

Impact of solvent polarity and substituents on polycyclic aromatic hydrocarbons' emission and absorption spectrums

A DISSERTATION

PRESENTED IN PARTIAL COMPLIANCE OF THE CRITERIA

FOR GRANTING THE DEGREE

OF

MASTER OF CHEMISTRY

IN

APPLIED CHEMISTRY

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I, **Manju (2K22/MSCCHE/52)** am the student of Masters in chemistry, hereby proclaim that the project Dissertation entitled " **Impact of solvent polarity and substituents on polycyclic aromatic hydrocarbons' emission and absorption spectrums**" which I submitted to the Department of Applied Chemistry, Delhi Technological University in partial fulfilment of the perquisites for granting the degree of Master of Science of Technology, is distinctive and has not been took from any source without adequate citation. This project has never previously served as the foundation for awarding any Degree, Diploma, Fellowship, Associateship or any other equivalent title or recognition.

Place: Delhi**Date: 25 MAY 2024****MANJU****2K22/MSCCHE/52**

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I authorize that the Project Dissertation entitled " **Impact of solvent polarity and substituents on polycyclic aromatic hydrocarbons' emission and absorption spectrums** " which is submitted by **Manju (2K22/MSCCHE/52)**, DEPARTMENT OF APPLIED CHEMISTRY, Delhi Technological University, Delhi in partial fulfilment of the perquisites for granting the degree of Master of Science of Technology, is a documentation of the project work completed by a student under my guidance. To the best of my knowledge, this work has not been registered for any degree or diploma, either at this university or elsewhere.

Place: Delhi**Date- 25 May 2024****PROF. ANIL KUMAR****SUPERVISOR**

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MANJU

Objectives

- ✓ Absorption spectrum and emission spectrum of Naphthalene, Anthracene and their derivatives.
- ✓ Impact of solvent polarity on absorption spectrum of Naphthalene, Anthracene and their derivatives.
- ✓ Impact of solvent polarity on emission spectrum of Naphthalene, Anthracene and their derivatives.
- ✓ Effect of amino – substituent on absorption spectra of Naphthalene and Anthracene.
- ✓ Effect of amino – substituent on emission spectra of Naphthalene and Anthracene.

ABSTRACT

The Ultraviolet absorption spectra and emission spectrum of polycyclic aromatic hydrocarbons (PAHs) are studied at different solvents i.e. acetone, hexane, dimethyl sulfoxide, ethyl acetate, of varying polarity. The effect of amino substituents at naphthalene and Anthracene have also been investigated. The solvent polarity impacts the absorption maxima and intensity maxima of emission spectra by change in physiochemical properties of solvent like dipole moment, charge transfer, H-bonding. The relation between absorption wavelength and emission intensity with solvent polarity indicates that there are solute-solvent interactions in the prepared solution. The orientation polarizability was associated with bathochromic or hypsochromic shift and Stoke's shift. The effect of solvents on the absorption band shifts reflects how much charge of solute particles are reorganized in response to electrical stimulation. The nature of substituents also influences the emission and absorption spectrum. These co-relations are studied in detail in this project. The emission and absorption spectrum of PAHs in 3 varying polarity solvents are in accordance with the previously reported results.

Keywords:

PAHs, Naphthalene, Anthracene, absorption spectra, emission spectra

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Figure 5.2.2: Emission spectrum of amino-naphthalene in DMSO, ethyl acetate, hexane.

Figure 5.2.3: Emission spectrum of amino-anthracene in DMSO, ethyl acetate, hexane.

LIST OF ABBREVIATIONS

PAH	Polycyclic Aromatic Hydrocarbon
UV	Ultra-violet
NAP	Naphthalene
PHE	Phenanthrene
PYR	Pyrene
DTU	Delhi Technology University
ACY	Acenaphthalene
ANT	Anthracene
FLU	Fluoranthene
FL	Fluorene
PER	Perylene
Vis	Visible
IR	Infra-red
NMR	Nuclear Magnetic Resonance
pH	Potential of Hydrogen
EMR	Electromagnetic radiation

CHAPTER 1

INTRODUCTION

Polycyclic aromatic hydrocarbons, also known as PAHs, comprise organic contaminants arising from both natural and man-made activities, including urbanization and industrialization[1]. They typically come from the processes that include combustion[2]. PAHs are persistent, semi-volatile contaminants found in the environment. They consist of 2 or more than 2 fused rings of benzene with lipophilic and hydrophobic double bond across the hydrocarbon rings. When three or less fused rings are present in a PAH, it is categorized as low molecular weight, and when four or more fused rings are present it is designated as high molecular weight[3]. One common low molecular weight PAH with three fused rings is phenanthrene (PHE), which is found in high concentrations in PAH containing surroundings[1], [4]. Four fused benzene rings make pyrene (PYR) a high molecular weight PAH, which is generated when fossil fuels like biomass or low rank coal are partially burned at high temperatures, particularly during gasification or pyrolysis process[1], [5]. The ratio of hydrophobicity to lipophilicity increases with molecular weight[3].

PAHs mainly include Naphthalene (NAP), Acenaphthalene (ACY), Pyrene (PYR), Anthracene (ANT), Fluorene (FL), Perylene (PER), Fluoranthene (FLU) etc. along its derivatives [1], [2]. In this paper, we are focusing on naphthalene, anthracene and their amino derivatives. NAP is produced from tar of coal that comes from robust petroleum components during refining. This is used in 2-naphthol production, pigments and as a precursor for many dyes [1], [6]. ANT is an organic contaminant in water that is primarily produced during partial combustion of organic materials.

ANT was recently categorized as an essential contaminant because of its carcinogenicity, mutagenicity, bioaccumulation and toxicity [7]. Moreover, due to its chemical stability, ANT is exceedingly hydrophobic and has minimal biodegradability [1], [8]. These two polycyclic aromatic hydrocarbons, naphthalene, anthracene, are then substituted with amino group to know the impact of substituents on emission and absorption spectrum.

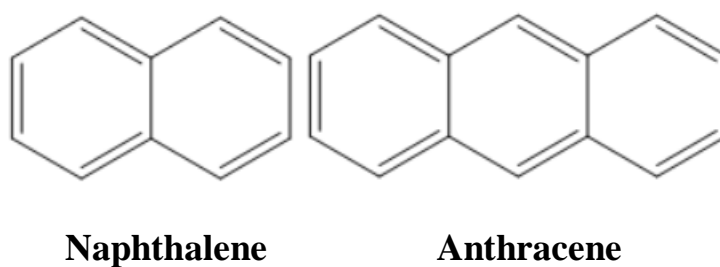


Fig.1(a): Structure of Naphthalene and Anthracene.

