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Studies of Titanium Dioxide Nanoparticles and Surfactants Effects, Singly and in Combinations, on Luminescence Intensity of Some Aromatic Compounds.

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by

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ABSTRACT

Studies of Surfactants and Titanium Dioxide Nanoparticles Effects, Singly And in Combinations, on Luminescence Intensity of Some Aromatic Compounds

by

Charles Anim Odame-Ankrah

Luminescence techniques are sensitive, selective, and widely used in analysis. Luminescence intensity is attenuated by quenchers. This research has focused on the use of surfactants such as CTAB, SDS, and TX-100 singly or together with TiO_2 nanoparticles to evaluate their individual and combined effects on some fluorescent aromatic compounds such as pyrene, fluoranthene, anthracene, phenanthrene, and carbazole. Rutile phase TiO_2 was synthesized using the low temperature sol-gel method. Carbazole and phenanthrene were severely quenched by all surfactants singly or in combination with TiO_2. Anthracene and fluoranthene showed some enhancement in their luminescence intensity. The most dramatic effect was observed on the fluorescence intensity of pyrene. Pyrene showed enhanced fluorescence after degassing the solution alone or with the addition of the surfactants alone or in combination with TiO_2 after degassing. These results showed that surfactants and TiO_2 nanoparticles either singly or in combination should be useful for analysis employing luminescence techniques.

DEDICATION

To Benedicta my dearest wife and Kwasi my beloved son

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My deepest gratitude goes to Dr. Chu Ngi-Ho for his fatherly and professional guidance throughout this work. Without him, all what I have done would not have been meaningful.

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CHAPTER 1

INTRODUCTION

The recent quest to improve and advance existing methodologies for sample analysis in terms of accuracy, precision, and rapid analytical response had driven researches in the areas of analytical chemistry and other fields. Most often, existing techniques tend to be time consuming and then often with low limit of detection. One of the powerful analytical techniques that had been found useful in almost every discipline is fluorescence which is a type of luminescence generally known as fluorometry. It is highly selective and sensitive and has a very wide linear dynamic range. This uses absorption of light by molecules that cause them to be excited. In the process of de-excitation, they emit photons which can give that both qualitative and quantitative measurements characteristic of the compound of interest. This light absorption-emission principle has been used in diverse fields especially by chemists and biochemists as an analytical tool for identifying, quantifying and, studying the behavior of millions of compounds. It is a very simple and easy to use method.

In terms of instrumentation, a spectrophotometer (fluorometer) is used to make fluorescence measurements. A homemade fluorometer could be designed for laboratory measurement purposes even though it may not be as accurate and precise as a commercial factory-made spetrophotometer. Source of light used for excitation of the compounds too are pertinent when it comes to fluorescence. Every compound has a unique wavelength of excitation and emission. This simplicity and accuracy of fluorometric technique has made it a widely used method when it comes to analysis of compounds that can fluoresce.

In the forensic sciences fluorescence is employed primarily to investigate crime scenes and other very critical decisions are made based on these findings. Many crimes and mysteries have been resolved due to the use of fluorometric techniques. Quenching that was considered a demerit of fluorescence now has a very useful analytical implications based on qualitative and quantitative analysis especially in biochemistry. Low resolution structure of membrane proteins are determined using fluorescence quenching (1). Anthracene quenching probes are being developed using parallax analysis of nitroxide-labeled phospholipid induced fluorescence quenching (2). Another breakthrough in the field of mining is the invention of the laser induced breakdown spectroscopy (LIBS) that now saves time and money associated with ore analysis. LIBS is now used to analyze ore on the spot based on fluorescence technology (3). In most cancer researches especially lung cancer, this is the main method being relied upon for quick response in relation to early lung cancer detection (4).

The merits of fluorescence technique cannot be overemphasized. But as usual it has its unique problems. A compound could fluoresce under a given condition such as the light source used. A compound can only fluoresce given the appropriate light source for excitation as in the analysis of any compound and the ability of the compound to emit light as photons. Its excitation wavelength is critical in determining that compound qualitatively or quantitatively. More so, only limited number of the excited compounds could fluoresce, thereby limiting the use of fluorometry as a general analytical technique. As mentioned earlier, quenching by impurities or the matrix is another source of worry. Some compounds also decompose after excitation by altering the stability of the compounds in the excited state. Instrumentation had

been a big source of worry too, because orientation of the components also affects the output signal of the technique.

Polycyclic Aromatic Hydrocarbons

Most aromatic organic compounds that have shown very intense fluorescence are polycyclic aromatic hydrocarbons (PAHs) such as pyrene, anthracene, phenanthrene, fluoranthene, fluorene, etc as shown in Figure 1.

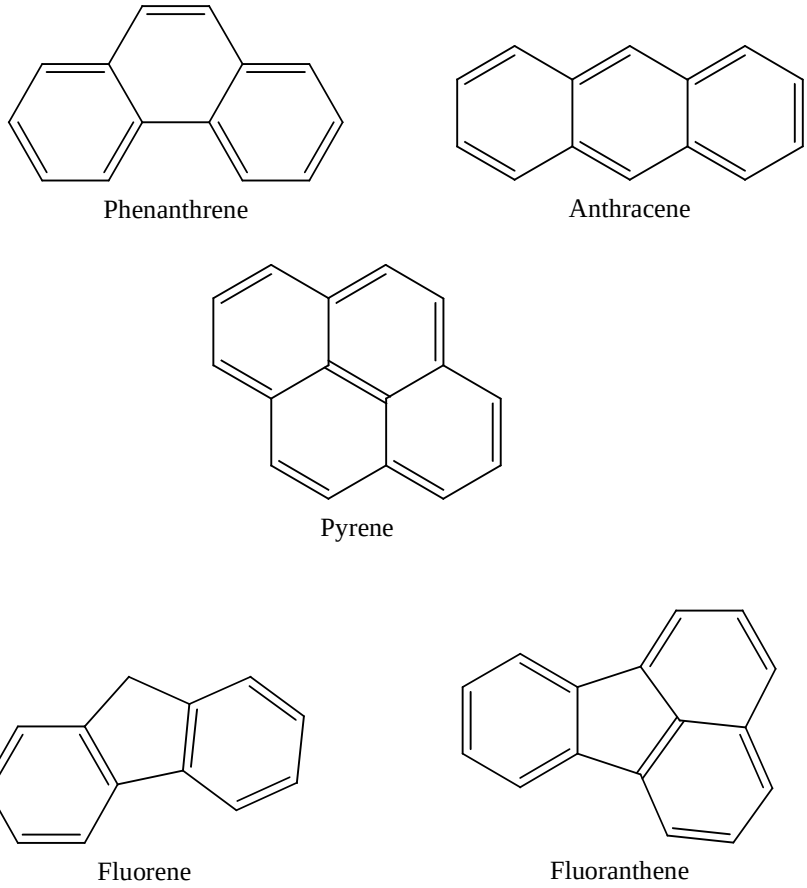

Figure 1: Structures of some polycyclic aromatic hydrocarbons

The main sources of aromatic hydrocarbons are furnaces, cigarette/tobacco smoke, coal burning, volcanic eruptions, petroleum production, and even decaying matter. PAHs have

generated a lot of concern especially in relation to human exposure and environmental toxicological impacts. Pyrene in itself is not a carcinogen but its derivatives such as benzo(a)pyrene have been labeled as hazardous. It is related to the class of compounds classified as being carcinogenic. (5-7).

Aromatic Heterocyclic Organic Compounds

Other class of fluorescent compounds is the aromatic heterocyclic organic compounds of which acridine, carbazole, carboline, indole, and indoline are typical examples shown in Figure 2.

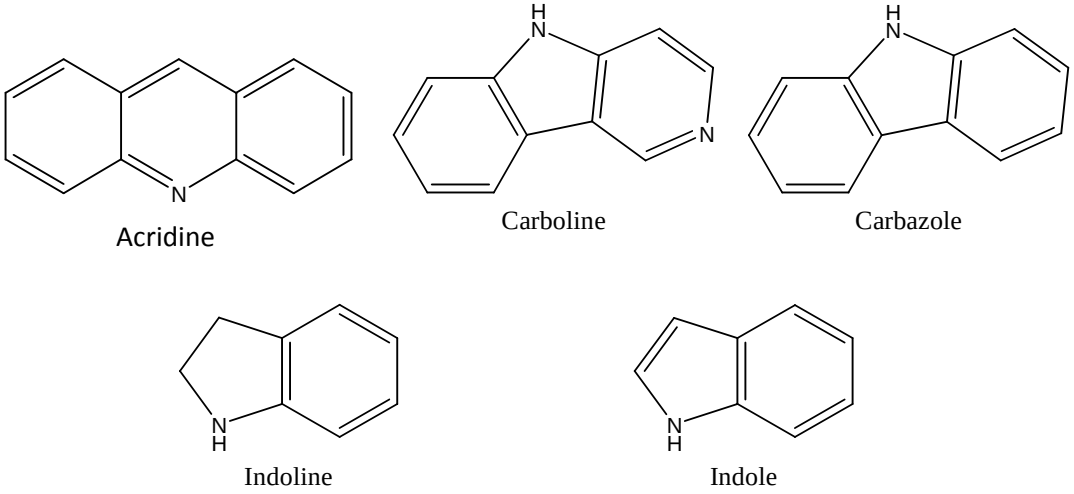

Figure 2: Examples of aromatic heterocyclic organic compounds

Most of these compounds have been shown to be extremely carcinogenic but acridine also has antiseptic properties (8).

These compounds show strong fluorescence and have been extensively researched. Some are easily quenched in the presence of molecular oxygen and hence need a supporting matrix to enhance or stabilize its transition to the excited singlet state and subsequently

fluoresce thereby overcoming competing transitions such as intersystem crossing that tends to quench them (9).

Micellar medium

One of the widely used matrixes to affect fluorescence intensity is surfactants through micelle formation. The surfactants, which are surface acting agents, have shown various degrees of impact on the fluorescence of these compounds due to their ionic properties be it cationic, anionic, or neutral. They serve as organized medium that may 'protect' the molecules from the impurities or other quenching factors (10). Examples of these surfactants are 1-octanesulfonic acid sodium salt (OSA) and sodium dodecylsulfate (SDS) that are anionic, and hexadecyltrimethylammonium bromide (CTAB) that is cationic. Their structures are shown in Figure 3.

Critical Micelle Concentration of Surfactants

This is the concentration above which the surfactants for aggregates called micelles. These aggregates could be normal micelle formation as in the case of cationic surfactants where the hydrophilic head form the inner core with the hydrophobic tails forming the outer sphere. In the case of reverse micelle formation, the inner core is the hydrophilic heads with the hydrophobic tails forming the outer sphere. The critical micelle concentrations of CTAB, SDS are 9.2×10^{-4} M and 8.1×10^{-3} M respectively. Triton X-100 is a non-ionic surfactant with a molecular formula of $C_{14}H_{22}O(C_2H_4O)_n$, The critical micelle concentration of Triton X-100 is 3×10^{-4} M. (11).

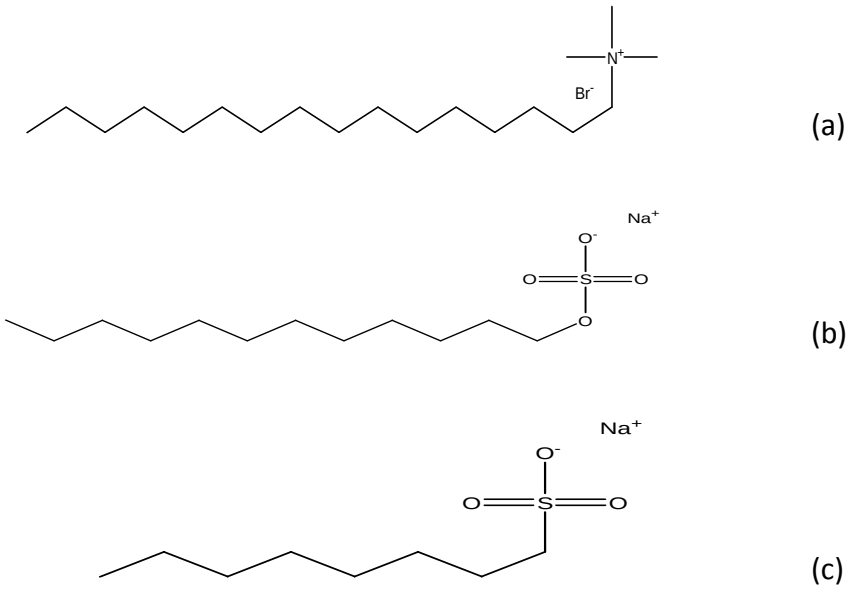

Figure 3: Molecular Structure of (a) hexadecyltrimethylammonium bromide (CTAB), (b) sodium dodecylsulfate (SDS), (c) 1-octanesulfonic acid sodium salt (OSA)

Micelles have the ability to incorporate and or to arrange solutes into their interior or on their colloidal surface. When a solute passes from the aqueous medium to the micellar medium, some changes are usually observed in several properties of the solute such as its reactivity, solubility, or spectroscopic characteristics. Thus in fluorescence there have been observable increases in the sensitivity. Also the relative viscosity of these micellar microenvironments can inhibit quenching by molecular oxygen (12-15).

Despite these improvements in this technique, nanotechnology, a modern area where a lot of ongoing research is being conducted to understand the behavior of compounds at the nano scale level, has been found to have some fluorescence applications.

