to reproduce the monomer phthalocyanine complex using the same method as described by Kuznetsova et. al., was unsuccessful as indicated by the low extinction coefficient value (691 nm) for the salt ($11,000 \text{ M}^{-1}\text{cm}^{-1}$ in distilled water).

zinc octacarboxy phthalocyanine sodium salt

Reaction Scheme 1: Proposed mechanism for the Zinc octacarboxylate phthalocyanine following the protocol outlined by Kuznetsova et al.

Various techniques were used to purify the Zinc tetraimide phthalocyanine compound synthesized using Kuznetsova et. al.'s protocol. The crude tetraimide sample was washed with benzene in order to remove the unreacted 1-bromonaphthalene from the reaction mass and was followed by acid/base ($\text{HCl}/\text{NH}_4\text{OH}$) precipitation which ensured the removal of water soluble reactants, mostly urea, zinc acetate, sodium sulphate,

pyromellitic dianhydride and excess metal. Soxhlet extraction was used to further purify the tetraimide substance. The tetraimide compound was hydrolyzed and converted to its salt (via 1% NaOH) by using the literature protocol followed by Kuznetsova et. al. The extinction coefficient (691 nm) value of the purified salt compound was calculated in water to be only $21,000 \text{ M}^{-1}\text{cm}^{-1}$ [$\text{Zn}(\text{C}_{40}\text{H}_8\text{N}_8\text{O}_{16}\text{Na}_8)$]. Because soxhlet extraction proved ineffective, purification using flash chromatography was attempted. The final product had only a slightly improved extinction coefficient (691 nm, $32,000 \text{ M}^{-1}\text{cm}^{-1}$).

It was noted that the high temperature conditions of the Kuznetsova et. al., method seemed to decompose the product. Therefore, synthesis of the tetraimide compound was attempted using milder temperature conditions (190 °C for 4 hours). The tetraimide phthalocyanine was then hydrolyzed according to Kuznetsova et. al. After the end of hydrolysis, there was evidence of thermal degradation as visually indicated by a color change from dark green to yellowish green along with a measured weight difference. Therefore, milder basic conditions as proposed by V.Iliev and A. Mihaylova [21] were used to hydrolyze the tetraimide compound. Using these milder conditions, there was no visual evidence of discoloration in the reaction mixture at the end of 1.5 hours (80 °C). UV-vis spectrum of the compound was obtained in water and the extinction coefficient (695 nm) value ($119,000 \text{ M}^{-1}\text{cm}^{-1}$) is a significant improvement but still less than the expected value of approximately $200,000 \text{ M}^{-1}\text{cm}^{-1}$ [37].

It was hypothesized that the complexes synthesized using protocols outlined by both V. Iliev and A. Mihaylova and Kuznetsova et. al., were in fact polymers (i.e., dimers, trimers or of higher orders) and that this may have accounted for the difficulty in purification. This was supported by the ratio of carbon to nitrogen from the elemental

analysis for the synthesized complex (4.55/1) with that the theoretically calculated for polymeric phthalocyanine derivatives provided by W.C Drinkard et. al. [22], (see Table 4).

Table 4: Comparison of the Carbon: Nitrogen (C/N) Ratios for the Synthesized Compound (A), (see Section 2.7.5) with the Calculated C/N Ratios of Phthalocyanine Polymers (B).

Atomic Ratios	
C/N (A)	C/N (B)
Zn (C ₄₀ H ₈ N ₈ O ₁₆ Na ₈), FW= 1105.84 g/mol [Calculation: Found: C: 39.78%, H: 1.20% and N: 10.20%]	[Molecular formula, FW, polymer units]
	4.98/1 [Zn(C ₄₀ H ₁₆ N ₈ O ₁₆),FW = 930 g/mol, 1]
4.55/1	4.37/1 [Zn ₂ (C ₇₀ H ₂₆ N ₁₆ O ₂₄), FW = 1606 g/mol, 2]
	4.18/1 [Zn ₃ (C ₁₀₀ H ₃₂ N ₂₄ O ₃₂), FW = 2278 g/mol, 3]

Pyromellitic dianhydride in the presence of excess ammonia (formed by the decomposition of urea at high temperatures) will form dicarboxyimide diimino isoindoline which will readily form two fused phthalocyanine rings as shown in Scheme 2 below.

Reaction Scheme 2: Proposed structure for the dimer sodium salt of Zinc carboxylate phthalocyanine.

The method of D. R. Boston and J. C. Bailer [38] was followed using tetracyanobenzene instead of pyromellitic anhydride and urea. The reaction between zinc acetate and tetracyanobenzene (TCB) in the presence of ethylene glycol is depicted in Scheme 3 below. The hydrolysis of TCB in wet ethylene glycol generated low concentrations of ammonia which in turn induced cyclization of the remaining nitrile groups forming an iminoisoindoline moiety. As shown in Scheme 3 below, continued heating of the isoindoline **4** results in the formation of the desired ZnPc product **5**.

When comparing the infrared spectra of the crude Zinc tetraimide and the purified (by acid washing) Zinc tetraimide complex it was observed that the imide stretch for the impure Zinc tetraimide appeared at 1772 cm^{-1} . The peak was seen to be broad and wide, in contrast with the sharp and intense imide peak that appeared at 1702 cm^{-1} for the acid washed complex. UV-vis spectrum was determined and the extinction coefficient value (693 nm) in DMF was calculated to be $122,000\text{ M}^{-1}\text{cm}^{-1}$.

Table 5: IR Data for Zinc Tetraimide Phthalocyanine Using KBr Pellets at Room Temperature (see Appendix I).