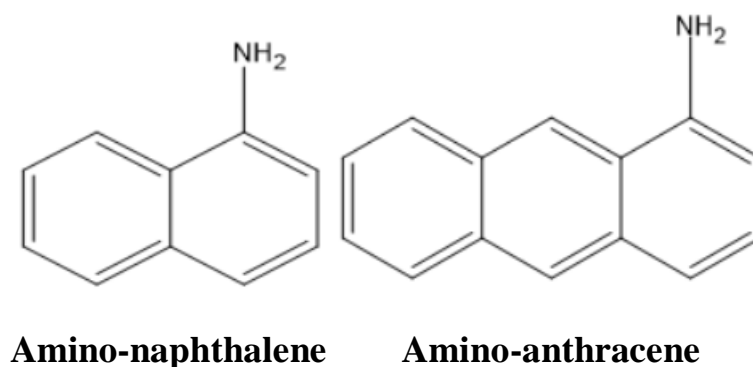


Fig.1(b): Structure of Amino-naphthalene and Amino-anthracene.

The term “solvation” refers to the process of more or less tightly bound solvent shells encircling the dissolved solute species as a result of intermolecular and interionic attractive forces between the solutes and solvents [9]. The ability of a solvent to dissolve apolar or dipolar and charged or neutral entities is known as solvent polarity [10]. Dipole moments, relative permittivities, and refractive indices are used as physical parameters of solvent polarity because electrostatic solvation models are straightforward. The solute/solvent interactions occur at molecular-microscopic level [9], [10]. A more practical definition of solvent polarity would be the solvent’s total solvation capability, also known as solvation power, which would include every potential specific intermolecular force and non-specific intermolecular forces in solute-solvent but would exclude all the interactions that would result in a clear chemical modification of the solute [9].

Solvent polarity characteristics were determined using solvent-sensitive reference chemicals that absorb or emit radiations in several spectral regions that correspond to UV-vis, IR, Fluorescence and NMR respectively [10]. Here we are going to focus on UV-Vis and Fluorescence spectroscopy. UV-Vis spectroscopy is employed for quantitative analysis of various analytes. The absorbing molecule comprises of a chromophore, which is responsible for the absorption of light in UV-Visible spectrum. When two or more chromophores are separated by many bonds, the absorption is cumulative. However, when chromophores are separated by a single bond, the effects are more noticeable. This shifts the maximum absorption to longer wavelength, making it suitable for spectrophotometers. This effect is known as bathochromic shift, which is characterized by a rise in maximum intensity and often known as hyperchromic effect. The opposing changes, known as hypsochromic shift and hypochromic effect, are common when a chromophoric system is altered, such as by changing pH [11]. The process of photo emission known as Fluorescence happens when molecules relax from electronic excited states. These photonic activities include the polyatomic fluorescent compounds from electronic to vibrational states [12].

In this dissertation work, we will discuss:

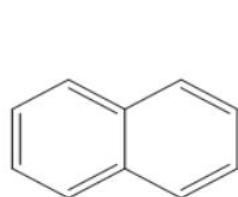
- I. The impact of solvent polarity
- II. The impact of substituents

in detail on the emission and absorption spectra/spectrum of naphthalene, anthracene and their amino derivatives.

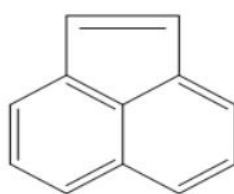
Chapter 2

POLYCYCLIC AROMATIC HYDROCARBONS

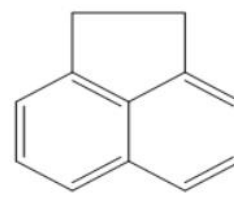
PAHs are organic molecules commonly perceived in the soil, water and air [13]. These are carcinogenic in nature [14], [15], [16], [17]. 16 PAHs have been identified by USEPA as the most important chemicals to be examined in a variety of environmental matrices. These chemicals include fluorine, anthracene, benzo(a)anthracene, naphthalene, phenanthrene, chrysene, acenaphthene, dibenzo(a,h)anthracene, pyrene, acenaphthylene, benzo(b)fluoranthene, benzo(a)pyrene, fluoranthene, indeno(1,2,3-c ,d)pyrene, benzo(k)fluoranthene, and benzo(g,h,i)perylene [18].