Nanoparticles and Quantum Dots

Nanoparticles, nanocomposites, nanotubes, and a host of other type structures have unique properties and are being researched for their usefulness in drug discovery, cancer treatment, sensors, automobiles, aircrafts, and all the other areas of everyday life. (16)

Nanoparticles

Nanoparticles are the basic structure of all particles. The properties of nanoparticles depend on structure and composition. Their size, shape, and morphology are the parameters of identifying them. Their interfacial or interphase properties differ from the macroscopic bulk properties due to their size and ability to interact with the domain of which they are found. The iteration of nanoparticles at the nanoscale level is through weak Van der Waals forces, electrostatic forces, or covalent forces. The nature of the medium such viscosity or polarisability of the fluid dictates the properties of aggregation associated with the particle size or surface modification interactions. The nanopaticles interact freely with the solution but the interactions are mainly controlled by the nature this solution and this result in a characteristic property of the nanoparticle in that solution. Nanoparticle are formed naturally or though synthetic means. The synthetic methods of producing nanoparticles pose a big challenge to researchers because their behavior of these nanoparticles are much undetermined and not well understood (17).

Quantum Dots

Inorganic particles, which are known as Quantum dots, have shown optical and electric properties as their size approaches the nanoscale facet. Quantum dots are now intensively

being studied for their applications in electro-optics and biomedical imaging (18). The particle in a box problem in quantum mechanics that illustrates that kinectic energy increases as consequence of a decrease in the box size is the foundation of quantum dots. If a box has a length of $L = \Delta x$ and electron momentum, $p = mv$, the kinetic energy is now non-zero and has finite value:

$$E = \frac{\hbar^2}{2mL} \qquad 1$$

Where M is the electron mass and $\hbar$ is the Planck's Constant and assuming a box length of L. This equation defines the basics of size-color intensity relations of quantum dots. Quantum dots further explain and extend the particle in a box confinement idea to colloidal chemistry. Examples of quantum dots systems are CdSe, CdS, CdSe/ZnS, and CdS/ZnS with particle sizes ranging from 2.0-7.8 nm (19)

Applications of Quantum Dots

The most successful application of quantum dots is its use as biological tags that involves modification the quantum dot surfaces for specificity for imaging biological targets (20). Another very important application is their use in electro-optic devices such as Light-Emitting Diode (LED), Photovoltaics(PV), and lasers. This has provided a large-scale but cheap means of producing semiconductors thin films (21).

TiO_2 Nanoparticles

A typical example of a metal oxide nanoparticle is titanium dioxide TiO_2 nanoparticle. Diebold reported that TiO_2 is used as a photocatalyst, heterogeneous catalyst, gas sensor, in

solar cells, and various other items and devices such as probes (10). It exists mainly in three forms; rutile and anatase (which are both photocatalytic in nature) and brookite, which is not (22). Rutile appears as a white shiny crystalline material with very good light scattering effects. Nanosized TiO_2 has been found to be very important especially in environmental cleaning agents and in the decomposition of some pollutants. It is also used as pigment in paints, as sun block (sunscreen) in many cosmetic lotions, and again as a photocatalyst (10, 23). A new x-ray molecular probe has been developed using TiO_2 nanoparticles. It is used in the detection of the location certain proteins that play an important role in diagnostics early stages of cancer in humans (24). Recent studies also show that TiO_2 has shown potency in eradicating cancer cells even though its applications in humans are limited due to its photocatalytic nature (25).

Toxicology of Nanoparticles

While there are numerous and promising applications, little is known, however, about their toxicity or their long-term effect on both living systems and the environment. Vicki et al. did research on mice and they found that mice exposed to TiO_2 nanoparticles showed minimal lung inflammation but recovered within a few weeks after the exposure (26). Wang and co-workers also showed that TiO_2 nanoparticles could travel to brain tissue and damage them after inhalation (27).

There is a lot of ongoing research on toxicology of nanoparticles in general. One of the challenges of nanostructures synthesis is the high cost of production. Other alternative methods of producing these nanostructures effectively and with easy instrumentation for their characterization are also of concern.

CHAPTER 2

PROPERTIES OF TiO_2 NANOPARTICLES AND LUMINISCENCE TECHNIQUES

Oxides of Titanium

Titanium is a transition metal with atomic number (Z) of 22 and relative atomic mass of 47.9 g/mol. The morphological characteristics of Titanium dioxide nanoparticles have been studied and are based mainly on its surface properties (10).

TiO_2 is polymorphic in nature with rutile, anatase, and brookite as the main phases it exists in. Brookite is non-photocatalytic and hence has found little application in research studies. Of these phases, rutile has widely been used as a pigment in paint and plastic and in cosmetic lotion as a sunscreen agent primarily due to its high light scattering or reflective effect. It has high dispersibility in water. TiO_2 nanoparticles have been thoroughly studied and shown to photocatalytically decompose toxic substances such as hydrogen sulphide (H_2S) gas. Rutile has a high dielectric constant and its tetrahedral shape is linked edge to edge in the crystal lattice. (22)

Methods for Synthesis of Titanium Oxide Nanoparticles

Phase transformation between anatase and rutile is a major problem in the synthesis of the pure phase titanium oxide. Different methods have been proposed for the synthesis of either pure anatase phase titania or pure rutile phase titania. The following are few methods that have been employed to effectively obtain rutile or anatase depending on experimental conditions.

Organometallic Synthesis

This method employs the use of low-valent organometallic precursors to synthesize TiO_2 nanoparticles at low temperatures. Bis-(cyclooctatetraene)titanium was used together with dimethyl sulfoxide in organic solution at room temperature to produce nanosized TiO_2. Supporting ligands such as tribuytlphosphine, tribuytlphosphine oxide, and trioctylphosphine oxide were used to arrest the precipitation that leads to formation of amorphous anatase phase TiO_2. These basic ligands ensured that crystalline TiO_2 nanoparticles were the main product of this method of synthesis. (28)

Hydrothermal Synthesis

This method also employs low-temperature and low pH techniques in producing pure phase rutile TiO_2 using the amorphous anatase phase as a raw material. The amorphous phase was combined with modifiers such as hydroxyl and carboxyl functional group-containing organic species to produce rutile nanoparticles. The particle size and distributions were in relation with the polarity and acidity of the organic modifiers that help determine which particular size of the nanoparticles are produced. (29)

Electrochemical Synthesis

The potentiostat method was used to also produce pure rutile phase TiO_2 nanoparticles. The TiO_2 thin films produced were of about 50-150 nm in particle size. These TiO_2 nanopartcles were used in modification of screen printed carbon electrodes (SPE) and were then used to immobilize flavin adenine dinucleotide (FAD) (30).

Reverse Micelles

Titanuim isopropoxide mixed with reverse micellar gels was used as the precursor in the synthesis of TiO_2 mesoporous films. The TiO_2 mesoporous films were deposited on glass templates that were dipped in the reverse micellar gels mixed with titanuim isopropoxide. This method makes it possible for studies on the photocatalytic effects of TiO_2 and its application in the treatment of waste water and degradation of crude oil fragments (31).

Low Temperature Sol-Gel

As with all synthetic methods, the methods discussed above have their exceptional scope and limitations. Pursuant to the exploration of low-temperature, simple, and reproducible procedure, as well as to establish a protocol for the synthesis pure phase rutile TiO_2 nanoparticle, Tang et al. proposed the following method. It involves the hydrolysis of $Ti(OC_4H_9)_4$ solution at a temperature range of 45-50^{0}C to produce the pure phase rutile TiO_2. The acidic hydrolysis was performed using 2M HNO_3 solution. The ratio of $Ti(OC_4H_9)_4$ to water and HNO_3 is a very important factor to obtaining only the rutile phase TiO_2. Gopal et al. further showed that the ratio of $Ti(OC_4H_9)_4$ to water must remain constant. Thus as the amount of any of the components of this ratio increase, the other must equally be increased to ensure a balance in the equilibrium that favors the rutile phase TiO_2 formation. The average particle size obtained from this method was approximately 50 nm. The characterization was done using X-ray diffraction (XRD). The results showed that there was no phase transformation even when it was calcined at elevated temperature of about 650^{0}C. This was the solution to the problem of the anatase-rutile phase transformations normally observed with TiO_2 nanoparticles (32, 33).

Luminescence Technique

Fluorescence spectroscopy is widely used as an analytical technique because of its good sensitivity and selectivity, very wide linear dynamic range, low limit of detection usually being one to three orders of magnitude better than those possible in absorption spectroscopy. In 1852, G. Stokes introduced the concept of fluorescence as result of his observation of the mineral fluorspar exhibiting a blue-white light emission. Stoke's work laid the foundation for fluorescence technique after his acclaimed Stokes Law that states that "the wavelength of emitted light is always longer than the excitation wavelength." He also showed the relationship between concentration and the luminescence intensity (34).

A molecule can fluoresce if it is irradiated with the appropriate wavelength of light. After irradiation, the molecule absorbs the light and becomes excited. Approximately 10% of the molecules irradiated could fluoresce. Most of this energy is lost as result of collision with the matrix molecules. In the excited state, the molecule has different possible pathways of deexcitation and fluorescence is just one of the possible routes back to the ground state. Light absorption is very fast, about 10^{-15}seconds and the fluorescence lifetime is also about 10^{-6}-10^{-9} seconds which indicates fluorescence is short-lived. The general equation below shows the mean lifetime of the excited state and also illustrates the relationship between the fluorescence intensity *I* and the lifetime τ:

$$I = I_o\, e^{-t/\tau} \qquad 2$$

I is the fluorescence intensity at time t, I_o is the maximum fluorescence intensity during the excitation, t is the time after removal of the exciting radiation, and τ is the average lifetime of the excited state (35).

As mentioned earlier, there are various pathways of deexciation of which some are classified as radiative and non-radiative. Examples of radiative pathways are fluorescence and phosphorescence while vibrational relaxation, internal conversion, and intersystem crossing are non-radiative pathways. Figure 4 is the Jablonski Diagram that shows the complete mechanism of fluorescence (35-37).

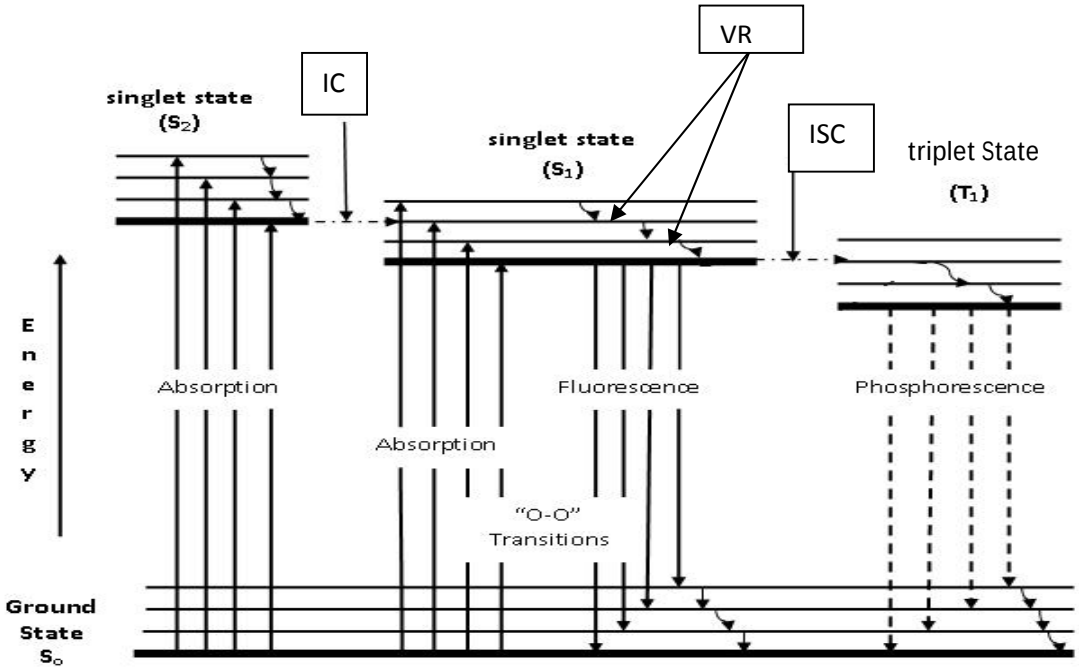

Figure 4: A simplified Jablonski Diagram

Vibrational relaxation (VR) happens within a time frame of about 10^{-13} to 10^{-12} seconds which makes vibrational relaxation very competitive with the other processes. Internal conversion (IC) is also fast and happens within 10^{-12} to 10^{-11} seconds. Intersystem crossing (ISC)

takes within a period of about 10^{-5}-10^{-3} seconds hence it compete with the fluorescence pathway that takes about 10^{-9} to 10^{-6} seconds. Intersystem crossing involves a change in the spin of the excited species from singlet to the triplet state. Intersystem crossing may not necessarily lead to phosphorescence but it's a requisite precursor for phosphorescence to occur. The "O-O" transitions occur when a molecule was excited at any of the vibronic levels of the ground state and after fluorescence or de-excitation, it returned to the same state. (38)

Quenching by Molecular Oxygen

A photochemical change observed in fluorescent compounds that gives rise to a gradual decrease in intensity is caused by the bright light used for excitation (39). This is the most common limitation of fluorescence techniques. Photochemical decomposition, viscosity, and quenching are the main concerns of this technique. Photochemical decomposition and viscosity usually affect the excited molecule by gradual decrease in the intensity. Viscosity of the medium usually reduces the number of molecular collisions and this helps to either enhance or decrease fluorescence of compounds. (34, 36)

Quenching had been described as the decay of an electronically excited state of a molecule. The reduction of the intensity of quantum yield of light emission is as a result of quenching. Several factors have been responsible for quenching of fluorescent molecules. Mechanistically, quenching is described as the dissipation of the excess energy of an excited species. The most known conditions that are responsible for a decrease in fluorescence intensity of most molecules are but not limited to temperature quenching, oxygen quenching,

concentration quenching, and impurity quenching. The various pathways taken by an excited molecule back to the ground state is shown in Figure 5.