	Frequency in cm^{-1}	
	Impure tetraimide complex	Tetraimide complex after acid/base extraction
O-H stretch	3740	3439
C=O imide stretch	1772 broad peak	1702 sharp peak

The next step in synthesis involved the hydrolysis of the Zinc tetraimide phthalocyanine complex **6**. Using D. R. Boston and J. C. Bailer's method, the Zinc carboxy phthalocyanine tetraimide compound was hydrolyzed using 18 M KOH. There was evidence of thermal degradation after 8 hours as indicated by a color change from dark green to yellowish green. Also, there was a considerable decrease in recovered weight (2.42 g to 0.20 g; yield 7.58%) which was indicative of decomposition during hydrolysis under strong basic conditions (18 M KOH). This method for hydrolysis was modified using a milder basic conditions as proposed by V. Iliev and A. Mihaylova (2 M NaOH). No discoloration was noticed at the end of the reaction (8 hours, yield 23.1%). The carboxy phthalocyanine was converted to its sodium salt by using the protocol outlined by Kuznetsova et. al. UV-vis spectrum (Figure 12) of the salt compound **7** was obtained and the extinction coefficient (696 nm) value in water was determined to be $191,000 \text{ M}^{-1} \text{ cm}^{-1}$. The monomeric nature of the compound was confirmed by elemental analysis (below) and further supported by the calculated atomic ratio of carbon to nitrogen (5.0/1). The calculated value for the C/N ratio was in agreement with the theoretical values shown in Table 4 for a monomer form of zinc phthalocyanine, thus confirming the monomeric nature of our complex. The calculated elemental analysis of the sodium salt of $\text{ZnPc}(\text{COO}^-)_8$ did not agree with that found but could be fitted assuming the hydrated Zinc 2,3,9,10,16,17-(hexacarboxylate)-23,24-(dicarboximide) phthalocyanine sodium salt. The complex purity was judged to be sufficient to carry out quantitative studies due to the high extinction coefficient of the photosensitizer ($191,000 \text{ M}^{-1} \text{ cm}^{-1}$).

Zinc 2,3,9,10,16,17-(hexacarboxylate)-23,24-(dicarboximide) phthalocyanine sodium salt

Reaction Scheme 3: Mechanism for the synthesis of sodium salt of Zinc 2,3,9,10,16,17-(hexacarboxylate)-23,24-(dicarboximide) phthalocyanine sodium salt, the photosensitizer.

Figure 12: UV-vis spectrum of the photosensitizer in water.

3.2 Aggregation of the Photosensitizer from pH 4 to 11

Figure 13: UV-vis spectra showing the behavior of the photosensitizer at room temperature in a pH 4-11 water-alkaline medium.

The nature of the photosensitizer in solution depends on the degree of ionization of the carboxyl groups of the phthalocyanine [43]. This is illustrated by Figure 13 which shows a change in photosensitizer absorption spectrum with decreasing pH. Under acidic conditions (pH 4), the carboxylic groups are likely protonated and this favours aggregation [10, 43]. As discussed previously, these aggregates do not have the

properties that allow them to form singlet oxygen in their excited state [28, 31]. To see if the absorption changes seen in Figure 13 were a consequence of the protonation equilibrium of the carboxylate groups, the photosensitizer was dissolved in DMF and to it different concentrations (1 drop-10 ml) of N-butylamine were added (Figure 14).

Figure 14: Spectra showing the behavior of the photosensitizer in DMF at room temperature using different concentrations of N-butylamine (BA) in 50 mL total volume of solution.

N-butylamine ($pK_a = 10.7$) is able to completely deprotonate the peripheral carboxyl substituents in the photosensitizer ($pK_a \sim 4.8$) [41, 43]. As shown by Figure 14, there is practically no change in the photosensitizer absorption spectrum with the addition

of N-butylamine. It is concluded that electronic transitions responsible for the Q-band of phthalocyanine are unaffected by the protonation equilibrium of the carboxylic groups and that the changes seen in Figure 13 are due to changes in the monomer/aggregate equilibrium.

3.3 Influence of Concentration on the Monomer-Dimer Equilibrium at pH 11

Figure 15: A: Band profiles with respect to the various concentrations of the photosensitizer in a pH 11 water-alkaline solution using different cells in aqueous solution at room temperature. B: Band profile with respect to the lowest concentration (10^{-7}) of the photosensitizer in a pH 11 medium. C: Plot of the logarithm of absorbance measured at 696 nm versus the logarithm of the photosensitizer concentration. A Cell with a 5 cm path length was used for 10^{-6} and 10^{-7} M solutions. Cells with 0.2 cm and 1 cm path lengths were used for 10^{-4} and 10^{-5} M solutions respectively. The absorbance was normalized relative to that of the 1 cm cell by dividing the measured absorbance by the path length of the cell used in the measurement.

The effect of concentration on the absorption spectra was studied for the photosensitizer in aqueous pH 11 solution and is shown in Figure 15A and 15B. The spectra for the lowest concentration (10^{-7} M) and the highest concentration (10^{-4} M) of the photosensitizer show an intense peak at 696 nm with no apparent shoulder, which is consistent with the monomer UV spectrum for the photosensitizer (Figure 12).

From the intercept of the linear best fit of the data in Figure 15C, an extinction coefficient of $179,000 \text{ M}^{-1}\text{cm}^{-1}$ is calculated, which is lower than that obtained from a solution of the photosensitizer at approx. 10^{-6} M ($191,000 \text{ M}^{-1}\text{cm}^{-1}$). This deviation maybe due to the formation of dimer at higher concentrations but considering the 1000-fold change in concentration to produce this effect, the influence of photosensitizer concentration on the monomer-dimer equilibrium must be small.

3.4 The Equilibrium Studies and Surfactants

3.4.1 Anionic and Non-Ionic Surfactants

Surfactants are classified according to their dissociation in water and are divided into four groups: (1) anionic; (2) nonionic; (3), cationic; and (4) amphoteric. Because the phthalocyanine is anionic, it was hypothesized that a cationic surfactant would be required to prevent aggregations. To confirm our hypothesis and to support our use of cationic surfactants, we decided to perform the SOOT experiments using anionic and nonionic surfactants. As hypothesized these surfactants were unsuccessful in protecting the photosensitizer against photodegradation during the SOOT experiment and thus no further characterization was performed using these classes of surfactants.

3.4.2 Monomer-Dimer Equilibrium and Cationic Surfactants

As seen in Figure 13 above, there exists a monomer-aggregate equilibrium where the photosensitizer is mostly an aggregate at low pH conditions (i.e., pH 4). To see if this

monomer-dimer equilibrium can shift towards mostly monomer species in solution and to study the state of the monomer-dimer equilibrium, the cationic surfactant CTAB was utilized at pH 4.