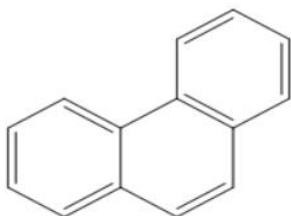
Naphthalene



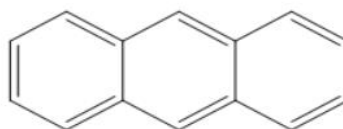
Acenaphthylene



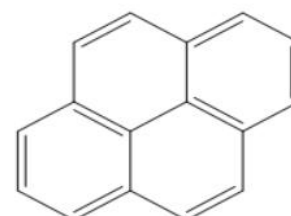
Acenaphthene



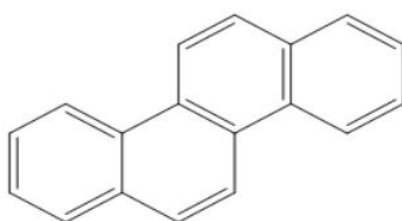
Phenanthrene



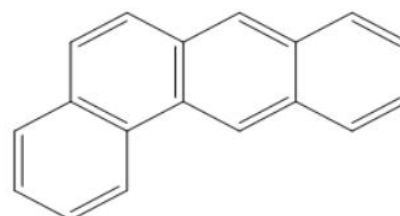
Anthracene



Pyrene



Chrysene



Benzo[a]anthracene

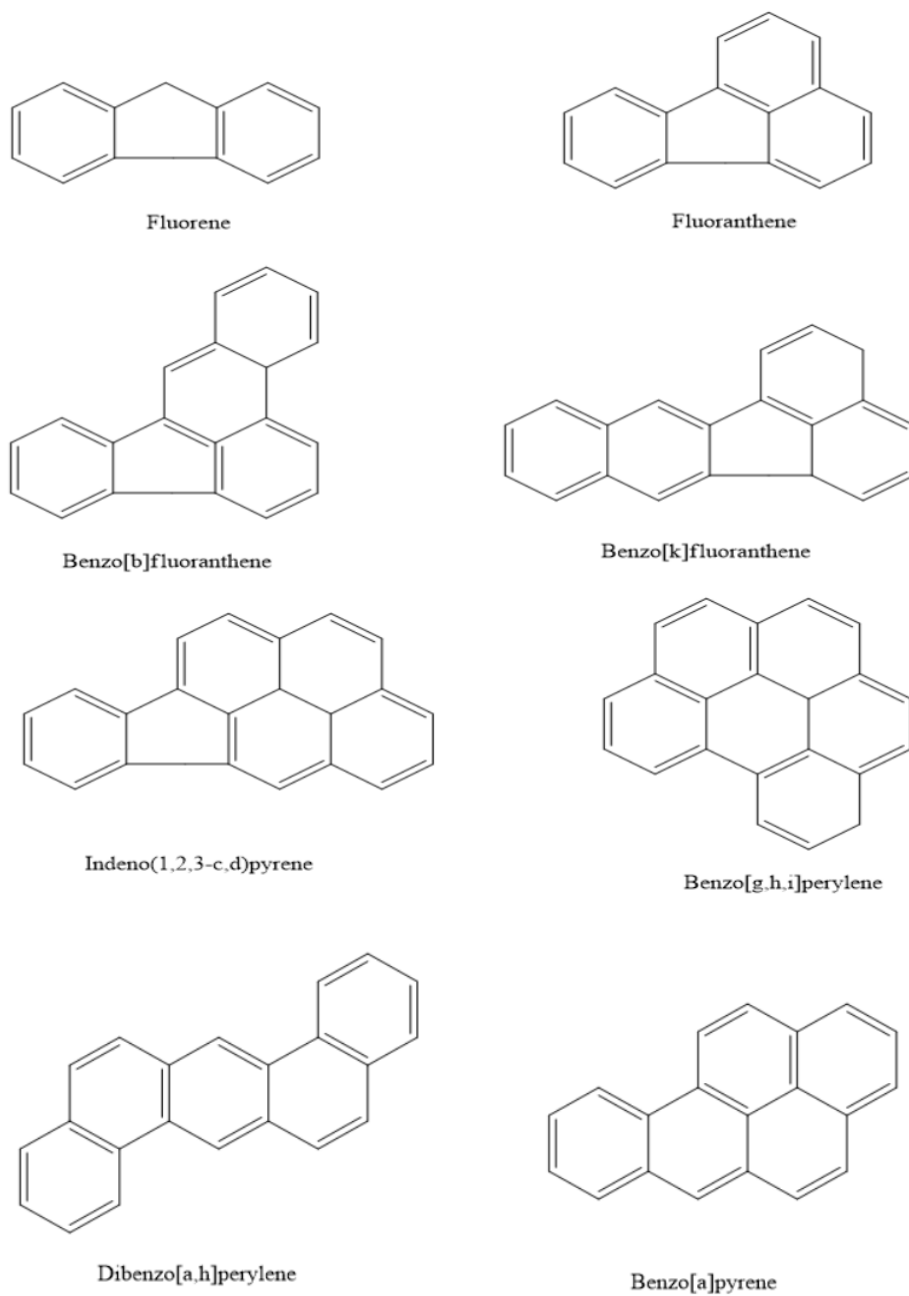


Fig.2: Structure of 16 PAHs

In recent times, the quantity of PAHs derived from fossil fuels and partial combustion has increased [13]. PAHs in the ecosystem are classified into four distinct categories [19];

- ✓ Petrogenic (produced from fuels)
- ✓ Pyrogenic (obtained from partial combustion)
- ✓ Biogenic (derived from organic metabolism)
- ✓ Diagenetic (derived from sediment transformation)

2.1 Sources of PAHs

PAHs may originate from both sources natural and human-caused (anthropogenic) including wood burning and coal [20], [21], [22], [23], [24], [25], [26], combustion of diesel oil and petrol [27], [28], [29], and industrial operations [30], [31]. Natural sources of PAHs include forest fires [32], [33], combustion of waste, eruptions and hydrothermal activities [33], [34], [35], [36]. PAHs global distribution can be attributed to both natural and anthropogenic sources, as well as global transport process. They are mostly created as a result of combustion of fossil fuels via heating operations, waste disposal and automotive exhausts. These environmental pollutants are widely disseminated and have negative biological consequences, carcinogenicity, toxicity and mutagenicity. The PAHs' concentration in environment varies based on factors like development of industries, proximity of the source and the mode of transport [37]. PAHs are found in large quantities in fossil fuel products, automotive traffic emission and refining, biomass combustion [38], tobacco [39], [40], wood smoke [24], [41], charcoals [42], wood [23], [25] and garbage [43].

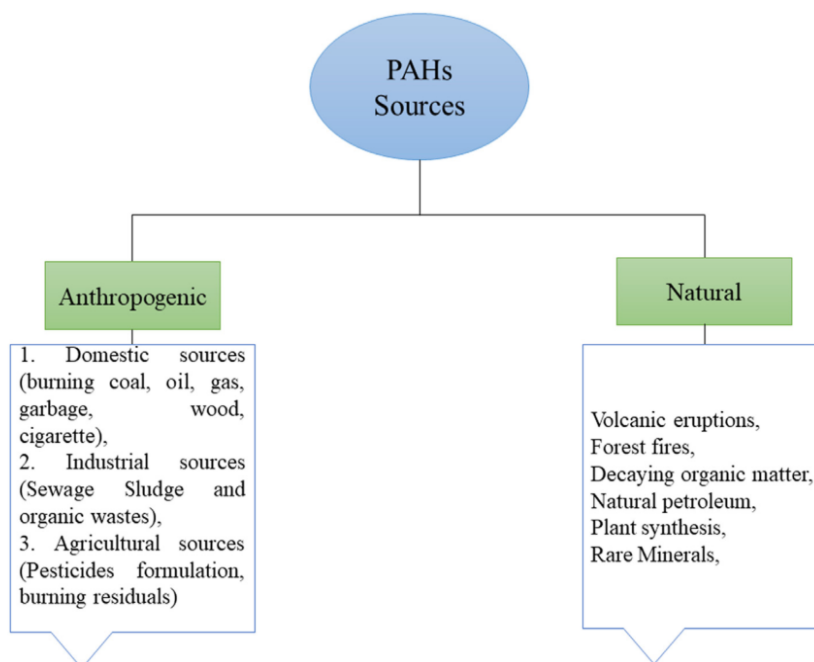


Fig. 2.1: PAHs' sources [1].

2.2 PHYSIOCHEMICAL Properties

The physiochemical characteristics are crucial in forecasting how PAH will behave in the environment [44], [45], [46]. They consist of carbon and hydrogen, but they can easily substitute with nitrogen, oxygen, and sulfur in benzene ring to create heterocyclic aromatic compounds, which are typically classified alongside PAHs. Furthermore, alkyl-substituted PAHs are commonly detected in environment matrices with PAHs [47]. Common characteristics of PAHs include less vapour pressure, extremely lower solubility, high melting and boiling temperature, and so on [3]. PAHs have tendency to decrease in aqueous solubility and vapour pressure as molecular weight grows; nonetheless they are resistant to oxidation and reduction grows with raise in their molecular weight. Thus, the water solubility these falls with every extra ring [18].