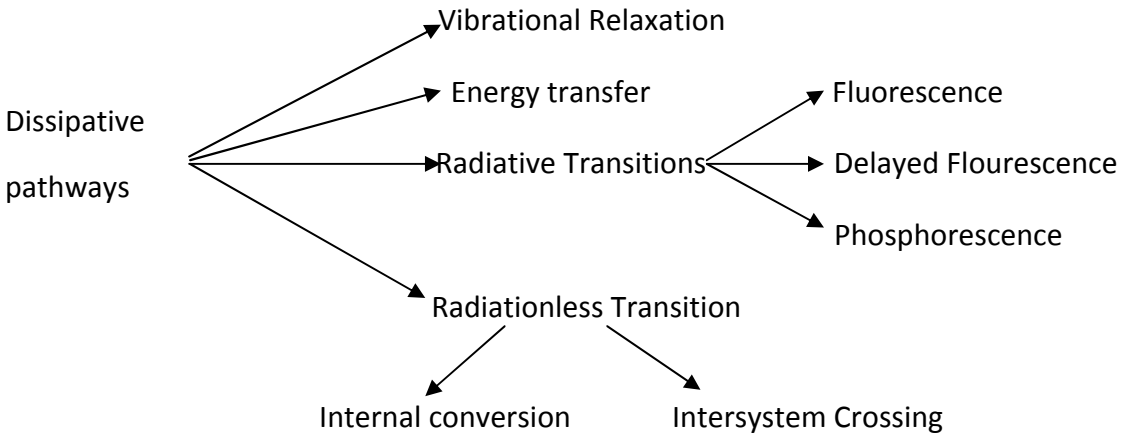

Figure 5: Vrious dissipative pathways of an excited molecule to the ground state

Fluorescence, delayed fluorescence and phosphorescence are radiative transitions. Radiationless transitions are internal conversion and intersystem crossing, vibrational relaxation, and energy transfer quenching.

Quenching Process

Photochemical quenching involves the formation of non-flourescent product between the excited species and the quencher as shown in the flow chart of Figure 6.

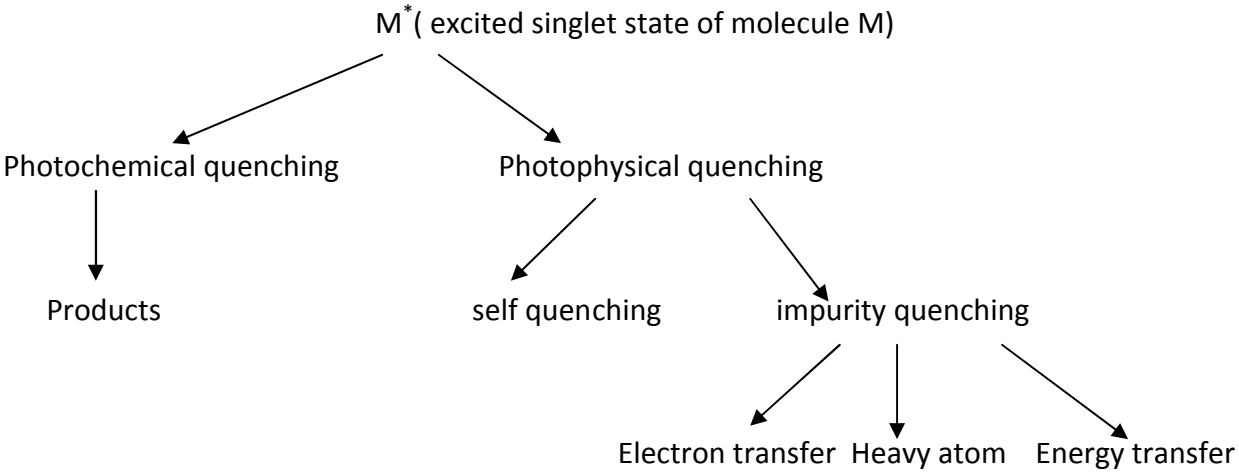

Figure 6: Flow chart of photochemical quenching pathway

Photophysical quenching involves self-quenching and impurity quenching. Self-quenching is usually observed when two excited species combine to form a non-fluorescent product thereby de-exciting to the ground state with no emission of photons. Impurity quenching involves electron transfer quenching, heavy-atom quenching, and energy transfer. Heavy atoms in solvents tend to enhance phosphorescence and diminish fluorescence. Heavy atom solvents usually induce a significant increase in intersystem crossing (38-40).

Mechanism of Oxygen Quenching

Ground state oxygen gas is actually a triplet and highly paramagnetic. Oxygen is present in solutions with concentrations of about 10^{-3} M and usually reduces fluorescence of typical compound by about 20%. Aromatic hydrocarbons are commonly susceptible to oxygen quenching (41). Oxygen is ubiquitous and the most known efficient quencher. Pyrene has shown to be one of the most severely quenched by oxygen (15). In fluorescence experiments, the presence of dissolved oxygen often reduces the fluorescence intensity of the compound in the solution. This quencher induces photochemical oxidation of the fluorescence species.

Oxygen is very small and has large diffusion coefficient. The most probable mechanism of oxygen quenching is the enhancement of intersystem crossing that does not necessarily lead to photoluminescence because oxygen in itself is a very effective triplet state quencher (42). Mechanisms recently proposed to account for the quenching of excited singlet state by oxygen molecule are the following:

1. Excited Singlet chemically Oxidized

$$^1A^* + O_2 \longrightarrow A^+ + O_2^- \quad (3)$$

2. Energy transfer from $^1A^*$ to O_2

$$^1A^* + {}^3O_2 \longrightarrow {}^3A^* \text{ to } O_2 \quad (4)$$

$$^1A^* + {}^3O_2 \longrightarrow {}^1A + {}^1O_2^* \quad (5)$$

3. Enhanced intersystem crossing in $^1A^*$

$$^1A^* + {}^3O_2 \longrightarrow {}^3A^* + {}^3O_2 \quad (6)$$

4. Enhanced internal conversion

$$^1A^* + {}^3O_2 \longrightarrow {}^1A + {}^3O_2 \quad (7)$$

5. Formation of a complex between O_2 and the ground state ^1A

The properties of both the species and the medium dictate which of the above equations apply in the quenching of a particular excited fluorescence species (43, 44). Of all the reactions above, the most probable equation that could account for the quenching route of molecular oxygen is the enhanced intersystem crossing (S^*_1 to T^*_1). This is the most probable route that conforms to photochemical data on the studies of the mechanism of oxygen quenching (34-36, 45).

Analytical sensitivity can be increased by removal of oxygen that can be achieved by degassing a solution using inert gas such as nitrogen or helium for about 5-10 minutes. When micelles are employed, they help in the enhancement of fluorescence intensity of a compound. Degassing of the system is very cumbersome as it results in the formation of lather with the addition of these surfactants that makes measurements very tedious. Special techniques are therefore required in the degassing of solutions involving addition of surfactants.

Research Proposal

The preceding discussions call for an attempt to investigate the applicability of using titanium dioxide nanoparticles together with surfactants to investigate their effects on the selected aromatic compounds. To achieve this aim, the following research proposal was put up to guide in the studies of such effects of the titanium nanoparticles on these aromatic hydrocarbons:

- Investigate the effects of TiO_2 nanoparticles singly on fluorescence of some aromatic organic compounds
- Investigate the influence of surfactants singly on fluorescence of these compounds
- Investigate the combined effects of surfactants and TiO_2 nanoparticles on these compounds
- And finally check the surfactants and TiO_2 effects singly and in combinations, on degassed solutions.

CHAPTER 3

EXPERIMENTAL PROCEDURE

The experimental procedures carried out to synthesize pure phase rutile TiO_2 nanoparticles and then establish the validity of the fluorescence method are highlighted in this chapter. The fluorescence method is assessed based upon its linearity, precision, accuracy, and its applicability to the determination of the fluorescence signals of the various samples.

Various surfactants have been used to enhance fluorescence signal (14, 15, 40,). The effect of several surfactants on the florescence signal was examined in this study. Three different surfactants were used in this study, namely hexadecylmethylammonium bromide (CTAB which is cationic, sodium dodecyl sulfate (SDS), anionic and one neutral surfactant: Triton X-100).

Reagents Used

All the chemicals and reagents used were ACS certified and of the highest purity grade available from commercial sources and so were used without further purification.

1. Deionized water, acquired from US Filter Company (Pittsburgh, PA).
2. Titanium isobutoxide $Ti(OC_4H_9)_4$ (Aldrich 97%) and Sodium dodecyl sulfate (SDS) and hexadecyltrimethylammonium bromide (CTAB) from Aldrich Chemical Company (Milwaukee, WI).
3. Triton X-100, Eastman Kodak Company (Rochester, NY).
4. 95% Ethanol, Laboratory grade purchased from Fischer Scientific.

Synthesis of Rutile TiO_2

TiO_2 nanocrystals were prepared by following the procedures described by Tang et al. that involve mixing titanium isobutoxide and nitric acid (HNO_3) in water. $Ti(OC_4H_9)_4$ was added dropwise to 2 M nitric acid (HNO_3) while the solution was stirred continuously. This resulted in the formation of a transparent solution. The molar ratios of $Ti(OC_4H_9)_4$: (HNO_3) :H_2O was 1: x: 50 with $2 \leq x \leq 5$ ratio held constant(31). This ratio ensured that pure rutile phase TiO_2 was produced. Too acidic a solution can cause the formation of the anatase phase (32). The transparent solution was hydrolyzed by heating it to a temperature of about 50^0C in a water bath. A two-layered solution (an upper organic layer and a lower sol) was obtained after the hydrolysis. The sol was separated from the organic layer by decantation and was then heated to about 50^0C without stirring for about 6-7 hours. A transparent gel was obtained and was dried in an oven overnight at temperature of 50^0C. White crystalline TiO_2 was obtained and used for the various studies.

Preparation of Working Solution

All the samples used in the preparation of the working solutions are organic in nature except TiO_2. The working solutions were prepared using 95% ethanol as the solvent. TiO_2 has very good dispersibility in water but practically insoluble in ethanol. The 5% water in the ethanolic solution ensured even distribution of the nanoparticles in the solution. Equimolar solutions of each PAH sample was prepared then used for the analysis.

TiO_2 Nanoparticles Solution

TiO_2 working solution was prepared on a daily basis. 19.0 mg of TiO_2 was weighed into 50-mL-volumetric flask and 95% Ethanol was added to the mark. This solution was then poured into a 100 mL-beaker and sonicated for about 20 minutes and then filtered.

Pyrene Solution

Approximately 48.54 mg of pyrene was weighed into a 50 mL-beaker. It was dissolved in 95% ethanol by sonication with a total volume of 50 mL.

Anthracene Solution

Anthracene is not as soluble as pyrene in 95% ethanol so 42.78 mg was weighed and dissolved in 50 mL of 95% ethanol in a 50 mL-volumetric flask by sonication.

Phenanthrene Solution

Phenanthrene solution was prepared by weighing 42.78 mg of phenanthrene and dissolving it in 50 mL of 95% ethanol in a volumetric flask.

Carbazole Solution

The carbazole solution was similarly prepared by dissolving 40.13 mg of carbazole in 50 mL of 95% ethanol solution in a volumetric flask.

Fluoranthene Solution

Fluoranthene solution for the analysis was prepared similarly by weighing 48.54 mg of fluoranthene and dissolving it in 50 mL of 95% ethanol solution in a volumetric flask.

Preparation of Surfactant Solutions

All surfactants were prepared to be approximately 10 times their critical micelle concentration (CMC) to ensure the formation of micelles after tenfold dilution. The surfactant concentration must be greater than the critical micelle concentration in order to obtain a micelle.

0.336 g of CTAB was carefully weighed into a 50-mL beaker, and then 25 mL of deionized water was added. The solution was sonicated for 5 min and then transferred into a 100-mL volumetric flask and was diluted to the mark with deionized water.

2.336 g of SDS was carefully weighed into a 50-mL beaker, and then 25 mL of deionized water was added. The solution was sonicated for 5 min and then transferred into a 100-mL volumetric flask and was diluted to the mark with deionized water.

122.16 µL of Triton X-100 was carefully measured into a 100-mL volumetric flask and diluted to the mark with deionized water.

Standard Solutions for Calibration Curve and Linearity Studies

The linearity of the fluorescence signal was determined with pyrene using different concentrations. The following procedure was used to generate a series of standard solutions for the calibration curve. Aliquots of the pyrene working solution of 100, 200, 400, 500, and 700 µL were measured into six different 10-mL volumetric flasks with a micropipette and then diluted to the mark to make five standard solutions of 0.05, 0.10, 0.20, 0.25, and 0.35, µg/mL, respectively. The sixth sample had no pyrene and it served as the blank. These samples were then ready for fluorescence measurement.

Instrumentation

Fluorometry was the method employed in the analysis all the samples. Typically, fluorescence instrumentation used to measure fluorescence signals involves an excitation light source, an excitation wavelength selector, a sample holder to contain the sample solution, and a detector which usually a photomultiplier tube (PMT). There is also a means to select the fluorescence wavelength to be monitored, a detector capable of producing a signal proportional to the intensity of light radiating it, and associated electronics and readout devices. This is aligned in such a way that the excitation source and the emission source are at right angle. A representation of the instrumentation is shown in Figure 7 below.