Figure 16: Spectra showing the effect of different concentrations of CTAB on the photosensitizer at pH 4.

Figure 16 shows varying concentrations of CTAB (0.004 M–0.006 M) complexed with the photosensitizer and its effects on dimerization at pH 4 as compared to a control containing only photosensitizer. The dimerization of the phthalocyanine decreases with

increasing amounts of CTAB. This is indicated by the Q-band shifting from 620 nm to 690 nm and the enhancement of its intensity as CTAB concentration increases in solution. Preliminary studies, however, indicated that CTAB precipitated from solution as a sulfate salt during the SOOT experiments, and so this equilibrium was examined with DTAB under the same conditions.

Figures 17 and 18 shows the absorption spectrum behaviour of the photosensitizer in a pH 4 medium at room temperature using different concentrations of DTAB (0.5 mM-28 mM) and is due to changes in the monomer-dimer equilibrium.

Figure 17: Spectra showing the behavior of photosensitizer in a pH 4 medium at room temperature using different concentrations of DTAB demonstration the monomer-dimer equilibrium.

Figure 18: Spectra showing the behavior of photosensitizer in a pH 4 medium at room temperature using different concentrations of DTAB demonstration the monomer-dimer equilibrium.

Because there are multiple sets of isosbestic points in Figures 17 and 18, we concluded that there exist more than two species in solution [42]. The scheme below shows some possible species that may be present in solution containing DTAB. As seen in Figures 17 and 18, there is no spectral change observed in the UV spectra of the sensitizer above the DTAB concentration of 30 mM. At the concentrations of photosensitizer and surfactant used in this experiment (see above) along with the fact that at concentrations greater than 4 mM, only one set of isosbestic point is observed, it can be

hypothesized that the equilibrium that exists is simply a micelle encapsulated dimer-monomer.

From the scheme presented above, it is suggested that in addition to the monomer species in solution there are also DTAB encapsulated monomer, dimer or aggregate complexes present in the medium above the DTAB concentration of 4 mM.

A similar trend was observed as the one seen for CTAB (Figure 16) when the concentration of DTAB was increased in a pH 6 solution from 8 mM to 28 mM (Figure 19).

Figure 19: Spectra showing the effect of different concentrations of DTAB on the photosensitizer at pH 6.

There were no significant changes observed in the absorption spectra at higher concentrations of DTAB (above 28 mM). It was found, with both cationic surfactants (CTAB and DTAB) and at both pH conditions (pH 4 and pH 6), the equilibrium shifted towards having more monomer species in solution and the concentration of DTAB required to attain the extinction coefficient that is associated with mostly monomer species in solution appears to be lower at pH 6 when compared to pH 4.

3.4.3 Protonation-Deprotonation Equilibrium Studies

There are two equilibria that occur in an aqueous solution containing the photosensitizer, (1) protonation-deprotonation (pH dependent); (2) and monomer-dimer equilibrium (see above).

Figure 20: Spectra showing the behavior of the photosensitizer in different phosphate pH buffers (0.05 M) and 40 mM DTAB, at room temperature.

Comparing Figures 20 and 13, it can be seen that when using DTAB, the photosensitizer exists mostly as monomer in pH ranges 6-10 (Figure 20) while when in solution without surfactant there are dimer species present at pH 6-10 (Figure 13) indicating there is no protonation-deprotonation equilibrium in solution (i.e., Figures 13 and 20 would look similar if there was such an equilibrium). Only at pH 4, is a significant concentration of dimer present under both conditions (with and without surfactant); however, when comparing Figure 20 to Figure 13, there are more monomer species present in solution in the presence of surfactant.

3.5 pH Dependence on the Singlet Oxygen Quantum Yield

The number of singlet oxygen molecules produced per photon absorbed by the photosensitizer is given by the value of Q_s , the quantum yield of singlet oxygen formation. The Q_s value for the photosensitizer was determined by using the method described in Chapter 2, Section 2.5, and using methylene blue as calibrant ($Q_s = 0.52$ [33]) at room temperature in a pH 7 aqueous solution in the absence of DTAB and in a pH 11 water-alkaline solution in the presence of DTAB. The reaction conditions were kept constant throughout the experiment and an excitation wavelength of 650 nm was used because at this wavelength the absorptivities of methylene blue and the photosensitizer are approximately equivalent.

Figure 21: $^1\text{O}_2$ emission intensity of 4.5×10^{-5} M methylene blue (calibrant) under pH 7 in the absence of DTAB.

Figure 22: $^1\text{O}_2$ emission intensity from an aqueous solution of methylene blue (calibrant) in the absence of DTAB. Singlet oxygen decay spectrum data fit to an active curve assuming first order decay. Conditions: Methylene blue 4.5×10^{-5} M, Milli-Q distilled water (pH 7). The solid line is a best-fit of eqn. 13.

In both studies we did not find any photodegradation of the phthalocyanine complex or calibrant monitored using UV-vis, indicating good stability under the experimental conditions employed. Figures 21 and 22 illustrate the treatment of the raw data and the results are summarized in Table 6. The ratio of the slope of the test solution to the calibrant times the quantum yield of the calibrant gave the quantum yields of singlet oxygen formation that are compiled below in Tables 6 and 7.

As shown in Figure 21, the initial signal at time zero after excitation gave a large signal which did not correspond to the intensity of singlet oxygen emission but was instead due to an electronic artifact. The intensity at time zero was estimated by extrapolation of data after the electronic noise had dissipated (3 to 4 microseconds) by assuming first order exponential decay according to the equation below:

$$I = -Ae^{-kt} \quad (13)$$

Where “I” is the intensity of singlet oxygen emission, “A” is the intensity of emission right after the flash, time zero, k is the first-order rate of decay (1/k is the measure of lifetime for the singlet oxygen) and “t” is the time in μs .

Singlet oxygen signal intensity at time zero, A in eqn. 13 was plotted versus concentration of methylene blue and the photosensitizer at different pH in the absence of DTAB and in the presence of DTAB in a pH 11 medium respectively, giving straight line relationships and these are summarized in Figures 23 and 24.