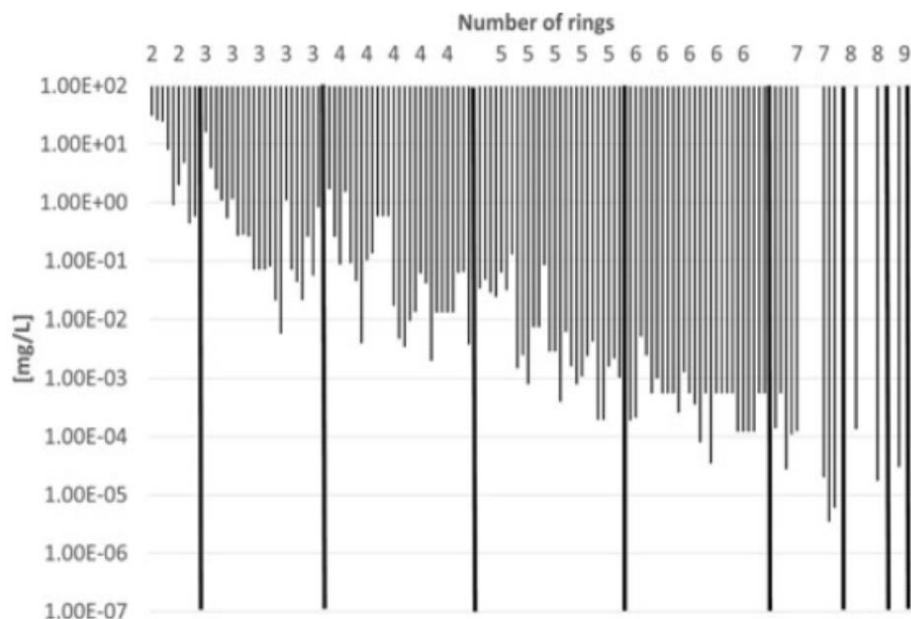


Fig.2.2 (a): PAHs' water solubility as a function of ring count [48].

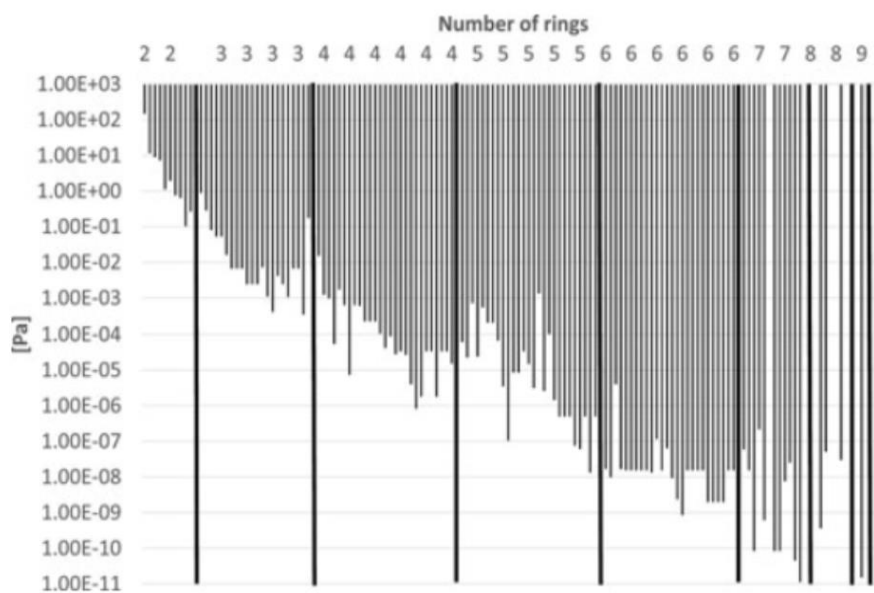


Fig. 2.2 (b): PAHs' Vapor Pressure as a function of ring count [48].

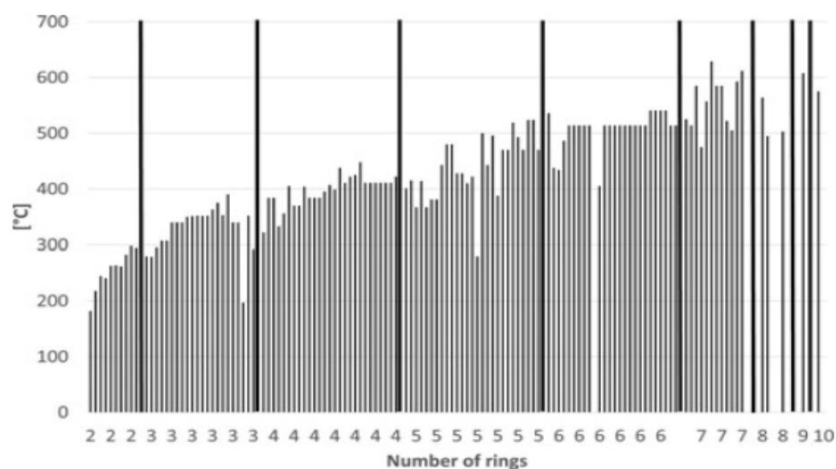


Fig.2.2 (c): PAHs' Boiling Point as a function of ring count [48].

Figure 2.2 (a), (b), (c) illustrate some of the PAHs' physio-chemical characteristics to show how they vary with ring number. Boiling points ranges of PAH's increases as the number of rings increases which can be seen in fig. 2.2 (c). Figure 2.2 (b) and 2.2 (a) depict that vapour pressure and water solubilities indicate steady decline from 2-ring PAH to 10-ring PAH [48].

2.3 EFFECT OF PAHs

2.3.1 Effect on Human Health

The impact of PAHs on health of humans is mostly determined by exposure duration, pace, concentration and individual toxicity [15], [49]. Pre-existing health state, personal

attributes, routines, other pollutants and age may all influence the impacts of PAHs on humans [49]. It is difficult to attribute health consequences to particular one PAHs, as most exposures involves many PAHs. However, exposure to high concentrations of particular PAHs has been connected throughout time to adverse effects [3].

Various effects of PAHs on health of human include [3], [15], [50]:

- ✓ Cancer
 - Oral Cancer
 - Leukaemia
 - Prostate Cancer
 - Lymphomas
 - Gastrointestinal Cancer
- ✓ Cataracts
- ✓ Decreased immune system
- ✓ Kidney damage
- ✓ Liver damage
- ✓ Asthma
- ✓ Immunotoxicity
- ✓ Genotoxicity
- ✓ Anaemia
- ✓ Nausea
- ✓ Diarrhoea

- ✓ Dermatitis
- ✓ Inflammation
- ✓ Vomiting
- ✓ Skin irritation
- ✓ Eye irritation