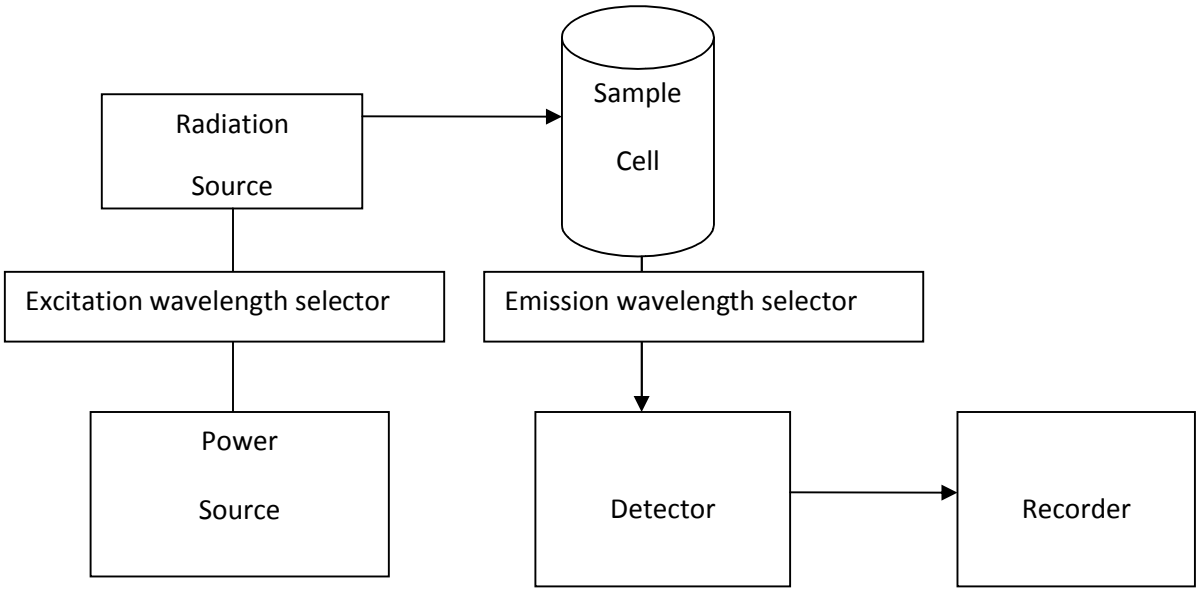

Figure 7: Schematic Diagram of the instrumental setup of a fluorometer

For our analysis, a commercial Perkin Elmer Spectrophotometer (PES) was used. It has a xenon arc lamp as its radiation source and it uses a photomultiplier tube (PMT) as its detector. Signals were recorded using a readout attached to the PES. It has an excitation and emission wavelength selectors and these selectors were varied to obtain the desired signal for each

sample analyzed. A non-fluorescent cuvette was used to contain the samples measurements. The excitation and emission slit were 2 nm wide each and were held constant for all the measurements. Background corrections were made using a blank solution of 95% ethanol solution and readings were corrected with this.

Data Analysis

The commercial PES was used to determine the intensity of fluorescence in the standard and sample solutions. All experiments were conducted in triplicate and the data reported are average values. Data were processed using Microsoft® Office Excel 2007 software for Windows® Vista (Microsoft Inc., Pedmond, WA). A plot of the calibration curves showing fluorescence signal and pyrene concentration was obtained from the standard solutions prepared. The various signal obtained from the various combinations of the TiO_2 nanoparticles and the surfactants together with the each were recorded and analyzed using Excel.

CHAPTER 4

RESULTS AND DISCUSSION

The various PAHs solutions used in the fluorescence studies were combined singly and in combinations with the surfactants and the TiO_2 nanoparticles solution and their fluorescence measurements were made. To establish first, an important aspect of fluorescence measurement, that the fluorescence intensity of a compound is proportional to its concentration, a set of pyrene solution of different concentration was prepared and their fluorescence measured. The results are shown in Table 1.

Table 1: Results of measurement of pyrene fluorescence for calibration

Volume of Pyrene (µL)	0	100	200	400	500	700
Signal Intensity	0	2.3	4.4	9.4	11.5	16.2

These results were used to plot a calibration curve. The results obtained from the calibration curve indicated that the Perkin Elmer Spectrophotometer (PES) had a very wide linear dynamic range with a regression coefficient of about 0.999. The linearity plot is shown in Figure 8. This procedure was repeated each time with samples of a different compound and the results were all linear and the sample solutions were kept within the corresponding limits of linear dynamic range.

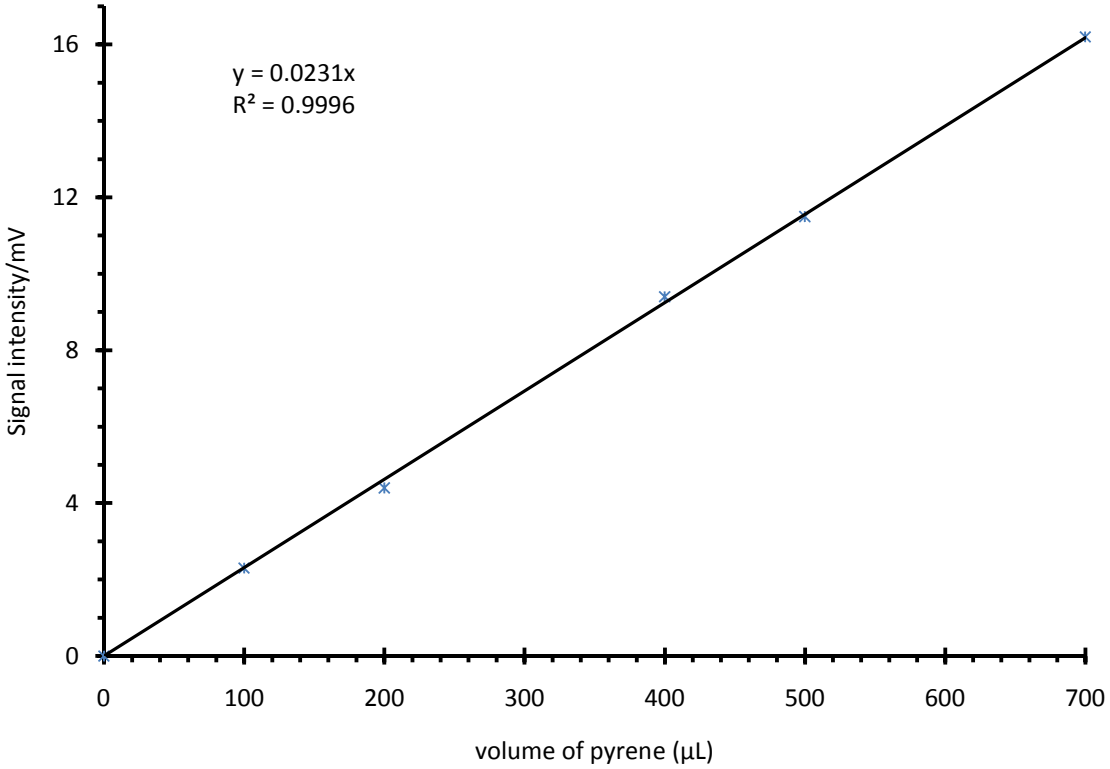

Figure 8: Calibration curve of Fluorescence Intensity Signal versus µL of Pyrene.

The sensitivity and selectivity of this instrument was fully optimized by the precision of the results obtained from this measurement. The results obtained from all the measurements made using the surfactants singly and in combination on the various aromatic compounds used for this work are shown and discussed. For all experiments, 1.0 mL of each aromatic compound sample was used at a time and diluted to the mark after addition of appropriate amount of surfactants or nanoparticles in a 10.0 mL-volumetric flask.

Studies on Fluorescence of Phenanthrene

Phenanthrene solutions prepared above were combined with TiO_2 nanoparticles solution singly and in combinations with surfactants to study the effect the TiO_2 nanoparticles

and the surfactants have on the fluorescence intensity. The results obtained in this study are shown in Table 2.

Table 2: Effects of surfactants and TiO_2 nanoparticles on fluorescence intensity of phenanthrene

VOLUME TO VOLUME RATIO	SIGNAL INTENSITY (Arbitrary units)		
PHENANTHRENE only	21.4		
1P:1T	17.2		
1P:2T	16.2		
1P:3T	16.0		
	CTAB)	TX-100	SDS
1P:1S	25.6 (1.20	21.4	26.5 (1.24)
1P:2S	19.8	22.0 (1.03)	24.2
1P:3S	18.3	21.9	24.0
1P:1T:1S	23.7 (1.21)	21.0	25.8 (1.11)
1P:1T:2S	22.5	18.5	23.7
1P:1T:3S	19.9	17.3	21.8

In Table 2, the different solutions made in 10-mL volumetric flasks were different combinations of the TiO_2 nanoparticles and surfactants. In Table 2, the ratios of the volumes of the compounds used are expressed as for example 1P:1T. The mixture with the ratio of 1 volume of phenanthrene to I volume of TiO_2 nanoparticles solution was made by diluting to the 10-mL mark after addition of 1 mL phenanthrene stock solution and 1 mL of TiO_2 nanoparticles

stock solution (1P:1T). For the mixture of 1 mL of phenanthrene, 1 mL of TiO_2 nanoparticles solution, and 1 mL of a surfactant stock solution, and diluted to the 10-mL mark of the volumetric flask was designated as 1P:1T:1S in Table 2. The same system of designation is used for all mixtures in all subsequent tables.

Effect of TiO_2 on Phenanthrene Fluorescence Intensity

The fluorescence intensity of phenanthrene by itself was 21.4. With the addition of TiO_2 nanoparticles, the fluorescence factors (FF) were calculated to be 0.8, 0.76, 0.75, and 0.74, with the addition of 1, 2, 3, and 4 mL of TiO_2 nanoparticles solution, respectively. This indicated that TiO_2 nanoparticlesare quenching the fluorescence of phenanthrene as shown in Figure 9. This means that the more TiO_2 nanoparticles added, the more severely the fluorescence signal of the phenanthrene was quenched. This quenching property can be attributed to the microenvironments of the mixture solution that give rise to interactions which may hinder the free excitation of the phenanthrene.

Effect of Surfactants on Phenanthrene Intensity

In Table 2, the highest ratio of fluorescence intensity of the added TiO_2 nanoparticles or surfactant to the pure phenanthrene solution is given in parenthesis for that solution. As the data of Table 2 showed, addition of one-to-one volume ratio of CTAB to phenanthrene solution gave a fluorescence factor of about 1.2. Further increment in the amount of CTAB resulted in the decrease of the fluorescence factor. Triton X-100 gave the highest fluorescence factor of 1.03 when 2 mL of the Triton X-100 solution was mixed with the phenanthrene solution.

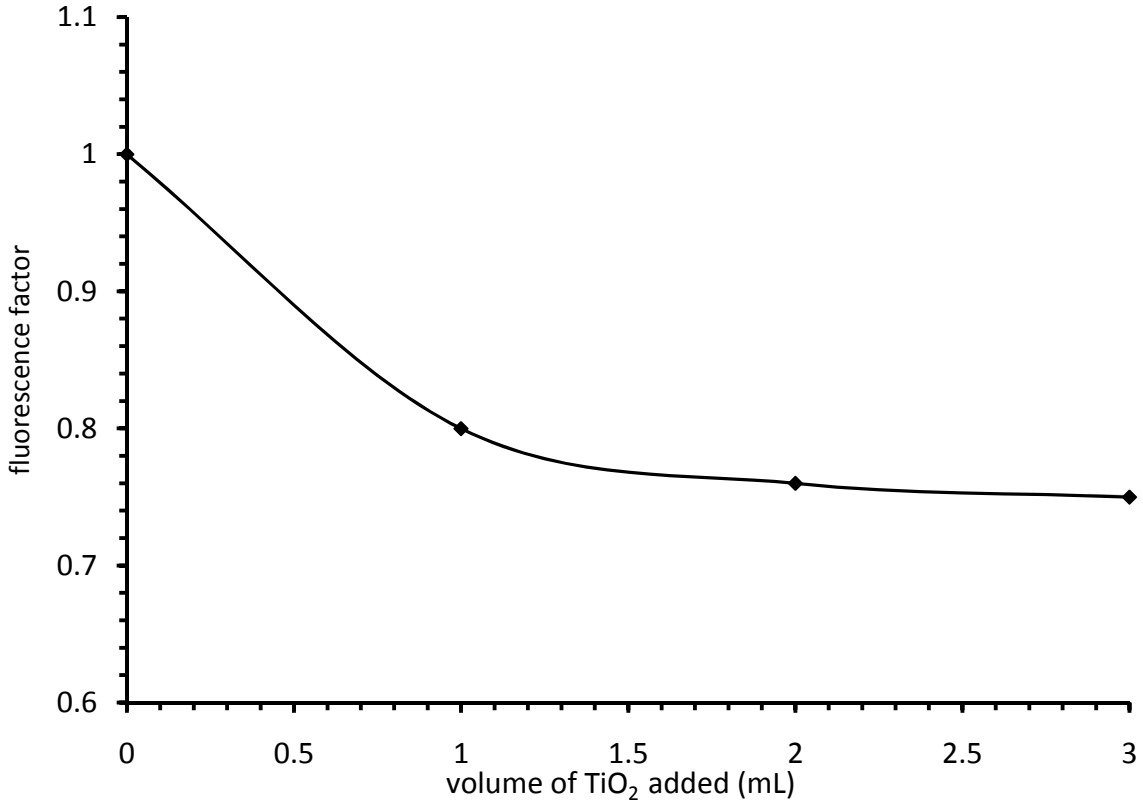

Figure 9: Plot of variation of fluorescence factor with TiO_2 on phenanthrene fluorescence versus volume of TiO_2 nanoparticles

Any other volume to volume ratios of the phenanthrene solution to Triton X-100 solution resulted in the attenuation of the fluorescence intensity. SDS increased the fluorescence factor for all the volume to volume ratios with phenanthrene solutions. The phenanthrene solution and the SDS solution with the one-to-one volume ratio gave the best signal with a fluorescence factor of about 1.24.