Figure 23: $^1\text{O}_2$ generation from Methylene Blue in aqueous medium and the photosensitizer in different water-alkaline pH media (pH 9, pH 10 and pH 11). Conditions: Photosensitizer: 0.037-0.041 mM.

Figure 24: $^1\text{O}_2$ generation from Methylene Blue and the photosensitizer in a pH 11 water-alkaline medium with the presence and absence of DTAB. Conditions: Photosensitizer in the presence of DTAB: 0.036-0.140 mM, photosensitizer in the absence of DTAB: 0.033-0.041 mM. Methylene blue: 0.0035-0.056 mM.

3.5.1 Calculation of the Quantum Yield of Singlet Oxygen Formation (Q_s)

Table 6: Calculated Values of the Quantum Yield of Singlet Oxygen for the Photosensitizer in Different pH Solutions in the Absence of Surfactant.

pH solutions containing the photosensitizer	Slopes (m)	Quantum Yields of Singlet Oxygen (Q_s)
pH 9	0.748	0.374
pH 10	0.873	0.437
pH 11	0.899	0.449
Standard	1.04	0.520 [33]

From the data in Table 6 it is clear that decreasing pH decreases the production of singlet oxygen. This is because as the pH of the solution drops, protonation of the photosensitizer takes place and the equilibrium present in the solution shifts towards the dimer formation as shown in Figure 13.

Table 7: Calculated Values of the Quantum Yield of Singlet Oxygen for the Photosensitizer in Different pH Solutions in the Presence of Surfactant.

pH solutions containing the photosensitizer	Slopes (m)	Quantum Yields of Singlet Oxygen (Q_s)
pH 11 (Without DTAB)	3.98	0.501
pH 11 (With DTAB)	3.76	0.474
Standard	4.12	0.520 [33]

From Table 7, it is clear that the singlet oxygen production levels remained approximately the same in the presence and absence of DTAB in a pH 11 medium. This indicates that the surfactant only plays a role in preventing photobleaching/photodegradation of the photosensitizer, while having minimal effects on the energy transfer mechanisms to create singlet oxygen.

Of note is that the maximum amount of singlet oxygen generated from the photosensitizer (as seen in Tables 6 and 7) is only slightly below the value measured for methylene blue. This variation, although not characterized, can be partially attributed to (a) difference in intersystem crossing to the triplet state from an excited state; or (b) difference in reaction conditions.

CHAPTER 4

4. SINGLET OXYGEN OXIDATION OF THIOSALTS **(SOOT)**

4.1 Photobleaching

4.1.1 Photobleaching in the Absence of Surfactant

Figure 25 shows the effect of irradiation on the photosensitizer over a period of 90 minutes using the SOOT test solution (see Chapter 2) but without added thiosulfate. A rapid decrease in the absorptivity of the Q-band is apparent indicating decomposition of the photosensitizer.

In an aqueous solution, superoxide ions are not stable and get rapidly converted to peroxide ions and oxygen (see Chapter 1, eqn. 8). These peroxide ions can either lead to (a) the chemical oxidation of thiosalts; or (b) the oxidation of phthalocyanine complex leading to photobleaching according to the reaction seen below:

Figure 25: Photobleaching of the photosensitizer under visible light irradiation (intensity = 166 klux), at 22 °C, in an oxygen saturated, pH 11 aqueous solution.

Figure 25 demonstrates that after 90 min of irradiation, bleaching of the photosensitizer is close to 95%. Consequently the production of singlet oxygen and hence sulfate ions is reduced by 95%. In previous studies, this problem of photobleaching was overcome by adding 0.12 M tetrabutylammonium bromide (Bu_4NBr) to the solutions prior to irradiation in the SOOT experiment [21]. Using such high concentrations of Bu_4NBr successfully reduced photobleaching but was considered an expensive answer to the problem and therefore, other surfactants and pH conditions were explored (discussion below).

4.1.2 Effect of pH on the Photobleaching of the Photosensitizer

In order to mimic environmental conditions such as the ones used in holding ponds of mine effluents, the effect of pH on the photosensitizer (i.e., photobleaching) was looked at under pH 10 and 11 conditions.

As shown in Figure 26, photobleaching is greater in pH 10 buffer solution compared to a pH 11 solution. This difference is probably due to the greater anion charge of the photosensitizer at pH 11 and the protection afforded to the photosensitizer by being surrounded by a more tightly bound sphere of tetrabutylammonium cations. With the greater loss of photosensitizer in pH 10 solution, sulfate yield at $T = 0\text{ }^{\circ}\text{C}$ and 4 hours irradiation was only 12% compared to that of a pH 11 solution, sulfate yield = 22%.

Figure 26: Bleaching of the photosensitizer (Q-band $\lambda = 696$ nm) with irradiation time in an oxygen saturated [A] pH 11 solution and [B] pH 10 borax buffer solution. Conditions: $T = 0$ °C; $5.7 \mu\text{M}$ photosensitizer; 0.12 M Bu_4NBr ; 1000 ppm $\text{S}_2\text{O}_3^{2-}$; irradiation intensity 166 klux .

4.1.3 Effect of Anionic, Non-Ionic and Amphoteric Surfactants on the Photosensitizer

The SOOT experiment was performed under visible light using the photosensitizer in the presence of three surfactants: (a) Triton X (non-ionic surfactant); (b) SDS (anionic surfactant); and (c) Tween 20 (non-ionic surfactant) (see detailed discussion of surfactants in chapter 1).

Figure 27: Photobleaching of the Zn phthalocyanine photosensitizer in the presence of Triton X-100 at critical micelle concentration. Conditions: $T = 0\text{ }^{\circ}\text{C}$, oxygen saturated pH 11 medium; 0.25 mM Triton X-100; 1000 ppm $\text{S}_2\text{O}_3^{2-}$, irradiation intensity 166 klux.

The spectra for all the three surfactants Tween 20 (CMC = 0.059 mM), SDS (CMC = 2.3 mM) and Triton X-100 looked similar to the one in Figure 27. It was observed in all three cases that there was a slight decrease in photobleaching when compared to Figure 25, but it was small compared to that of tetrabutylammonium cation. Therefore, from these preliminary tests, it was concluded that these three classes of surfactants were not significantly successful in inhibiting photodegradation and to further the research, the feasibility of cationic surfactants was explored.