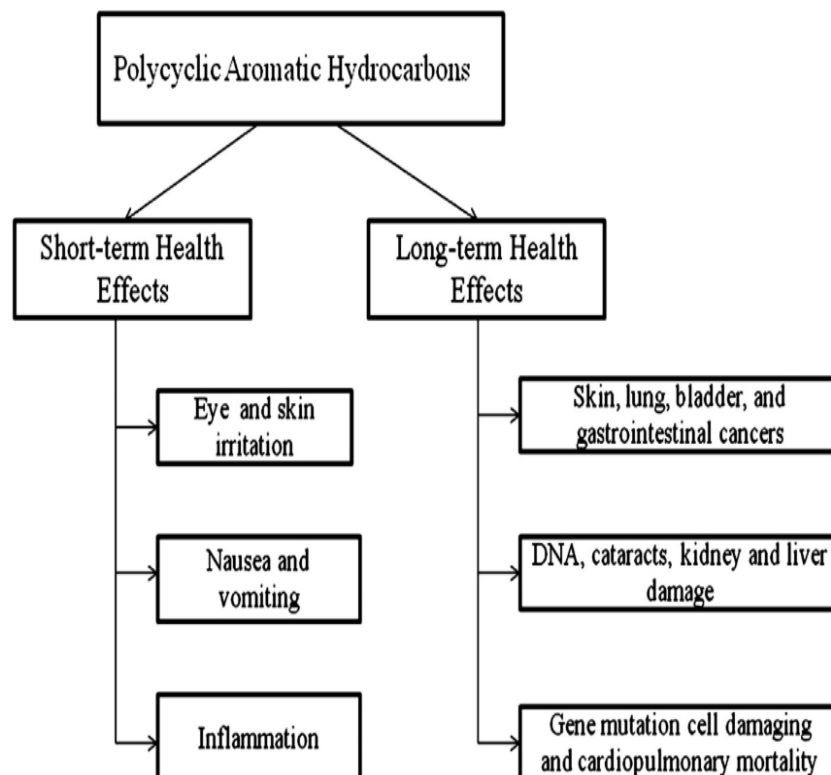


Fig.2.3.1: Effect of PAHs on Human Health [50].

2.3.2 Effect on Aquatic Ecosystem

PAHs are a type of persistent organic contaminants that contaminate the aquatic environment. The majority of PAHs found in aquatic environments arise from pyrogenic origin [51] .

Sources of PAHs in aquatic ecosystem is [2]:

- ✓ Oil
 - Oil Spill
 - Marine Oil
 - Bunker Fuel Spill
 - Crude Oil Spill
- ✓ Sediment
 - River Sediment
 - Lake Sediment
 - Marine Sediment
 - Harbor Sediment
- ✓ Wastewater

Effects of PAHs on aquatic organisms are:

- ❖ PAHs bio-accumulate in fish bile, liver or food of aquatic organisms [13], [52].
- ❖ PAHs might interrupt the reproduction of fish [53].
- ❖ PAHs are carcinogenic for aquatic organisms.

Chapter 3

LITERATURE SURVEY

3.1 IMPACT OF SOLVENT POLARITY ON ABSORPTION AND EMISSION SPECTRUM

Verdasco et al., 1995, shows that variations in absorption maxima, excitation maxima and emission maxima occur when solvent polarity is changed. Higher shifts are observed with dimethyl sulfoxide (DMSO) and acetone. Solvents with higher dipole moments also show increase in emission maxima and this effect in fluorescence emission maxima is greater than the absorption maxima. Some solvents have the ability to increase excited state ionization, which can increase the Stokes shift that is related to solvent changes. DMSO have more pronounced effect in this Stokes shift. It is depicted that the compound's excited state is more susceptible to the polarity of the solvent than their ground state.

Porobić et al., 2020, demonstrates that absorption and emission maxima show bathochromic shift when substituted with electron donor group in comparison to unsubstituted compounds. While in case of electron withdrawing substituents, show bathochromic shift in polar solvent and hypsochromic shift in non-polar solvents. The solvent's dipole moment and electrons mobility cause the solvent's polarity to have effect on Stokes shift.

Zakerhamidi et al., 2010, depicts that source of Stokes shifts is the way solvent polarity affects absorption and fluorescence. The difference of energy between ground states and excited states is influenced by solute-solvent interactions. Solvent polarity has more pronounced effect on emission spectra as compared to absorption spectra. High dipole moments increase the absorption and emission shifts. Hydrogen bonding also effects the absorption and emission spectra.

Saroj et al., 2011, shows that as polarity increases the absorption band shifts to higher bathochromic shift. Interactions like charge-transfer also increases the bathochromic shift. In the more polar solvents, more interaction will take place between the solute and solvent resulting into broad absorption spectra. When polar solvents were used instead of non-polar ones, the intensity of fluorescence increases. When solvent polarity increases, Stokes shift and emission bandwidth increases due to charge transfer.

Hammud et al., 2008, states that the absorption spectra band undergoes a red shift while moving from non-polar to polar solvent because the interactions between solute and solvent stabilise the π^* orbital in polar solvents. DMSO accepts hydrogen.

3.2 IMPACT OF SUBSTITUENT ON ABSORPTION AND EMISSION SPECTRUM

Verdasco et al., 1995, depicts that presence of substituent (amine group) on PAHs results in bathochromic shift in absorption maxima due to conjugation. Ionized amines have more positive charge which increase the resonance in response to that excited state becomes stable and, therefore, emission maxima changes.

Porobić et al., 2020, demonstrates that absorption and emission maxima shift to higher wavelength when the benzene is substituted with electron donor group at para position regardless of solvent while when it's substituted with electron withdrawing group then absorption and emission maxima will depend on solvent. The red shifts in emission and

absorbance spectra were predicted by electron donating substituents stabilizing the excited state by extended conjugation.

Zakerhamidi et al., 2010, shows that hydrogen bonds increase the absorption and emission spectra. So, if substituent can make H-bond with solvent then the absorption and emission maxima increase.

Saroj et al., 2011, depicts that electron withdrawing group show the absence of fluorescence due to efficient decay (non-radiative).

Cisse et al., 2020, shows that electron donating substituent decreases the Stokes shift and red shift was taken place in absorption and emission spectra while in case of electron withdrawing group Stokes shift increases and blue shifts takes place. Electron donating group lessen the difference in energy between the molecular orbital involved in π bonding and π^* antibonding.

Chapter 4

MATERIALS AND SYNTHESIS

4.1 MATERIALS USED

Naphthalene, Anthracene, Amino-Naphthalene, Amino-Anthracene, Acetone, Chloroform, Hexane, Dimethyl sulfoxide (DMSO), Ethyl acetate.

4.2 SYNTHESIS OF SAMPLES

1 mmol solutions of Naphthalene, Amino-Naphthalene, Anthracene, Amino-Anthracene were prepared.

4.2.1 Preparation of Naphthalene

0.773 mg of Naphthalene was dispersed in 4 ml of chloroform.

4.2.2 Preparation of Amino-naphthalene

0.573 mg of Amino-naphthalene was dispersed in 4 ml of chloroform.

4.2.3 Preparation of Anthracene

0.713 mg of Anthracene was dispersed in 4 ml of chloroform.