Effect of Combined TiO_2 and Surfactant on Phenanthrene Fluorescence Intensity

The combinations of the TiO_2 nanoparticles solutions and surfactants with phenanthrene and the resulting effects on fluorescence intensity were studied next. The

combination of TiO_2 nanoparticles with SDS that gave the highest fluorescence intensity was the 1P:1T:1S. The fluorescence factor of this was about 1.21, a decrease of about 2.4% compared to when only SDS was added to the phenanthrene without the addition of TiO_2 nanoparticles. This confirmed that TiO_2 nanoparticles had a negative effect on phenanthrene's fluorescence intensity. CTAB also gave a fluorescence factor of about 1.11 in the 1P:1T:1S solution. It also showed a decrease of about 7.5% compared when only CTAB was was added to the phenanthrene. The TiO_2 nanoparticles added to Triton X-100 had a more detrimental effect on the fluorescence intensity. It decreased the intensity by about 20% in the 1P:1T:1S solution.

Studies on Fluorescence of Anthracene

Anthracene, an isomer of phenanthrene, showed varied results with the addition of TiO_2 nanoparticles and the surfactants. The results obtained are shown in Table 3.

Effect of TiO_2 Nanoparticles on Anthracene Fluorescence Intensity

The fluorescence of pure anthracene solution gave a fluorescence intensity of 11.4. The addition of the TiO_2 nanoparticles solution to the anthracene solution gave fluorescence factors (FF), calculated to be 1.65, 1.57, 1.56, and 1.56, with the addition of 1, 2, 3, and 4 mL of TiO_2 nanoparticles solution, respectively. This indicated that TiO_2 nanoparticles were enhancing the anthracene fluorescence instead of quenching as in the case of phenanthrene. This result is also displayed in Figure 10. This result further showed that the 1A:1T gave the best signal enhancement. However, when more TiO_2 nanoparticles were added the fluorescence signal of the anthracene was attenuated.

Table 3: Effects of surfactants and TiO_2 nanoparticles on fluorescence intensity of anthracene

VOLUME TO VOLUME RATIO	SIGNAL INTENSITY (Arbitrary units)		
ANTHRACENE only	11.4		
1A:1T	18.8		
1A:2T	17.9		
1A:3T	17.8		
1A:4T	17.8		
	CTAB	TX-100	SDS
1A:1S	18.0	17.9	18.8
1A:2S	18.0	18.8	15.7
1A:3S	17.9	18.6	14.8
1A:2T:1S	19.8	18.8	20.3
1A:2T:2S	17.7	18.6	14.2
1A:2T:3S	17.7	18.6	10.1

The results shown in Table 3 indicated that the microenvironment of the anthracene such as the presence of oxygen may have inhibited its ability to fluoresce as well as it should. This means that the addition of TiO_2 nanoparticles might help in suppressing the interferents and thus enhancing the fluorescence signal. The action of TiO_2 nanoparticles on phenanthrene was different from that of anthracene. The difference between the two isomeric compounds is that of the linear (anthracene) versus the bent structure of phenanthrene that affects the delocalization of π electrons. It seems the TiO_2 nanoparticles may have helped with the

delocalization. This difference might be another reason the fluorescence intensity of anthracene was enhanced rather than attenuated by addition of the TiO_2 nanoparticles.

Effect of Surfactants on Anthracene Intensity

As recorded in Table 3, in 1A:1S solution of anthracene, addition of CTAB gave a fluorescence factor of about 1.59. Any increment in the relative amount of CTAB resulted in the fluorescence factor remaining almost constant.

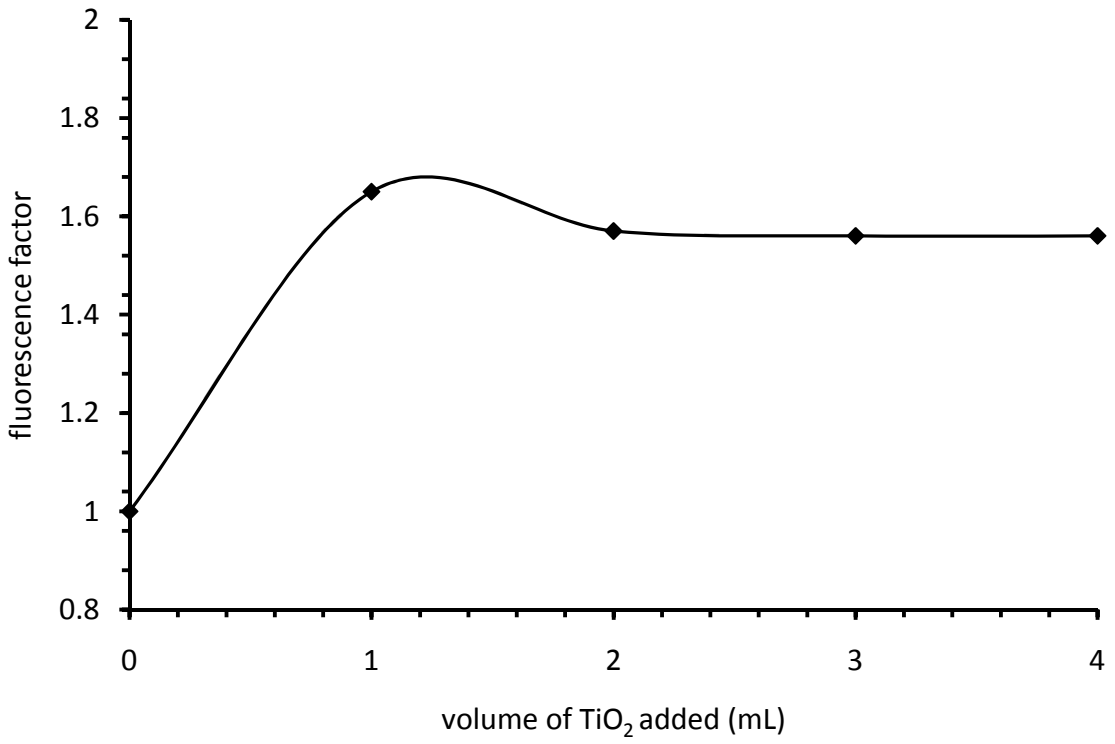

Figure 10: Plot of fluorescence factor versus volume of TiO_2 nanoparticles solution on anthracene fluorescence

Triton X-100 also gave a high fluorescence factor of 1.59 when 2 mL of the Triton X-100 solution was added to the anthracene solution. Increase of Triton X-100 beyond this resulted in a slight diminishing of the fluorescence intensity. SDS increased the fluorescence factor for only the one-to-one ratio with the anthracene solution. With this one-to-one ratio, anthracene yielded the best signal with a fluorescence factor of about 1.65 from the anthracene only reference solution. The action of surfactants on the enhancement of fluorescent intensity has often been attributed to their ability to shield the fluorophore in the micellar cavity from effect of quenchers like molecular oxygen. The enhancement seen in this set of experiment most likely was due to this protective action of the surfactants.

Effect of Addition of TiO_2 Nanoparticles and Surfactant Solutions on Anthracene Intensity

The combinations were made by keeping the volume ratio of the anthracene and TiO_2 nanoparticles solutions constant while varying volumes of the added surfactants. CTAB and SDS showed a significant increase in the fluorescence factor by about 10.0% and 8.0%, respectively. Triton X-100 showed no further enhancement in the signal intensity. The 1A:1T:1S with the surfactnat CTAB did affect the signal intensity by causing a sharp increase of about 73% with reference to the pure anthracene solution while showing a 64% increase when only TiO_2 nanoparticles was added to anthracene. It seems that the nonionic surfactant like Triton X-100 had the same enhacement effect on the fluorescence of anthracene. While the charged surfactants, cationic of anionic, had a significant effect on the fluorescence intensity of both anthrecene and fluoranthene, Triton X-100 only helped enhance the intensity of anthracene

Studies on Fluorescence of Fluoranthene

Fluoranthene, a polycyclic aromatic hydrocarbon (PAH), is an isomer of pyrene. It is strongly fluorescent and little is known about the toxicity of its derivatives. The combinations of the TiO_2 nanoparticles and the surfactants gave interesting results that are recorded in Table 4.

Table 4: Effects of surfactants and TiO_2 nanoparticles on fluorescence intensity of fluoranthene

VOLUME TOVOLUME RATIO	SIGNAL INTENSITY		
FLUORANTHENE only	8.1		
1F:1T	7.7		
1F:2T	8.3		
1F:3T	8.0		
	CTAB	TX-100	SDS
1F:1S	7.6	8.1	6.8
1F:1S	8.0	8	6.9
1F:1S	7.9	8.1	6.8
1F:2T:1S	6.8	8.0	6.1
1F:2T:2S	6.8	8.0	6.0
1F:2T:3S	5.2	7.9	6.0

Effect of TiO_2 on Fluoranthene Fluorescence Intensity

The addition of TiO_2 nanoparticles to the fluoranthene solution showed a decrease of about 4.9% in fluoranthene's fluorescence intensity as compared to that of fluoranthene solution alone. But when the volume ratio was increased (1F:2T), there was a slight increase of

about 2.5% in fluorescence intensity compared to the signal intensity obtained when only fluoranthene was present in the solution. In general, the addition of TiO_2 nanoparticles gave a fluorescence factor of about 1 compared to the reference fluoranthene solution. This result implied that TiO_2 nanoparticles did not affect the fluorescence of fluoranthene much at all.

Effect of Surfactants on Fluoranthene Intensity

As shown in Table 4, addition of CTAB in a one-to-one volume ratio with fluoranthene gave a fluorescence factor of about 0.94. Any increment in the relative amount of CTAB resulted in the fluorescence factor increasing slightly but dropped after adding 4 mL of CTAB. Triton X-100 gave the same fluorescence factor of 1.0 when varying amounts of the Triton X-100 solution was used in the measurements. SDS on the other hand severely quenched the fluorescence intensity compared to CTAB and Triton X-100. SDS decreased the fluorescence intensity by about 16%, a figure almost three times the decrease in fluorescence caused by addition of CTAB, which is 6.2%. Thus the addition of surfactants had a much different effect on fluoranthene than seen in anthracene.

Effect of Addition of TiO_2 Nanoparticles and Surfactant Solutions on Fluoranthene Intensity

The addition of both TiO_2 nanoparticles and surfactants to fluoranthene was studied by varying the volume of the surfactants added. CTAB combined with TiO_2 nanoparticles added to fluoranthene showed a sharp decrease of about 35.8% in the fluorescence intensity in the 1F:1T:3S solution compared to the pure fluoranthene solution and a 32.5% decrease if only 1 volume of TiO_2 nanoparticles solution was added to fluoranthene. Triton X-100 had virtually no effect on the signal intensity. SDS like CTAB in combinations with the TiO_2 nanoparticles did

affect the signal intensity of fluoranthene by causing a sharp decrease of about 30% with reference to the pure fluoranthene solution while showing a 22.1% decrease when only TiO_2 nanoparticles was added to fluoranthene. It seems that the nonionic surfactant like Triton X-100 has little effect on the fluorescence of fluoranthene while the charged surfactants, cationic of anionic, had a significant effect on its fluorescence. Some sort of charge transfer quenching might have occurred with the addition of these ionic surfactants

Studies on Fluorescence of Carbazole

Carbazole, a strongly fluorescent polycyclic aromatic heteroatomic compound, was the only heteroatomic compound used in this study. The results obtained are shown in Table 5.

Table 5: Effects of surfactants and TiO_2 nanoparticles on fluorescence intensity of carbazole

VOLUME TO VOLUME RATIO	SIGNAL INTENSITY		
CARBAZOLE	25.6		
1C:1T	17.8		
1C:2T	17.8		
1C:3T	18.2		
	CTAB	TX-100	SDS
1C:1S	11.8	24.8	13.3
1C:2S	19.0	25.1	15.6
1C:3S	19.2	25.3	17.2
1C:2T:1S	10.9	19.2	13.0
1C:2T:2S	15.6	19.5	14.1
1C:2T:3S	15.6	20.1	15.3

Effect of TiO_2 on Carbazole Fluorescence Intensity

The fluorescence intensity of carbazole was severely attenuated by the addition of the TiO_2 nanoparticles. It reduced the fluorescence intensity by an average of about 30% compared to the reference carbazole solution. This reduction gave fluorescence factor of about 0.7 when TiO_2 nanoparticles were added to the pure carbazole solution. Thus TiO_2 nanoparticles quenched the fluorescence of carbazole. This might be due to the lone pair of electrons on the carbazole nitrogen that can allow intersystem crossing to occur thus taking the excited molecule to the triplet state that can then be easily quenched. TiO_2 nanoparticles because of the lone pair of electron on its oxygen, might help to enhance the process of intersystem crossing thus quenching the fluorescence of carbazole even more

Effect of Surfactants on Carbazole Fluorescence Intensity

Both CTAB and SDS had severe quenching effects on the fluorescence of carbazole. CTAB and SDS reduced the fluorescence intensity on average by 53.9% and 48%, respectively, when the volume ratio of CTAB and SDS was 1C:1S to the carbazole solution. When the volume ratio of these two surfactants each was varied while the volume of carbazole was kept constant, the fluorescence intensity was still less than when only carbazole was used. Triton X-100 had little to no effect on the fluorescence intensity because carbazole has the nitrogen in its molecule and the nitrogen is highly electronegative, charge transfer or dipole-dipole interactions can easily take place with the ionic surfactants like CTAB (cationic) and SDS (ionic). Thus the fluorescence intensity was greatly quenched. Whereas Triton X-100 is nonionic, this effect is most likely not seen. The protective effect of micelles formation by the surfactants was not important at all with respect to carbazole. Although a hint of this can be discerned

when the concentration of the surfactants were increased by 3 times such as shown by an increase of fluorescence intensity from 11.8 (1C:1S) to 19.2 (1C:3S) of carbazole when CTAB was added

Effect of Addition of TiO_2 Nanoparticles and Surfactant Solutions on Carbazole Fluorescence Intensity

The combinations of TiO_2 nanoparticles and surfactants had the same attenuating effect on the carbazole intensity just as when either the TiO_2 nanoparticles or surfactants were added singly to the carbazole solution. The fluorescence intensity of carbazole was decreased by approximately 34% representing a fluorescence factor of 0.67. it seems even for the nonionic Triton X-100, the fluorescence intensity had decreased when both TiO_2 nanoparticles and it were present compared to only when Triton X-100 was present alone. Thus it seems that the TiO_2 nanoparticles had also a significant effect on the quenching of the carbazole fluorescence. This effect can also be observed for combination of TiO_2 nanoparticles with CTAB and SDS as the fluorescence intensity of carbazole was lower than the corresponding cases when the surfactants were present alone with carbazole. For example the fluorescence intensity was 15.6 (1C:2T:3S) versus 17.2 (1C:1S) for SDS. This effect on the fluorescence intensity of carbazole may in part be due to the catalytic property of TiO_2 nanoparticles in addition to the enhancement of intersystem crossing by both the TiO_2 nanoparticles and surfactants (16).