4.1.4 Comparison of Cationic Surfactants CTAB to Bu₄NBr (TBAB)

Next, the SOOT experiment was performed under visible light using the photosensitizer in the presence of two cationic surfactants: (A) TBAB; and (B) CTAB.

Figure 28: Bleaching of the photosensitizer (Q-band $\lambda = 696$ nm) with irradiation time in oxygen saturated A) TBAB (0.12 M) and B) CTAB (1 mM) pH 11 water-alkaline solution. Conditions: $T = 22$ °C; $5.7 \mu\text{M}$ photosensitizer; 1000 ppm $\text{S}_2\text{O}_3^{2-}$; irradiation intensity 166 klux.

As shown in Figure 28B, there is only a slight decomposition of the photosensitizer over a period of 5 hours and this is due to the enclosure of the photosensitizer by a cationic micelle. In a SOOT solution, there exist neutral oxygen and anionic superoxide/peroxide species. It has already been shown that there is no significant difference in singlet oxygen generation in the presence or absence of surfactant (Figure 24). This is because neutral oxygen can freely diffuse through a cationic micelle and react with the photosensitizer triplet state to produce singlet oxygen.

Hydrated peroxide anion, which is able to oxidize the photosensitizer (eqn.14), is repelled by the inner hydrophobic layer of the cationic micelle (see Figure 7C), which encloses the photosensitizer and so oxidation of the photosensitizer is inhibited.

The presence of CTAB with the photosensitizer after 5 hours of irradiation showed higher conversion to sulfate (i.e., 54%) at a low concentration (i.e., [CTAB] = 1 mM) when compared to the percentage conversion to sulfate (i.e., 38%) when using a higher concentration of Bu₄NBr (0.12 M).

CTA⁺ performs better than TBA⁺ because CTA⁺ (C₁₉) completely surrounds the photosensitizer by having an organized micelle structure that prevents the peroxide to permeate inside to reach the photosensitizer. TBA⁺ (C₄), on the other hand is a smaller molecule and is unable to create an organized micelle around the photosensitizer allowing areas, where the peroxide can permeate through to reach the photosensitizer causing photobleaching.

4.2 SOOT Experiment with CTAB at 0 °C

Studies carried out by Silver et. al., in 1985 revealed that the rate of thiosalt oxidation using thiobacilli decreased by a factor of 10 when the temperature of the thiosalt oxidation ponds dropped from 30 to 5 °C. Therefore, it was decided to test what happens to the photosensitizer at lower temperatures (0 °C) when irradiated.

Figure 29: Bleaching of the photosensitizer (Q-band $\lambda = 696$ nm) during the SOOT experiment with irradiation time in an oxygen saturated CTAB (1 mM) pH 11 water-alkaline solution. Conditions: $T = 0$ °C; 5.7 μM photosensitizer; 1000 ppm $\text{S}_2\text{O}_3^{2-}$; irradiation intensity 166 klux.

The absorption spectra of the photosensitizer at 0 °C in the presence of CTAB (1 mM) in a pH 11 water-alkaline solution (Figure 29) showed significantly greater photobleaching compared to the room temperature experiment (Figure 28). A background increase was also observed in the UV spectrum because of the presence of a white precipitate. This precipitate was isolated from the SOOT solution and its IR spectrum (see Appendix I, Figure C) showed the characteristic vibration bands of the sulfate ion

[65]. The IR spectrum of $[\text{CTA}]_2\text{SO}_4$, prepared by the addition of CTAB to a concentrated sulfate solution, was identical to that of precipitate isolated from the SOOT solution. At low temperatures, the precipitation of CTA cations from the SOOT solution causes the photosensitizer to become unprotected from the peroxide anion, leading to a significant increase in photobleaching. The percentage conversion of thiosulfate to sulfate for the SOOT experiment in the presence of CTAB and Bu_4NBr is given below in Table 8. It is likely that CTA cation precipitated out of aqueous solution at lower temperature because of the 19 carbons in its organic tail that made it less polar and reduced its solubility in water. It was decided to try SOOT experiments at 0 °C with a surfactant with a smaller carbon backbone (i.e., DTAB).

Table 8: Comparison of the Percentage Conversion of Thiosulfate to Sulfate (Gravimetric Analysis of Barium Sulfate) for the SOOT Experiment Carried Out at 0 °C and 22 °C in the Presence of CTAB and Bu_4NBr .

	0 °C	22 °C
Conversion of sulfate in the presence of CTAB	2%	86%
Conversion of sulfate in the presence Bu_4NBr	25%	82%

4.3 SOOT Experiment Evaluated in the Presence of DTAB

SOOT experiment was performed for a set of test solutions to determine the minimum concentration of DTAB required to successfully encapsulate the photosensitizer. Table 9 summarizes the results obtained after irradiating the solutions containing the photosensitizer for 8 hours in a pH 11 medium with different concentrations of DTAB.

Table 9: Illustration of the Percentage Conversion of Thiosulfate to Sulfate in the SOOT Experiment Carried Out in the Presence of Different Concentrations of DTAB.

[DTAB] in mM	Weight of BaSO₄ [g]	% thiosulfate conversion at 22°C
0	0.0010	0.18
4	0.0030	0.53
8	0.0080	1.42
12	0.2180	38.8
14	0.5100	90.8
16	0.5540	98.7
20	0.5580	99.4

As the concentration of DTAB increases in solution, the rate of photobleaching of the photosensitizer decreases, this in turn causes the generation of more singlet oxygen leading to more conversion of thiosalts to sulfate. The conversion reaches a plateau when the concentration hits the critical micelle concentration of 16 mM. Therefore, a

concentration of 16 mM was used in the subsequent SOOT experiments with DTAB at 0 °C and 22 °C (Figure 30).