4.2.4 Preparation of Amino-anthracene

0.773 mg of Amino-Anthracene was dispersed in 4 ml of chloroform.

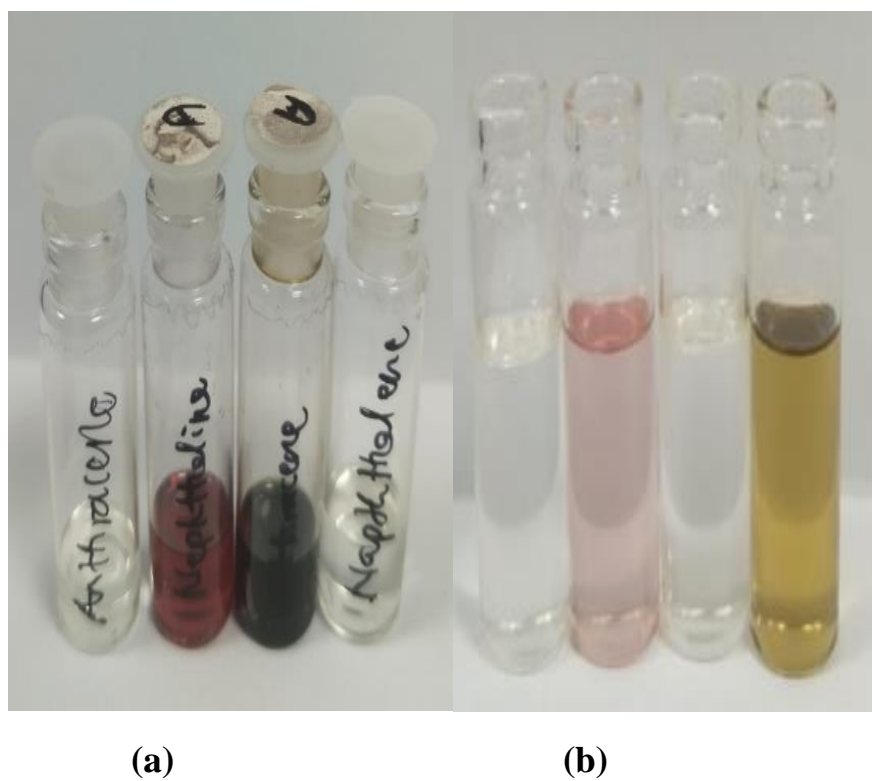


Figure 4(a): Solution of required PAHs (b) Solution of required PAHS in Chloroform.

4.3 CHARACTERIZATION METHODS

4.3.1 UV-Vis Spectroscopy

UV-Vis spectroscopy is commonly utilized to analyse various compounds. The fundamental principle of this spectroscopic technique is light absorption. This is the most ancient spectrophotometric technique to examine the lights' intensity in 10-40 nm (UV) and 400-800 nm (Vis) ranges, as a function of wavelength. The interactions between matter and EMR UV-vis range are the primary objective of ultraviolet-visible spectroscopy. A UV-Vis spectrometer's visual setup consists of one or more polychromatic source of light, wavelength selectors, detectors, sample holder, recorders. UV region includes 10-380 nm of spectrum. The UV spectrum is then categorized into 3 sub-parts: UVA, UVB, UVC. This UV-Vis spectral regions across the electronic energy levels figure out the absorption bands. UV and visible rays may react with matter in numerous ways, including reflection, transmission, emission and absorption as photoluminescence, diffusion at different wavelengths compared to the incoming monochrome radiations.

UV-Vis spectroscopy relies on the light's absorption, the quantity of the light absorbed corresponding directly to analyte's concentration in sample solution. Increasing analyte concentration, leads to linear increase in light's absorption and exponential decrease in light's transmission [59], [60].



Figure 4.3.1: UV-Vis Spectrophotometer.

4.3.2 Fluorescence Spectroscopy

Fluorescence spectroscopy is one of the primary key techniques used in biochemistry and biophysics. But nowadays, Fluorescence is widely applied in flow cytometry, sequencing of DNA, biotechnology, health care diagnostics, forensics and analysis of genetics. This is quite fast, sensitive, low-cost and highly specific technique. It is used for both types of analysis, quantitative as well as qualitative. Spectrofluorometer consists of light source, monochromators, sample cells and detectors.

Luminescence is light's emission from a substance, which can be categorized into Fluorescence and Phosphorescence. Fluorophores serve the major function in fluorescence spectroscopy. These are the components which enable them to glow. Mostly, Fluorophores are aromatic molecules. Absorption of Ultraviolet or Vis rays result in electrons' transition from singlet ground to excited state. This unstable state generates Ultraviolet or Vis light before returning to ground state. Fluorescence emission happens when fluorophores fall from electronic excited state to permissible

vibrational level of ground state. Fluorescence excitation spectra represent vibrational levels in ground state while fluorescence emission spectra represent vibrational levels in excited state [12], [61].



Figure 4.3.2: Spectrofluorometer.

CHAPTER 5

DISCUSSION AND RESULT

The experiment was carried out in Lambda 25 UV/Vis spectrometer and Fluorescence spectrometer.

5.1.1 IMPACT OF SOLVENT POLARITY ON ABSORPTION SPECTRUM

Absorption spectra of naphthalene, anthracene, amino-naphthalene and amino-anthracene is reported as a function of solvent polarity of hexane (low polar), acetone (intermediate polar), dimethyl sulfoxide (highly polar). The graph of absorbance vs wavelength was made in origin software.

The reported absorption maxima (fig. 5.1, fig. 5.1.1, fig. 5.1.2, fig 5.1.3) of naphthalene in DMSO, acetone and hexane are 278 nm, 210 nm, 238 nm respectively while in case of anthracene is 262 nm, 210 nm and 252 nm respectively. While, the λ_{\max} of amino-naphthalene in DMSO, acetone and hexane are 337 nm, 331 nm and 243 nm, λ_{\max} of amino-anthracene is 270 nm, 210 nm and 236 nm for DMSO, acetone and hexane respectively.

The data depicts that λ_{\max} is highest for DMSO which has the highest polarity. But the intermediate and lower polar solvents do not follow particular trend.

From the graphs and data, it is clearly understood that absorption spectra of PAHs do not only depends of polarity of the solvent. Many factors like, dipole moment, dielectric constant, charge transfer, refractive index, solvation energy, H-bonding, other specific or non-specific interactions, influence the Stokes shift value. DMSO also have hydrogen accepting tendency.

So, the solvents typically cause displacements in absorption peaks rather than fundamental shift in the spectrum.