Studies on Fluorescence of Pyrene

Pyrene, a fluorescent compound, is well known to be very susceptible to molecular oxygen quenching, as discussed earlier in Chapter 2, has been extensively studied (15). The results of the experiment done in this project are shown in Table 6.

Table 6: Effect of surfactants and TiO_2 nanoparticles on fluorescence intensity of pyrene

VOLUME TO VOLUME RATIO	SIGNAL INTENSITY		
Pyrene only	14.1		
$1P_Y$:1T	18.3		
$1P_Y$:2T	18.3		
$1P_Y$:3T	17.0		
$1P_Y$:4T	17.1		
	CTAB	TX-100	SDS
$1P_Y$:1S	44.0	18.0	24.6
$1P_Y$:2S	45.5	17.9	54.3
$1P_Y$:3S	57.2	18.1	60.8
$1P_Y$:4S	57.4	18.1	60.7
$1P_Y$:1T:1S	48.0	18.0	25.5
$1P_Y$:1T:2S	46.5	18.1	59.0
$1P_Y$:1T:3S	59.9	17.9	62.2
$1P_Y$:1T:4S	58.8	18.0	62.4

Effect of TiO_2 Nanoparticles on Pyrene Fluorescence Intensity

The addition of TiO_2 nanoparticles in various volume ratios of pyrene solution resulted in an average fluorescence increase of about 29.8% representing a fluorescence factor of about

1.25. The 1P:1T pyrene solution gave a significant increase in fluorescence. Further addition of TiO_2 nanoparticles did not help or reduce the fluorescence intensity to any significant extent

Effect of Surfactants on Pyrene Fluorescence Intensity

The surfactant, CTAB increased the fluorescence intensity steadily as the amount of the surfactant was increased until a maximum was reached when 3 mL of the surfactant was added. These data are shown in Figure 11.

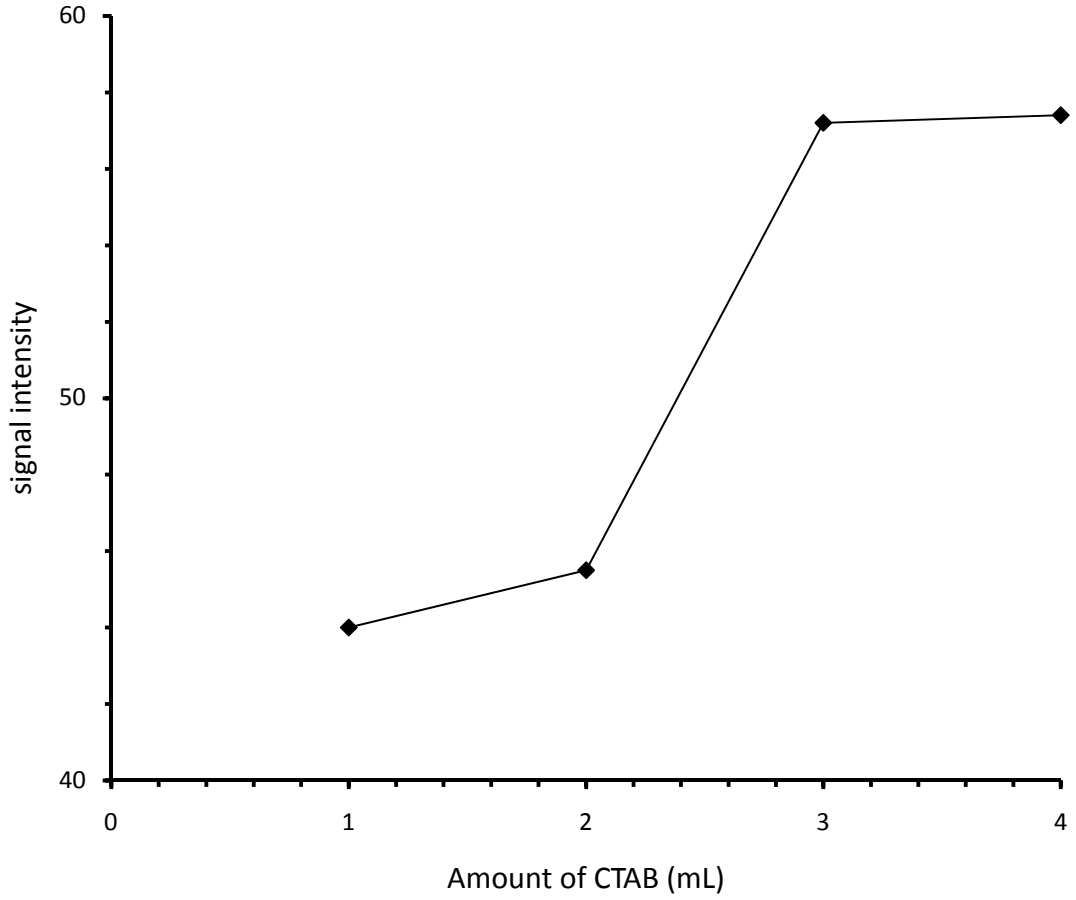

Figure 11: A plot of signal intensity with mL of CTAB added to the pyrene solution

This result further showed that pyrene is affected by the matrix and interferences from other molecules present in the solution. The micelles resulting from CTAB helped shield the

interferents that might be present in the solution and can act as quenchers, thereby enhance the pyrene fluorescence intensity. SDS also had very strong enhancing effect on the fluorescence intensity as shown in Figure 12.

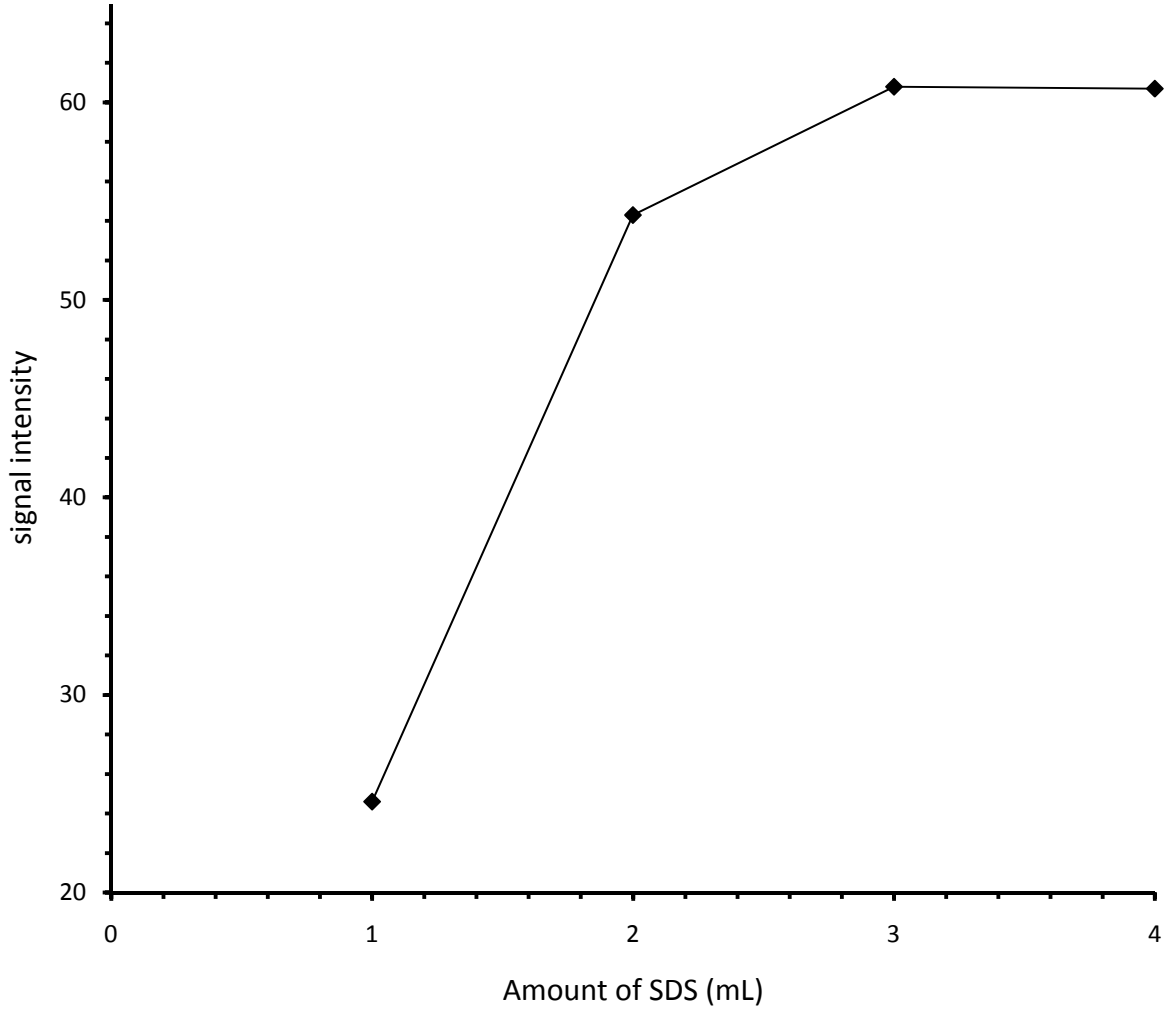

Figure 12: A plot of signal intensity versus amount of SDS in mL

The $1P_y$:3S of pyrene:SDS gave the highest fluorescence intensity of about 60.8, which is more than when CTAB (57.2) with the same $1P_y$:3S with pyrene. Those are enhancement of 331.2% and 305.6%, respectively. Triton X-100 did not have much enhancing effect compared to CTAB and SDS. Triton X-100 gave a fluorescence factor of about 1.28 (28%) with respect to

pure pyrene solution. Pyrene is well known to be easily quenched by molecular oxygen, hence it is reasonable that surfactants can enhance the fluorescence of pyrene by protecting pyrene from oxygen in their micellar cavities. Thus, the fluorescence signal from pyrene increases with the amount of surfactants present. Also ionic surfactants have a greater enhancing effect (>300%) than the nonionic surfactant (Triton X-100) (28%) because in a polar solvent, they form tighter and better protective micelles and can exclude the nonpolar oxygen far more effectively.

Effect of Adding both TiO_2 Nanoparticles and Surfactant Solutions on Fluorescence of Pyrene

The addition of TiO_2 nanoparticles and the surfactants also resulted in further increase in the fluorescence intensity of pyrene. The maximum fluorescence intensity resulted from the volume ratio combinations of pyrene with SDS which gave signal intensity 62.4 compared to the reference pyrene solution with an intensity of 14.1. CTAB gave a maximum value of 59.9 which was very close to the SDS value. Triton X-100 resulted in just a minimal enhancement compared to CTAB and SDS. It gave a fluorescence factor of 1.68 compared with 4.17 and 4.43 of CTAB and SDS respectively. The presence of TiO_2 nanoparticles actually hampers the action of the surfactants, particularly that of CTAB and SDS, the ionic surfactants. Only when the relative amount of CTAB and SDS was high enough did the fluorescence enhancement reach a slightly better value. For example, the signal from $1P_y$:3S was 57.2 for CTAB and 60.8 for SDS while the signal from $1P_y$:1T:3S was 59.9 for CTAB and 62.2 for SDS. The increase was insignificant showing that TiO_2 nanoparticles actually had a slight detrimental effect on the enhancement of pyrene fluorescence by the ionic surfactants

Studies on Degassing on Fluorescence of Selected PAHs

The effect of molecular oxygen quenching was evaluated by degassing the solution using nitrogen gas for various length of time ranging from one minute up to 5 or 6 minutes. CTAB and SDS were the surfactants used for this particular work. This was done to ascertain whether oxygen quenching could be reduced and fluorescence intensity enhanced further. Pyrene, anthracene, and phenanthrene were individually studied and the results obtained are presented and discussed.

Degassed Solution of Pyrene

The results obtained after subjecting pyrene to degassing for the various length of time are presented in Table 7. The results in Table 7 indicated that oxygen severely quenched the fluorescence of pyrene. The addition of the TiO_2 nanoparticles singly and in combinations with the surfactants enhanced the fluorescence intensity even without degassing but to a much smaller extent. The data of Table 7 are plotted in Figure 13 to show how the various additions affect the fluorescence intensity of pyrene with degassing time.

After degassing pyrene only solution for five minutes, it resulted in fluorescence factor of 8.2 compared to the reference pyrene solution when the solution was not degassed. Pyrene is relatively sensitive to molecular oxygen quenching thus degassing helped. TiO_2 nanoparticles singly added to pyrene gave a fluorescence factor of 1.09 even when the solution had not been degassed. After degassing the solution, a fluorescence intensity of 82.5 was obtained representing a fluorescence factor of 9.5. TiO_2 nanoparticles thus helped in enhancing the

fluorescence intensity by 9.5 times compared to 8.7 obtained when only pyrene solution was degassed for 5 minutes.