Figure 30: Bleaching of the photosensitizer (Q-band $\lambda = 696$ nm) during the SOOT experiment with irradiation time in an oxygen saturated DTAB (16 mM) pH 11 water-alkaline solution. Conditions: 5.7 μ M photosensitizer; 1000 ppm $S_2O_3^{2-}$; irradiation intensity 166 klux.

From Figure 30, it is evident that DTAB is efficient, even after 8 hours, in protecting the photosensitizer from photobleaching at 0 °C and 22 °C, that results in a 67% and 93% conversion of thiosulfate to sulfate respectively, as compared to the minimal % conversion achieved using CTAB (i.e., 2% at 0 °C, see Table 8).

4.4 Comparison of the Photosensitizer to the Tetracarboxylate ZnPc in the presence of DTAB

Experiments were carried out to compare the photoactivity of Dr. MacLean's $\text{ZnPc}(\text{COONa})_4$ photosensitizer (5.7 μM) with the photosensitizer (5.7 μM) in the presence of DTAB (16 mM). The SOOT conditions (see Chapter 2) other than the photosensitizer were equivalent in both cases. After irradiating the reaction solutions containing $\text{ZnPc}(\text{COONa})_4$ for 8 hours in the presence of DTAB, gravimetric determination of barium sulfate was performed. The percentage conversion of thiosulfate to sulfate at 0 °C with $\text{ZnPc}(\text{COONa})_4$ was determined to be 33% (compared to the photosensitizer conversion of 67%). Therefore, it is evident that the photosensitizer converts a higher amount of thiosulfate to sulfate in oxygen saturated pH 11 medium with minimum photodegradation observed after 8 hours when compared to $\text{ZnPc}(\text{COONa})_4$. The reason for this difference may lie with magnitude of Q_s but it also possible that the photosensitizer is better protected by a DTA^+ micelle owing to its greater negative charge.

4.5 SOOT Experiment Evaluated in the Presence of DTAC

It might be possible that the bromide anions from the surfactant (DTAB) could participate in the SOOT processes, perhaps by being oxidized by singlet oxygen or peroxide. Replacing the bromide anions with chloride anions should have a significant effect on the SOOT process if bromide anions do participate because of the difference in their oxidation couples as shown below:

Looking at the reduction potentials of the halides and those of the oxidants peroxide and singlet oxygen, it seems unlikely that oxidation of the halides would occur. However peroxide's reduction couple is pH dependent and increases to +1.76 V vs NHE under acidic conditions [58, 64]. To remove the possibility of halide oxidation, it was decided to perform the SOOT experiment at 22 °C with the chloride and bromide salts of DTA⁺ (see Figure 31).

Figure 31: Bleaching of the photosensitizer (Q-band $\lambda = 696$ nm) during the SOOT experiment at 22 °C with irradiation time in an oxygen saturated DTAB (16 mM) and DTAC (16 mM) pH 11 water-alkaline solution. Conditions: 5.7 μ M the photosensitizer; 1000 ppm $S_2O_3^{2-}$ irradiation intensity 166 klux.

There was no dramatic change in the production of sulfate measured at the end of 5 hours between the two different counterions (91% and 92% for DTAC and DTAB respectively). From this it was concluded that the oxidation of bromide anions or chloride anions, if any, is negligible.

CHAPTER 5

5. CONCLUSION AND FUTURE STUDIES

5.1 Conclusion

In this research project, important insights were gained towards the synthetic route and characterization of the photosensitizer, which had superior qualities than the previously studied $\text{ZnPc}(\text{COONa})_4$. Research carried out by Brian MacLean showed dimerization of $\text{ZnPc}(\text{COONa})_4$ (Figure 4) in aqueous solution that is undesirable as the photophysical properties of excited dimers are not appropriate for photosensitization of singlet oxygen. Thus, the $\text{ZnPc}(\text{COONa})_4$ was modified to the photosensitizer used in this research project and as shown, this modification increased the overall negative charge on the photosensitizer, which increased the repulsion between complexes and reduced the tendency towards dimerization in aqueous solution.

The effect of irradiation on the photosensitizer was studied during the SOOT experiments using an optimum pH (pH 11) where the complex was mostly in its monomer form and which would mimic environmental conditions of holding ponds. Within the first 90 minutes the complex was completely photobleached. Therefore, in order to protect the photosensitizer from photodegradation, the feasibility of using surfactants was explored. A much lower concentration of cationic surfactants such as CTAB (1 mM) and DTAB (16 mM) was required as compared to Bu_4NBr (0.12 M) to protect the photosensitizer from peroxide. The SOOT experiment was carried out under

different temperature conditions (0 and 22 °C) in the presence of CTAB, TBAB and DTAB using the photosensitizer and the percentage conversion at 0 °C of thiosulfate to sulfate (by gravimetric analysis of barium sulfate) for solutions containing CTAB, TBAB and DTAB was calculated to be 2%, 25% and 67% respectively; thus making DTAB a more practical alternative than the previously used Bu_4NBr .

Experiments were carried out to compare the photoactivity of the $\text{ZnPc}(\text{COONa})_4$ with the photosensitizer in the presence of DTAB (16 mM). The percentage conversion of thiosulfate to sulfate at 0 °C with $\text{ZnPc}(\text{COONa})_4$ was determined to be 33% (compared to the photosensitizer conversion of 67%). Therefore, it is evident that the photosensitizer is more efficient in the SOOT process (higher conversion of thiosulfate to sulfate).

The singlet oxygen production levels remained approximately the same in the presence and absence of DTAB ($[\text{DTAB}] = 16 \text{ mM}$) with $Q_s = 0.47$ and 0.50 , respectively; thus suggesting that the primary function of the surfactant in the SOOT process was to protect the photosensitizer from photobleaching.