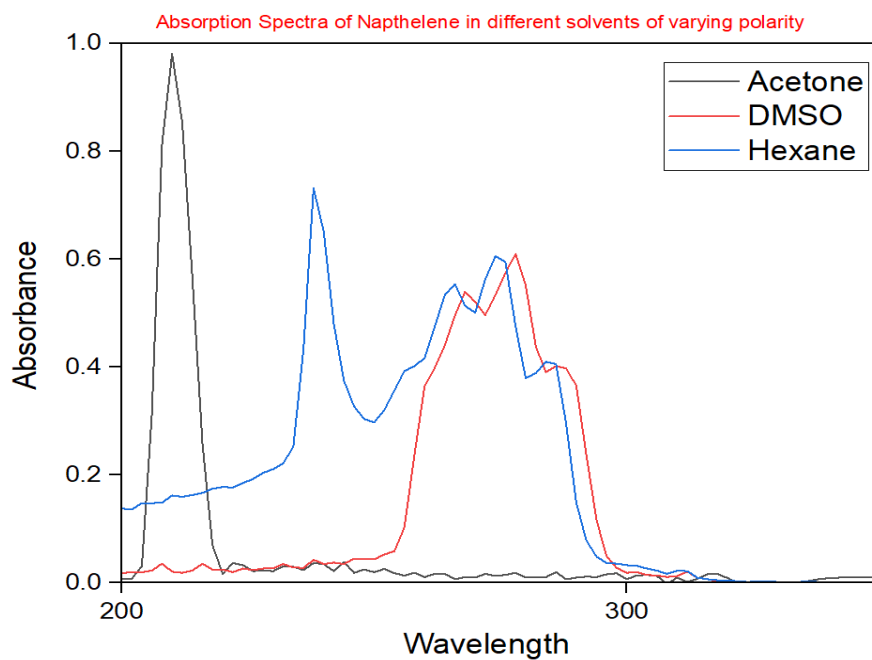


Fig. 5.1 Absorption spectrum of naphthalene in DMSO, acetone and hexane.

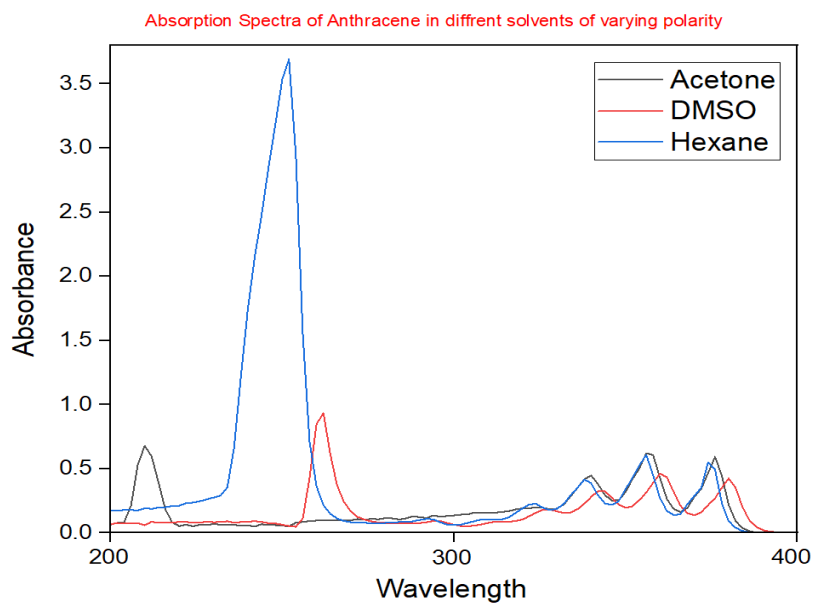


Fig. 5.1.1 Absorption spectrum of anthracene in DMSO, acetone and hexane.

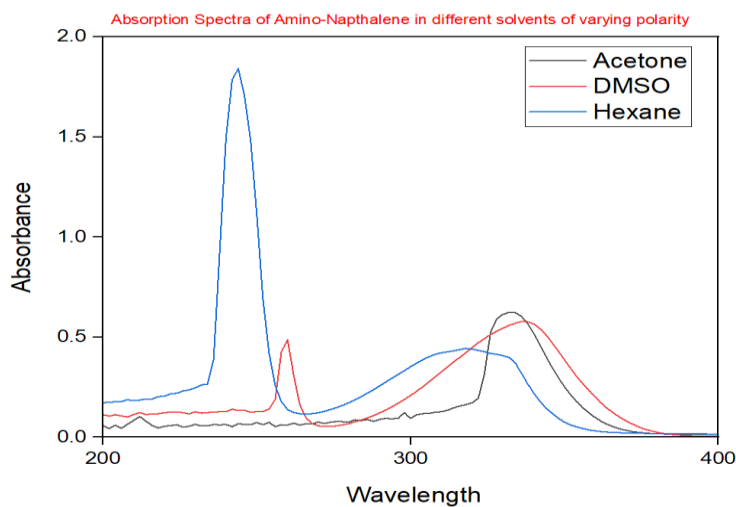


Fig. 5.1.2 Absorption spectrum of amino-naphthalene in DMSO, acetone and hexane.

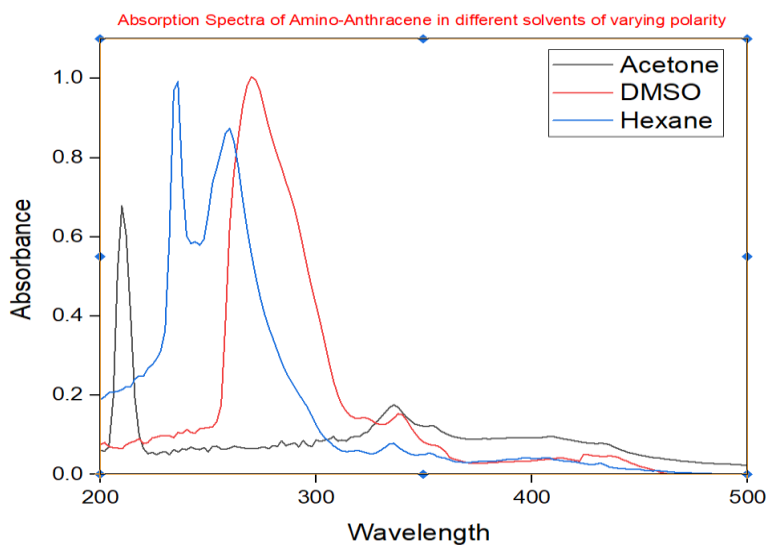


Fig. 5.1.3 Absorption spectrum of amino-anthracene in DMSO, acetone and hexane.

5.1.2 IMPACT OF SOLVENT POLARITY ON EMISSION SPECTRUM

Emission spectra of naphthalene, anthracene, amino-naphthalene and amino-anthracene is reported as a function of solvent polarity of hexane (low polar), ethyl acetate (intermediate polar), dimethyl sulfoxide (highly polar). The graph of intensity vs wavelength was made in origin software. Emission spectra were found structureless for naphthalene at 330 nm, anthracene at 405 nm, amino-naphthalene at 415 nm and amino-anthracene at 438 nm approximately respectively as seen in graphs. The shape and location of bands are approximately same in case of each molecule which indicates that transition of naphthalene, anthracene, amino-naphthalene, amino-anthracene takes place in same electronic level in all solvents.