Table 7: Results of fluorescence measurements on different pyrene solutions after degassing

Degassing time (min)	Signal reading					
	A	B	C	D	E	F
0	8.7	9.5	14.2	24.9	21.5	33.4
1	18.7	36.5	58.2	65.1	63.3	86.1
2	45.5	67.3	87.7	99.3	98.4	130.6
3	61.5	73.0	95.0	104.6	102.1	130.0
4	66.0	79.2	98.4	105.1	108.8	136.1
5	71.3	82.5	98.4	105.1	108.8	136.0
A= pyrene only						
B= pyrene + TiO_2						
C= Pyrene + SDS						
D= pyrene + CTAB						
E= pyrene + TiO_2 + SDS						
F= pyrene + TiO_2 + CTAB						

The addition of both TiO_2 nanoparticles and CTAB together to pyrene also gave a fluorescent signal factor of 15.6 times that of pyrene alone without degassing. This was the highest intensity obtained after degassing for all the different addition combinations to the pyrene solutions with 6 minutes of degassing. These results indicated that after thoroughly degassing a solution, effect of adding TiO_2 nanoparticles either singly or in combinations with the

surfactants CTAB and SDS further enhanced the fluorescence signal intensity. These results showed that oxygen quenching was a very important factor in reducing the fluorescence of pyrene.

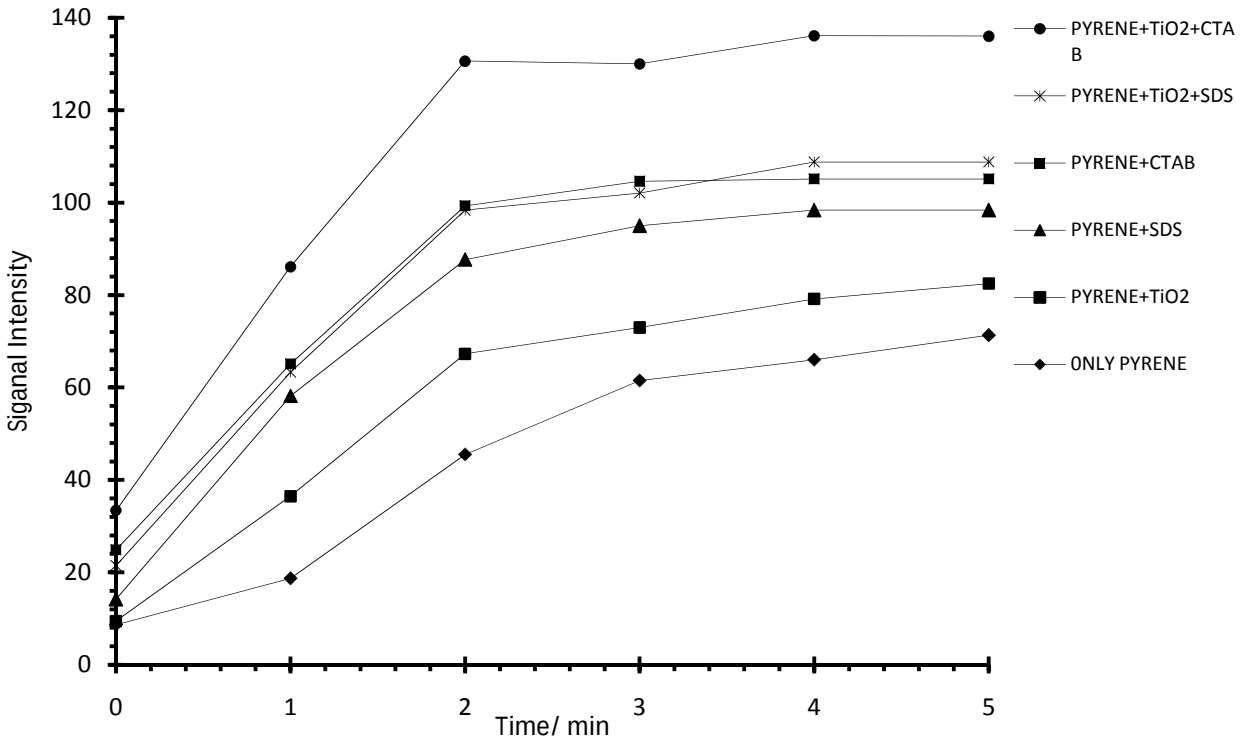

Figure 13: A plot of the variation of fluorescence intensity versus degassing time of pyrene

Degassed Solution of Anthracene

The results obtained after subjecting anthracene to degassing for the various length of time are presented in Table 8.

The results show that after adding TiO_2 nanoparticles to the solution of anthracene, there was an increase in the intensity of the fluorescence signal. The increase was not as sharp as compared to that obtained from the pyrene.

Table 8: Results of fluorescence measurements on different anthracene solutions after degassing

Degassing time (min)	Signal reading					
	A	B	C	D	E	F
0	31.9	42.1	36	32.5	34.1	33.8
1	42.7	42.7	36.7	35.6	34.7	38.7
2	43.5	43.8	38.6	38.7	35	40.8
3	44.4	44.5	38.7	40.5	40.4	45.1
4	44.4	44.5	38.7	44.8	40.5	45.2
5	44.4	44.5	38.6	44.8	40.5	45.2
A= Anthracene only						
B= Anthracene + TiO_2						
C= Anthracene + SDS						
D= Anthracene + CTAB						
E= Anthracene + TiO_2 + SDS						
F= Anthracene + TiO_2 + CTAB						

This showed that anthracene is also quenched but not as severely as pyrene by molecular oxygen. Generally, the average fluorescence factor obtained for the entire various volume ratio combinations was from 1.21 to 1.42 with the anthracene solution having both TiO_2 nanoparticles and CTAB added as shown in Figure 14.

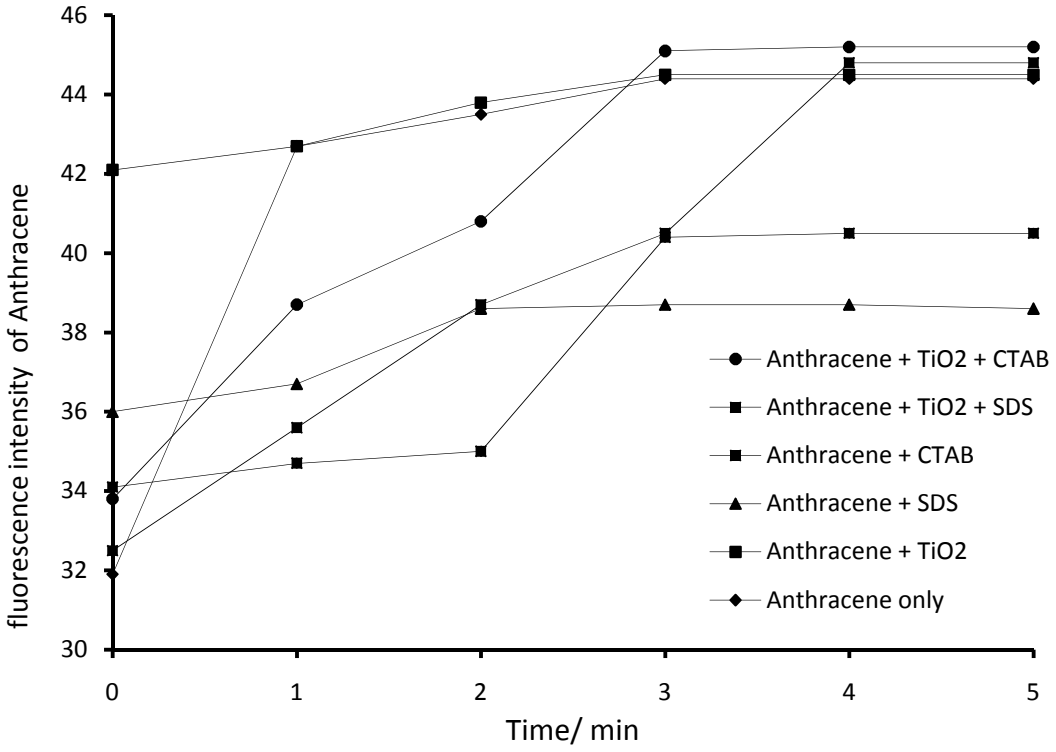

Figure 14: A plot of fluorescence intensity of various solutions of anthracene versus degassing time

Degassed Solution of Phenanthrene

After degassing the phenanthrene solution for the various length of time, the results obtained for the different solutions of phenanthrene are shown in Table 9. Phenanthrene and anthracence are isomers. This study was an attempt to observe if structural differences show different enhancement effects.

Table 9: Results of Phenanthrene fluorescence measurements during degassing

TIME (min)	Signal reading					
	A	B	C	D	E	F
0	28.9	22.4	32.1	27.7	32.0	32.7
1	65.2	70.1	70.1	60.3	64.4	69.9
2	65.7	71.0	72.2	64.5	70.7	76.9
3	67.9	71.1	72.4	65.4	71.8	77.0
4	69.6	71.1	72.4	66.2	72.1	77.1
5	69.6	70.0	72.4	66.2	72.1	77.2
A= Phenanthrene only						
B= Phenanthrene + TiO_2						
C= Phenanthrene + SDS						
D= Phenanthrene + CTAB						
E= Phenanthrene + TiO_2 + SDS						
F= Phenanthrene +TiO_2 + CTAB						

The results showed that the fluorescence intensity of phenanthrene was enhanced more than that of anthracene, its isomer. The solution of phenanthrene only gave fluorescence intensity factor of 2.4 after 5 minutes of degassing. The addition of TiO_2 and CTAB combined together with phenanthrene gave a maximum fluorescence intensity signal of 77.2 representing a fluorescence factor of 2.67 as shown in Figure 15.

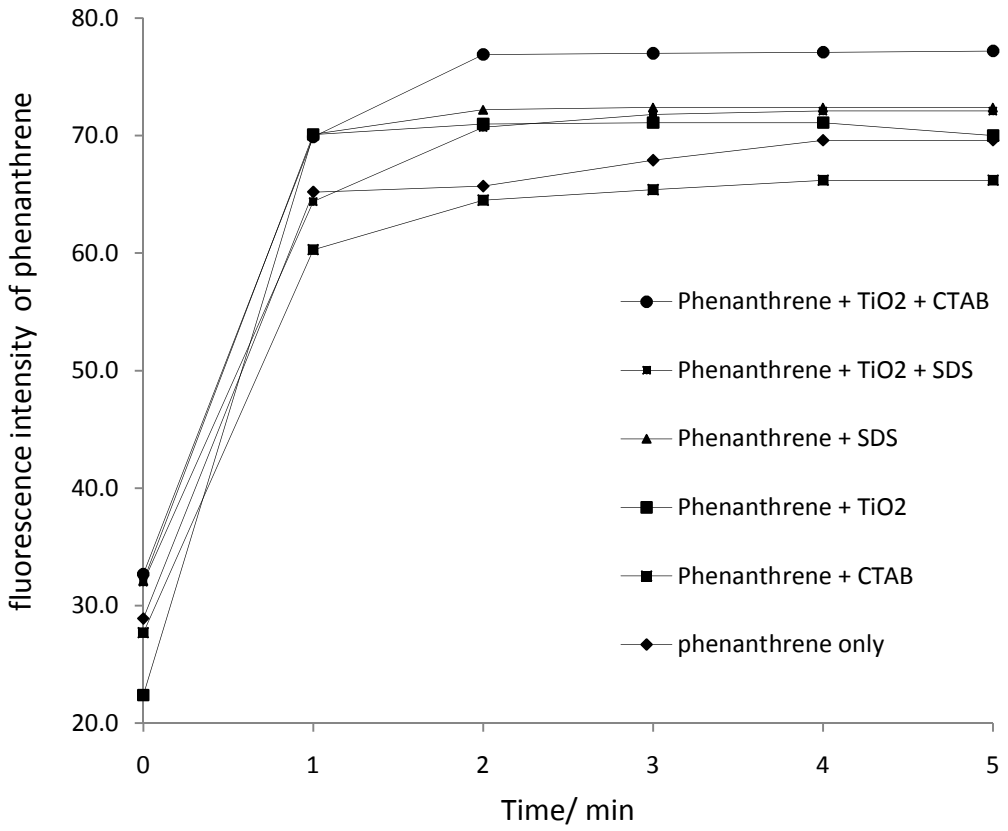

Figure 15: A plot of fluorescence intensity of phenanthrene versus degassing time

The effect of the presence of molecular oxygen in the solution on the fluorescence intensity on phenanthrene seemed to be greater than that of anthracene and thus showing greater enhancement factor with degassing (15). These results showed that phenanthrene and pyrene were quenched by molecular oxygen more so than anthracene, with pyrene more severe than phenanthrene. Anthracene, on the other hand, after degassing, showed only a little increase in fluorescence intensity. Anthracene solution, even after degassing and then allowing the solution sit exposed to air for a while, gave about the same fluorescence signal. However, for both pyrene and phenanthrene, when the fluorescence intensity was measured after exposing to air for a few minutes, showed a sharp decrease in the fluorescence intensity. This was due

to oxygen quenching. Another possibility, though very much smaller, was the possibility of slight decomposition of pyrene and phenanthrene in the presence of TiO_2 nanoparticles and after some exposure to intense excitation radiation (16).

CHAPTER 5

CONCLUSION

The effects of TiO_2 nanoparticles and surfactants in combination on the fluorescence of phenanthrene, anthracene, fluoranthene, carbazole, and pyrene have been studied. The results obtained from all the experiments were varied and interesting. Some of the results were in close agreement with expectations. However, some were interesting and not easy to explain completely and warrant further investigation.