Therefore, we have shown a stable surfactant-photosensitizer system that is successful in converting thiosalts to sulfates, where the surfactant protects the photosensitizer from photobleaching by preventing permeation of the peroxide through the micelles while allowing molecular oxygen to permeate through the micelles. Nevertheless, there exist many challenges that need to be dealt with in order to create an application based system that can be used in the holding ponds. Working with numerous surfactants it was observed that as the number of carbons in the organic tail increased, the solubility in water at 0 °C decreased. Although the large sized surfactants have a low

CMC (e.g. CTAB = 1 mM) and are comparatively low in cost (CTAB, \$49 for 100 or ~\$179/m³ of effluent), they are not efficient in forming a micelle around the photosensitizer at 0 °C and this eventually results in photobleaching of the photosensitizer. As previously discussed, DTAB is a small surfactant having 15 carbons in its tail and is more soluble in water at 0 °C. Unfortunately, it is expensive to use in the SOOT process (\$100 for 20 g or ~\$2400/m³ of effluent) because of its high CMC (16 mM). As mentioned in the introduction, the goal is to obtain a method of treating mining effluent at a cost of only 0.30/m³ of effluent. Using surfactants in the SOOT process is economically impractical and alternative methods are the subject of future studies.

5.2 Future Studies

The chemistry of singlet oxygen is rich and its potential uses have recently been realized. Much needs to be done to modify and improve existing photosensitizers to better suit their properties and desired applications. This of course requires better understanding of the mechanism of the photosensitizer quenching and photobleaching.

Future studies may involve a dendrimer wrapping around the photosensitizer via covalent bonding with the carboxylates, where the dendrimer would protect the photosensitizer from photobleaching and would remove the need for surfactants [23]. The dendrimer may wrap more than one photosensitizer molecule depending on its chain length thus reducing cost further. Also the dendrimer-photosensitizer being large (typically > 40 nm) may be easily filtered out prior to release of the effluent into the rivers. Along with industrial advantages, dendrimers offer Environmental Health and Safety (EHS) benefits where surfactants are highly toxic to aquatic life while dendrimers

being large typically do not elicit toxic affects. However, during the SOOT experiment the mechanism of diffusion of oxygen and peroxide in and out of the dendrimer would require detail understanding of the polymer and further studies would need to be implemented with respect to photobleaching of the dendrimer-photosensitizer system.

Also, the photosensitizer may be absorbed onto the surface of particles (such as quantum dots) that would mediate reactions on the nanoparticle surface (where the photosensitizer is rendered active by coupling between the nanoparticles and photosensitizer) [24] and mitigate the release of the photosensitizer into waterways (i.e., by recovering or destroying the particles and constituents sorbed onto its surface). Of course, a detailed understanding of the coupling between nanoparticles and photosensitizers, such as possibly energy quenching, will need to be thoroughly investigated. Substances such as cadmium-selenide quantum dots are currently prime candidates in EHS research due to their ease of detection [24].

APPENDIX 1

Figure A: IR spectrum of the impure Zinc tetraimide

Transmittance / Wavenumber (cm-1)

Figure B: IR spectrum of the tetraimide complex after acid/base extraction

Figure C: Infrared spectrum in KBr of $[\text{CTA}]_2\text{SO}_4$

Figure D: IR spectrum in KBr of [DTA][BPh₄].

REFERENCES

1. Braun, A., and Tcherniac, J., Ber. Deut. Chem. Ges. 40 (1907), p. 2709
2. Byrne, G., T., Linestead, R., P., and Lowe, A., R. J. Chem. Soc. (1934), p. 1022
3. Chanda, A., O'Driscoll, K., F., and Rempel, G., L. J. Mol. Cat. A. 7 (1980), p. 389
4. Dinardo, O., CANMET, Personal communication
5. Hackett, J., and Turro, C. Inorganic Chemistry. 37 (1998), p. 2039
6. Haque, K., E., and Dinardo, O. Div. Rep. MMSL 96-039 (OP&J), CANMET, Energy, Mines and Resources Canada (1997)
7. Iliev, V., Prahov, L., Bilyarska, L., Fischer, H., Schulz-Ekloff, G., Wohrle, D., and Petrov, L. J. Mol. Cat. A. 151 (2000), p. 161
8. Iliev, V., and Ileva, A. J. Mol. Cat. A 103 (1995), p. 147
9. Lebedeva, N., S., Pavlycheba, N., A., Petrova, O., V., Vyugin, A., I., Kinchin, A., N., Parfenyuk, E., V., Mayzhlish, V., E., and Shaposhnikov, G., P. Mendelev Communications. 13 (2003), p. 237
10. Leznoff, C., C., Lever, A., B., P. Phthalocyanine: Properties and Applications, 2nd edition. Wiley-VCH, 1993
11. Lissi, E., A., Encinas, M., V., Lemp, E., and Rubio, M., A. Chem. Rev. 93 (1993), p. 699
12. Mckeown, N. Phthalocyanine Materials. Cambridge University Press (Jul 13 1998)
13. Robertson, J., M. J. Chem. Soc. (1935), p. 615

14. Rolia, E. Div. Rep. MRP/MSL 84-144 (TR). CANMET, Energy Mines and Resources Canada (1984)
15. Rosen, Milton J. Surfactants and Interfacial Phenomena. John Wiley & Sons. 1-7 (1978), p. 234
16. Silver, M. Appl. Environ. Microbio. 50 (1985), p. 663
17. Spiller, W., Wohrle, D., Schulz, G., Ford, W., and Stark, J. Journal of photochemistry and photobiology A. (1996), p. 161
18. Wasserlauf, M., and Ditrizac, J., E. Canadian Metallurg. Quart. 23 (1984), p. 259
19. Wong, W., S. Division Report MRP/MSL 81-112 (TR), CANMET, Energy, Mines and Resources Canada (1981)
20. <http://sales.hamamatsu.com>
21. Iliev, V., and Mihaylova, A. Journal of Photochemistry and Photobiology A: Chemistry. (2002). Vol 149, Issues 1-3, p. 23
22. Drinkard, W., C., and Bailer, J., C. J. Amer. Chem. Soc. 81 (1959), p. 475
23. Zhang, Guo-Dong, Harada, A., Nishiyama, N., Jiang, Dong-Lin., Koyama, H., Aida, T., and Kataoka, K. Jour. Cont. Rel. 93 (2003) 2, p. 141
24. Hodon, M., Horvath, E., Haspel, H., Kukovecz, A., Konya, Z., and Kiricsi, I. Chem. Phys. Lett. (2004) 4-6, p. 512
25. Black, Shaun, D. Properties of Detergents (Ampiphiles). University of Texas Health Centre at Tyler
26. Huang, X., Yang, J., Zhang, W., Zhang, Z., and Zesheng, M. Journal of Chemical Education. 76 (1999), No.1, p. 93
27. Moser, F.H., Thomas, A.L. The Phthalocyanines. CRC press (1968)