From the graphs, it is clearly depicted that the fluorescence intensity decreases with increase in polarity or vice-versa. Intensity of naphthalene, anthracene, amino-naphthalene, and amino-anthracene follows the same trend. Intensity peak is low for highly polar solvent i.e. DMSO followed by intermediately polar ethyl acetate and peak is highest for weakly polar hexane. The hypsochromic shift and increase in intensity takes place for low polarity solvent.

Distinctive interaction between solvent and fluorophore either specific or non-specific results in decrease or increase of intensity and Stokes shift.

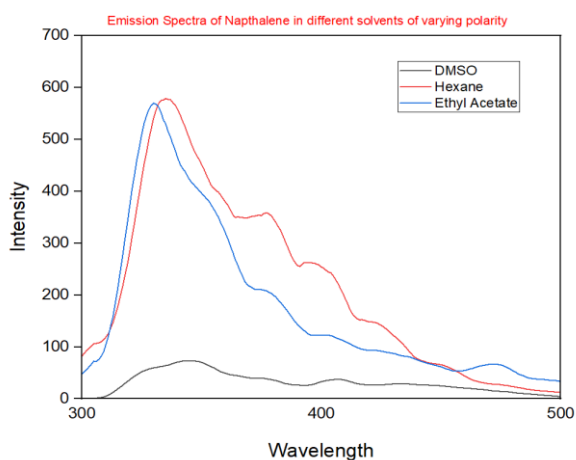


Fig. 5.2 Emission spectrum of naphthalene in DMSO, ethyl acetate, hexane.

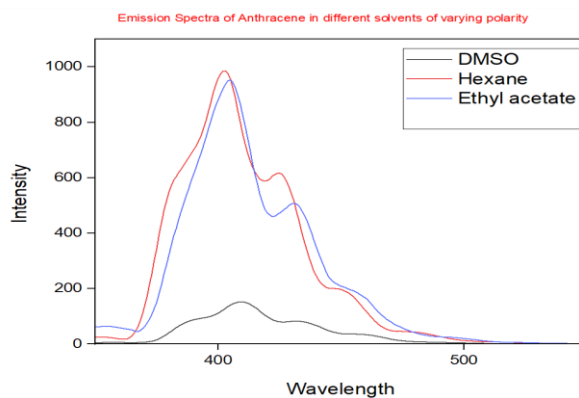


Fig. 5.2.1 Emission spectrum of anthracene in DMSO, ethyl acetate, hexane.

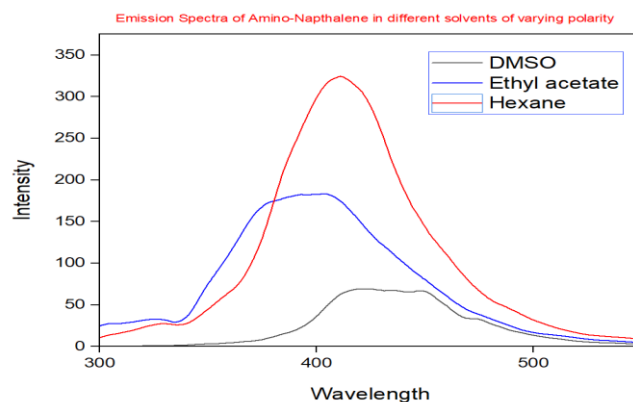


Fig. 5.2.2 Emission spectrum of amino-naphthalene in DMSO, ethyl acetate, hexane.

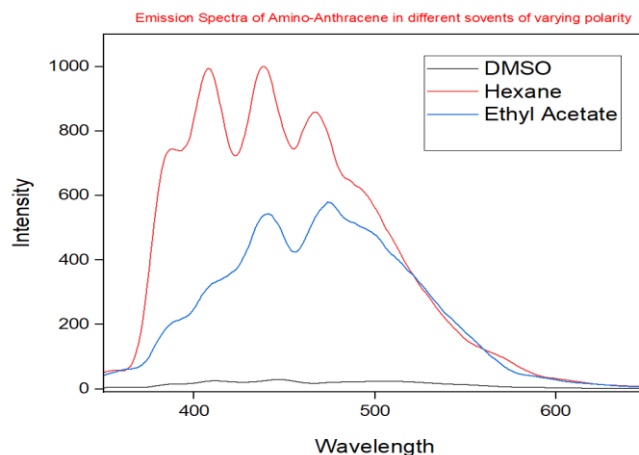


Fig. 5.2.3 Emission spectrum of amino-anthracene in DMSO, ethyl acetate, hexane.

5.1.3 IMPACT OF SUBSTITUENT ON ABSORPTION AND EMISSION SPECTRUM

The nature of the substituent present on the PAHs impacts the spectrum. The substituent is either electron donor or electron acceptor influences the emission and absorption spectrum. The amino (NH_2) present on naphthalene and anthracene is electron donating in nature. As we studied in literature survey that electron donating substituent decrease the Stokes shift value due to extended conjugation.

From fig. 5. and fig 5.1.2. it is understood that absorption maxima of naphthalene in DMSO and acetone decreases as substituted with amino group. Stokes shift also decrease in case of amino substituted naphthalene. In case of anthracene, the effect is not so pronounced.

Fig. 5.2 and fig. 5.2.2 shows the blue shift in emission intensity i.e. emission intensity decreases take place due to the presence of amino substituent in naphthalene. The same behaviour of decrease in emission intensity is observed in case of anthracene and amino-anthracene.

From fig. 5.2.1. and fig. 5.2.3, it is seen that due to addition of amino group, some extra peaks or shifts are detected due to conjugation.

CHAPTER 6

CONCLUSION

In this paper, we reported the structures of PAHs, effects of PAHs on human and aquatic organisms and the photophysical characteristics of PAHs. PAHs photophysical characteristics like water solubility, vapour pressure and boiling points depends on the number of fused rings present in PAHs. Boiling point ranges increase with increase in benzene rings while water solubility and vapor pressure decrease with increase in benzene rings. The effect of solvent polarity at low polarity (hexane), intermediate polarity (acetone, ethyl acetate), and high polarity (DMSO) solvents on emission and absorption spectrum of naphthalene and anthracene is explained in detail. Alongside with it, substituent present on PAHs also influence the emission and absorption spectrum. The results obtained show that solvent polarity and nature of substituent play very crucial role. As the solvent polarity increases, naphthalene, anthracene and their derivatives depict the positive solvatochromism. With increase in dipole moment, charge transfer interactions and H-bonding, the Stokes shift of absorption maxima and emission maxima increases. The electron donating and electron withdrawing effect of substituent influences the absorption spectra and emission spectrum, decrease and increase the Stokes shift value respectively.

Chapter 7

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