The fluorescence of phenanthrene was quenched by the addition of TiO_2 nanoparticles with the highest fluorescence factor of 0.8 but the TiO_2 nanoparticles enhanced the fluorescence of phenanthrene, its isomer. The addition of more TiO_2 nanoparticles, however, attenuated the fluorescence of phenanthrene. The addition of TiO_2 nanoparticles to the fluoranthene solution decreased the fluorescence intensity by 4.9%. On the average the fluorescence intensity of fluoranthene was slightly affected by the addition of TiO_2 nanoparticles. The addition of TiO_2 nanoparticles to carbazole resulted in quenching of the fluorescence of carbazole by an average of 30% compared the reference carbazole solution. This might be due to the lone pairs of electrons on the carbazole nitrogen which can allow intersystem crossing to occur which may have caused triplet state quenching. The addition of TiO_2 nanoparticles to pyrene solution had the most enhancement in the fluorescence intensity compared to all the compounds used in this research. The fluorescence intensity of pyrene was increased by about 29.8% representing a fluorescence factor of 1.25 compared to the reference pyrene solution. This might be due to how severe oxygen could quench the fluorescence of

pyrene and as such the addition of TiO_2 nanoparticles might have helped protect the fluorophore from the quenchers.

Surfactants also had generally, enhancement effect on all the compounds used for this research except carbazole. The fluorescence of phenanthrene was enhanced by all the surfactants with the one-to-one volume ratio of fluorophore to surfactants solution (1P:1S), with SDS giving the best signal with fluorescence factor of 1.24 compared with the same ratios with CTAB and Triton X-100. The fluorescence of anthracene likewise was enhanced by the addition of surfactants. The 1A:1S combinations of SDS again gave the best fluorescent signal with a fluorescence factor of 1.65 compared with the anthracene reference solution. The fluorescence of fluoranthene was quenched by almost all the surfactants in contrast to the enhancement in fluorescence intensity by the addition surfactants to anthracene solution. The SDS reduced the fluoranthene fluorescence by 16%, CTAB by 6.2%, while Triton X-100 had on the average no effect on the fluorescence intensity. Carbazole was quenched significantly by the TiO_2 nanoparticles and also all the surfactants added singly or in any combination. For example 1C:1S of CTAB and SDS solutions quenched the fluorescence of carbazole by 53.9% and 48%, respectively. Triton X-100 had very little to no effect on the fluorescence of carbazole. The nitrogen atom on carbazole, the only aromatic compound studied with such structure, allows intersystem crossing to the triplet state is suspected to be responsible for all the quenching effects observed.

The surfactants CTAB and SDS had very strong enhancing effect. In fact the most dramatic enhancement in fluorescence signal by the surfactants was on pyrene compared to all

the other aromatic compounds used in this work. The surfactant CTAB increased the fluorescence signal of pyrene steadily as the volume CTAB was increased. SDS had a better enhancement than CTAB. The fluorescence signal obtained for $1P_y$:3S using SDS was 60.8 compared to 57.2 with addition of CTAB in volume ratio the same $1P_y$:3S with pyrene. These ionic surfactants had a greater enhancing effect (>300%) than the nonionic surfactant (Triton X-100) (28) on pyrene. This is because in a polar solvent these surfactants form tighter and better protective micelles and can exclude the nonpolar oxygen far more effectively.

The effect of adding both TiO_2 nanoparticles and surfactants together with each of the aromatic compounds used for this research followed almost the same trend obtained when either the TiO_2 nanoparticles or the surfactants were employed in the analysis singly. The most enhancement by these combinations was obtained with pyrene with a fluorescence intensity of 62.4 when 1Py:1T:1S of SDS was used and 59.9 when CTAB was used. Even then the enhancement increase in the presence of TiO_2 nanoparticles was not considered that significant

Degassing to exclude molecular oxygen in relation to selected aromatic compounds had dramatic effects on some of them. The solutions of pyrene, phenanthrene, and anthracene were studied with addition of TiO_2 nanoparticles and the surfactants and then the solution was degassed. The fluorescence intensity of pyrene was increased by an average fluorescence factor of 1.1 when TiO_2 was added without degassing the solution. After the pyrene solution was degassed, it gave a fluorescence factor of 8.2 which was less than the fluorescence factor of 9.5 obtained when TiO_2 nanoparticles were added to the pyrene solution and also degassed. This means that TiO_2 nanoparticles did help to diminish quenching by themselves without

degassing. Thus we observed a slight increase in fluorescence intensity of pyrene when the nanoparticles are even without degassing.

Surfactants also helped enhance the fluorescence intensity of pyrene. The surfactant CTAB singly gave the highest fluorescence factor after degassing of 12.1 compared to 11.3 obtained when SDS was used singly. When TiO_2 nanoparticles were added together with CTAB or SDS, pyrene gave fluorescence factors of 15.6 and 12.5, respectively. The additional increase in fluorescence intensity was due to the addition of TiO_2 nanoparticles. These results show that molecular oxygen quenching on pyrene is so severe that the sensitivity of fluorescence measurements depends greatly on how well the solution is degassed.

The addition of TiO_2 nanoparticles to anthracene solution resulted in an increase of the fluorescence intensity signal by 10.2 units. But after degassing both solutions, the final signal intensities were almost the same. After the solutions containing SDS-anthracene, CTAB-anthracene, TiO_2-SDS-anthracene, and TiO_2-CTAB-anthracene, the fluorescence factors obtained were almost equal. This means that molecular oxygen was not the main or sole quencher of the anthracene fluorescence intensity.

The studies on phenanthrene fluorescence intensity also revealed that molecular oxygen severely quenched the fluorescence intensity. After degassing all the TiO_2 nanoparticles singly and surfactant combinations solutions of the compound, an average fluorescence factor of 2.4 was obtained. The phenanthrene-TiO_2-CTAB combination gave the highest fluorescence factor of 2.7. The results also showed that after degassing the phenanthrene solution the

surfactants and TiO_2 nanoparticles might have helped to protect the fluorophore or make the fluorophore more rigid and thus enhanced the fluorescence intensity further.

In general, CTAB and SDS had varying effects on the selected aromatic compounds used in this research. The general effects of CTAB and SDS on these chosen aromatic compounds were enhancing the fluorescence intensity signal. Triton X-100, the neutral surfactant, did not have much effect on the fluorescence intensity in any combination on the selected compounds singly or in combination with TiO_2 nanoparticles one way or the other.

The use of 95% ethanol provided another means of conveniently degassing solutions containing surfactants without the formation of lather. This will help solve the problem of associated with solutions containing surfactants that needs to be degassed for further research work.

From the data obtained, it can be concluded that the more condensed, conjugated, and delocalized the structure of a polycyclic aromatic hydrocarbon, the more severely it is quenched. For instance, pyrene was more severely quenched compared to its isomer fluoranthene in the presence of oxygen. Phenanthrene, likewise, was also quenched to a greater extent compared to anthracene.

Finally, TiO_2 nanoparticles can enhance the fluorescence intensity of pyrene, fluoranthene, phenanthrene, and anthracene to small extent by themselves or aid in the enhancement by the surfactants with the exception of carbazole. Carbazole and similar heteroatomic compounds should present interesting further studies.

REFERENCES

1. Ladokhin, A. S. *Biophys. J.* 1999, 76(2): 946–955

2. Asuncion-Punzalan, E.; London, E. Biochemistry, 1995, 34(36), 11460–11466

3. www.csiro.au/science/LIBS.html (accessed October 22, 2008)

4. Lam, S.; Hung, J.; MacAulay, C.; Jaggi, B.; Palcic, B. Fluorescence Imaging Of Early Lung Cancer, Engineering in Medicine and Biology Society, 1990, 1142 – 1143

5. Agency for Toxic Substances and Disease Registry (ATSDR). *Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAHs)*. Public Health Service, U.S. Department of Health and Human Services, Altanta, GA. 1995.

6. Agency for Toxic Substances and Disease Registry (ATSDR). 1999. *Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAHs)*. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

7. U.S. Environmental Protection Agency. Deposition of Air Pollutants to the Great Waters. First Report to Congress. EPA-453/R-93-055. Office of Air Quality Planning and Standards, Research Triangle Park, NC. 1994.

8. Guilbault, G. *Practical Fluorescence, 2nd ed.; rev. and expanded*. Marcel Dekker, Inc., New York, 1990, 1-60.

9. Aiken, J.; Huie, C.. *Analytical Letters*, 1991, 24(1), 167-180.

10. Diebold, U., Surf. Sci. Reports, 48, 2003, 53.

11. Hinze, W. *Organized assemblies in chemical analysis*. *Overview of the utilization of reversed micellar media in analytical spectroscopy*, Jai Press Inc.: Greenwich, CT, 1994, 1, 3.

12. Bhowmik, B. B.; Ganguly, P. Photophysical studies of some dyes in aqueous solution of Triton X - 100. *Spectrochim. Acta, Part A* 2005, *62A* (4-5), 808-813.

13. Largiuni, O.; Udisti,R.;Traversi R.; Piccardi,G. Sensitivity enhancement of the formaldehyde fluorimetric determination by the use of surfactant, *Intern. J. Environ. Anal. Chem*, 2001, 82(2), 97-112.

14. Nobuhko. I.; Kina, K.; Sensitivity enhancement of the fluorometric determination of aluminum by the use of surfactant. *Analytical letters*, 1972, 5(9), 637-641.

15. Harnandan S.; Hinze,W. Micellar enhanced spectrofluorimetric methods: application to the determination of pyrene. *Analytical letters*, 1982, 15(A3) 221-243.

16. Lin, Y. L.; Wang, T. J.; Jin, Y. Powder Technol.123, 2002 194.

17. http://ec.europa.eu/health/ph_risk/committees/04_scenihr/docs/scenihr_o_003b.pdf

18. Guyot-Sionnest, P. Quantum Dots: An Emerging Class of Soluble Nanomaterials, Material Matters, 2007, 2 (1), 10.

19. Kittel C. Introduction to Solid State Physics, 8th edition, 2005, Wiley.

20. Bruchez M.; Moronne,M.; Gin,P.; Weiss, S.; Alivisators, A. P. Science, 1998, 281, 2013
21. Chan ,W.C.W.; Nie, S. M. Science, 1998, 281,2016

22. Reyes-Coronado, D.; Rodriguez-Gattorno, G.; Espinosa-Pesqueira, M.,E.; Cab, C.; de Coss, R.; Oskam, G. Nanotechnology. 19, 2008, 145605 (10pp)

23. Yin, H.; Wada, Y.; Kitamura, T.; Yanagida, S. J. Mat. Chem. 12, 2002, 378

24. Ashcroft Jared, M.; Weiwei, G.; Zhang, T.; Hughes, S. M.; Hartman, K. B.; Hofmann, C.; Kanaras, A. G.; Kilcoyne, D. A.; Gros, M.; Le, Y. Y.; Alivisatos, A. P.; Larabell, C. A. *Chem. Communications.* 7(21): 2008, 2471-2473

25. Thevenot, P.; Cho, J.; Wavhal, D.; Timmons, R.; Tang, L. Surface chemistry influences cancer killing effect of TiO_2 nanoparticles, *Nanomedicine: Nanotechnology, Biology and Medicine*, 4(3), 226-236

26. Vicki, G. H.; O'Shaughnessy, P. T.; Adamcakova-Dodd, A.; Pettibone, J. M.; Thorne, P. S. *Environmental Health Perspect*, 2007, 115(3) 397-402

27. Wang, J.; Gu, M.; Di, J.; Gao, Y.; Wu, Y.; Tu, Y.; Biosyst. Eng. 30, 2007, 289-50

28. Lin,Y.L.; Wang, T.J.; Jin, Y. *Powder Technol*.123, 2002, 194

29. Tang, J.; Redi, F.; Zhu, Y.; Siegrist, T.; Brus, L.E.; Steigerwald, M.L.; *Nano Letters* 5, 3, 2005, 543-548

30. Jiang, B.; Yin, H.; Jiang, T.; Jiang, Y.; Feng, H.; Chen, K.; Zhou, W.; Wada, Y.; Mater. Chem. And Phy. 98, 2006, 231-235

31. Kumar, S. A.; Chen, S. M.; Lo, P. H.; Nanotechnology 19, 2008, 255501(7pp)

32. Lin, Y. Food Chem.Toxicol. 34, 1996, 887-904

33. Tang, Z.; Zhang, J.; Cheng, Z.; Zhang, Z.; Mat. Chem. And Phy. 77, 2002, 314-317

34. O'Haver,T. C. The Development of Luminescence Spectrometry as an Analytical Tool. *J. Chm Edu.* 1978, 55(7), 423.

35. Gopal, M.; Mobey, C. W. J.; De Jonghe, L. C. *J. Mater. Sc*. 32, 1997, 6001-6008

36. Association of Official Analytical Chemists, 1984,. In official Methods of Analysis. 14th ed. AOAC, Arlington, VA. 43.039-43.047

37. Guilbault, G. Practical Fluorescence: Theory, Methods, and Techniques Marcel Dekker, Inc.: New York, 1973; pp 1-60.

38. Harris, D.C. Quantitative Chemical Analysis,7ed.; W. H. Freeman and Company: New York, 2007, pp 1-661

39. Gary, Christian D., *Analytical Chemistry*, 6th ed.; John Wiley & Sons Inc. 2003; pp 1-803

40. Skoog,D. A; Holler, F.J.;Crouch S. R. *Principles of instrumental Analysis*,6ed.;Thomson Higher Education: Belmont, CA, 2007 pp
41. Grewer, C.; Brauer, H-D. *J. Phys. Chem.* 1994, 98, 4230-4235.

42. Lakowicz J. R. Principles of Fluorescence spectroscopy, 3ed, 2006, 277-331

43. Aiken, J. Huie, C. Detection of Biririubin using surfactant fluoresecence enhancement and visible laser fluorometry. *Analytical Letters*, 1991, 24(1), 167-180.

44. Rubinson, K. A.; Rubinson, J. F. Contemporary Instrumental Analysis 1st ed Prentice Hall Inc: New Jersey, 2000 pp 330-350.

45. Torro, N. J.; Renner, C. A.; Waddell, W. H.; Katz, T. J. *J. Am. Chem. Soc*. 1976, 98, 4320.

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