28. West, W., and Pearce, S. *Journal of Physical Chemistry*. 69 (1894), p. 16
29. Schwartz, Melissa, L., Vigneault, B., and McGeer, J. (2006). Report CANMET-MMSL 06-053(CR)
30. Metal Mining Effluent Regulations. *Canada Gazette Part II*. SOR/2002 202 to 206 and SI/2002-90 to 96. (2002), p.1246
31. Thomas, J., L., and Allen, N., S. *Dyes and Pigments*. 53 (2002) p. 195
32. Helman, W., P., and Ross, A., B. *J. Phys. Chem. Ref. Data*. 24(1995), p. 663
33. DeRosa, M., and Crutchley, R., J. *Coordination Chemistry Reviews*. 233-234 (2002), p. 351
34. Torinuki, W., and Miura, T. *The Tohoku Journal of Experimental Medicine*. 140 (1983), p. 297
35. Schweitzer, C., and Schmidt, R. *Chem. Rev.*, 103 (2003), p.1685
36. Kuznetsova, N., A., Gretsova, N., S., Derkachena, V., M., Mikhaleenko, S., A., Solov'eva, L., I., Yuzhakova, O., A., Kaliya O., L., and Luk'yanets E., A. *Russian Journal of General Chemistry*. 172 (2002), p. 300
37. Ozoemena, Kenneth, I., and Nyokong, T. 6 (2003), p.1192
38. Boston, D. R., and Bailer, J., C. *Inorganic Chemistry*. 11 (1972), Issue 7, p. 1578
39. Sakamoto, K., and Ohno, E. *Progress in Organic Coatings*. 31 (1997), p.139
40. Mathai, S., Smith, T., A., and Ghiggino, K., P. *Photochem. Photobiol. Sci.* 6(2007), p. 995
41. Faure, S., Stern, C., Guillard, R., and Harvey, P., *J. Am. Chem. Soc.*, 126 (2004), p. 1253

42. Anderson, S., E., and Nyberg, G., L. Applications of Surface Science. 22-23 (1985), p. 325
43. Lebedeva, N., Sh., Petrova, O., V., V'yugin, A., I., Maizlish, V., E., and Shaposhnikov, G., P. Optics and Spectroscopy. 94(2003), p. 924
44. Jeffery, W., B., Micheal, F., Reynolds, J., R., and Kim, S. Langmuir-American Chemical Society. 15 (1999), p. 6460
45. Finlayson, Chris, E., Ginger, D., S., and Greenham, N., C. Chemical Physics Letters. 338 (2001), p. 83
46. Hong, Suc-Kyoung. Physica E. 28 (2005), p.66
47. Ozoemena, K., Kuznetsova, N., and Nyokong, T. Journal of Photochemistry and Photobiology A: Chemistry 139 (2001), p. 217
48. Maclean, B., and Crutchley, R., J. Chemistry Department of Carleton University. CAMNET-NRCan. October 31, 2002. <http://www.nrcan.gc.ca/ms/canmet-mtb/mmsl-lmsm/enviro/effluents/effthiosalts-e.htm>
49. Yates, Stephen, Good, Mary, L., Gaita, Romulus. World Intellectual Property Organization (WO 1990007144). June 28, 1990
50. Malinauskas, A. Journal of Applied Polymer Science. 73 (1999), p. 287
51. Mata, J., Varada, D., Ghosh, G., and Bahadur, P. Colloids and Surfaces A: Physiochemical and Engineering Aspects. 245 (2004), p. 69
52. Baudin, H., B. Comprehensive Summary of Uppsala Dissertations from the Faculty of Science and Technology. Acta University Upsaliensis Uppsala (2001)
53. Neta, P., Alberta, B., R., and Huie, R. J. Phys. Chem. 17 (1988), p. 1027

54. Saito, I., T., Matsuura, and Inoue, K. Journal of the American Chemical Society. 105 (1983), p. 3200
55. Afanas'ev, Igor, B. Superoxide Ion: Chemistry and Biological Implications Volume I. CRC Press, 1991
56. Eriksen, J., Foote, C., S., Parker, T., L. Journal of the American Chemical Society 99 (1977), Issue 19, p. 6455
57. Petlicki, J., and Van de Ven, Theo, G., M. Chem. Soc., Faraday Trans. 94 (1998), p. 2763
58. Doyle, F., M., and Wang, L. University of California. Proceedings VMIC 2003 (12th Int. VLSI Multilevel Interconnection Conference). (2003), p. 267
59. Snyder, Milton, K. Chemistry; Structure and Reactions. Holt, Rinehart and Winston, 1966
60. Kirk, Raymond, Eller, and Othmer, Donald, Frederick. Encyclopaedia of Chemical Technology. Published 1947
61. Barrett, Jack. Inorganic Chemistry in Aqueous Solution. RSC Publishing, 2003
62. Kerner, Nancy, Konigsberg, and Konigsberg, Nancy. Chemical Investigations. Benjamin/Cummings Pub. Co., 1985
63. Brady, George, S., Clausar, Henry, R., and Vaccari, John, A. Materials Handbook. McGraw-Hill Professional, 2002
64. Bockris, John, O'M., Conway, Brian, E., and Yeager, Ernest, B. Comprehensive Treatise of Electrochemistry. Springer, 1985
65. Pouchert, Charles, J. The Aldrich Library of Infrared Spectra - 3rd edition. Aldrich Chemical (1997) ISBN: 978-0-941633-39-0

66. Douglas, B., McDaniel, D., H., and Alexander, J., J. Concepts and Models of Inorganic Chemistry, 2nd ed. Wiley, 1983
67. Atkins, Peter. Physical Chemistry, 6th ed. W.H. Freeman and Company, 1997
68. Borgmann, U., Couillard, Y., Doyle, P., and Dixon, G. Environmental Toxicology and Chemistry. 124 (2005), p. 641