CO-SOLUBILIZATION OF ORGANIC COMPOUNDS IN SELF- ASSEMBLIES OF SURFACTANT SYSTEMS

DISSERTATION

Submitted in partial fulfillment of the requirements provided for the award of Degree of

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By

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Dedicated to my caring parents
and Beloved Brother

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CERTIFICATE FROM SUPERVISOR

This is to certify that the work presented in this dissertation entitled "CO-SOLUBILIZATION OF ORGANIC COMPOUNDS IN SELF ASSEMBLIES OF SURFACTANT SYSTEMS" is original and has been carried out by **Ms. Rohi Masrat** under my supervision. This piece of work is suitable for submission for the award of M.Phil Degree in Chemistry. It is further certified that the work has not been submitted in part or full for award of any degree in this or any other University.

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DECLARATION

I hereby declare that the work incorporated in the present dissertation was carried out by me in the Department of Chemistry, University of Kashmir, Srinagar 190006. The entire work or any part of it has never been submitted before for any prize or degree anywhere.

(Rohi Masrat)

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Nomenclature

C_t	Total Surfactant Concentration (mM/mmoldm^{-3})
N	Aggregation Number
ϑ_{alkyl}	Volume of Alkyl Chain Per Mole of Surfactant
cmc^{lit}	Literature Value of cmc (mM/ mmoldm^{-3})
cmc^{expt}	Observed Value of cmc (mM/ mmoldm^{-3})
S_t	Total Apparent Solubility of PAH (mM/ mmoldm^{-3})
S_{cmc} / S_w	Apparent Solubility of PAH at cmc(mM/ mmoldm^{-3})
K_m	Partition Coefficient
V_m	Molar Volume of water (L/mol)
X_m	Mole Fraction of PAH in Micellar Phase
X_a	Mole Fraction of PAH in Aqueous Phase
K_1	Binding constant/ Association constant
S^M	Average Number of PAH molecules Per Micelle
S^i	Multi-component Relative Solubiization Ratio
X^i_{mix}	Mole Fraction of component in 1:1 mixture
R^2	Regression coeffient
ΔG^s_{excess}	Excess Gibbs Free Energy Change of Solubilization
R	Universal Gas Constant
T	Absolute Temperature
χ^A , χ^B	Mole Fractions of two PAHs A and B within the Micelle on Solubilizate only Basis
K_d	Activity of singly Dispersed PAH
K_{eq}	Equillibrium constant for Solubilization
K_{eq}^{mix}	Equillibrium constant for cosolubilization
K_d^A , K_d^B	Activity of two PAHs A and B Dispersed in Bulk Phase

K_m^A, K_m^B Partition Coefficients of two PAHs A and B in mixed state

K_{ow} Octanol Water Coefficient

M_t Total Micelle Concentration

Greek letters

γ Surface Tension (dyne cm^{-1})

ω Interaction Parameter

Δ Change/Difference

γ_{NAP}, γ_{PY} Activity coefficient of Napthalene in mixed state

Abbreviations

HOC Hydrophobic Organic Compounds

PAH Polycyclic Aromatic Hydrocarbons

NAP Naphthalene

PY Pyrene

HLB Hydrophilic Lipophilic Balance

ATSDR Agency for Toxic Substances and Disease Registry

NAPL Non Aqueous Phase Liquids

CMC Critical Micelle Concentration

CTAB Cetyl Trimethyl Ammonium Bromide

SDS Sodium Dodecyl Sulfate

DDEAB Dodecyl Dimethyl Ethyl Ammonium Bromide

MSR Molar Solubilization Ratio

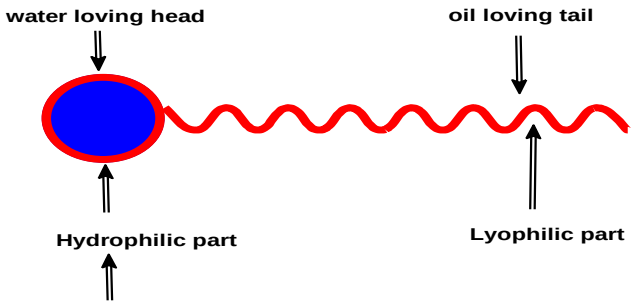
EPA Environmental Protection Agency

IARC International Agency for Research on Cancer

Chapter 1
Introduction

1.1 Surfactants and surfactant micelle:

Surfactants are heterogeneous, long chain molecules,[1,2] that at low concentration in solution, have the property of adsorbing onto the surface / interface of a system in an oriented fashion altering the surface / interfacial energy to a marked extent.[3,4] Another property of surfactants is that its unimers tend to form aggregates. These characteristic features of surfactant stem from the fact that such molecules are amphiphilic in character, i.e., they possess hydrophilic (which is relatively small ionic or polar head group) and hydrophobic parts (which is usually a long hydrocarbon tail).[5,6] Such compounds are also known as emulsifiers, since they have tendency to accumulate at the interface of immiscible fluids facilitating emulsification of such fluids. A schematic diagram of a typical surfactant is shown in **Figure 1.1.**



Hydrophobic part = hydrophobe

Figure 1.1: *Schematic diagram of surface-active molecule*

Research on surfactants is a rapidly developing due to their booming applications in many important practical and fundamental sciences like petroleum oil recovery, corrosion inhibition, water and environmental pollutions, understanding the mysterious role of biological membranes, biotechnology, and other systems. Moreover, research on surfactant behaviour is completely multidisciplinary in nature.

1.1.1. Classification of surfactants:

Depending on the charge of head groups, the surfactants are classified as:

(i) Anionics: In anionic surfactants, the surface-active portion of the molecule bears a negative charge. Anionic surfactants of best formulations can be obtained from alkyl and alkylaryl chains in $C_{12} - C_{16}$ range. Some of the more commonly used anionic head groups are sulfates and ethoxylates. The counterions most frequently involve sodium, potassium, ammonium, calcium and various protonated alkyl amines. sodium and potassium imparts water solubility, where as calcium and magnesium promote oil solubility. Amine/alkanol amine gives both oil and water solubility. Anionics are commonly used in cleaning products, such as shampoos, laundry detergents and soaps because of their ability to remove dirt from soft mediums such as fabrics. e.g ; sodium dodecyl benzene sulfate (SDBS), sodium dodecyl sulfate (SDS) ,Bile salts etc.

(ii) Cationic: Cationic surfactants have positively charged head groups. Some common cationic surfactant head groups includes amines and quaternary ammonium ions , amines only function as a surfactant in the protonated state, and hence cannot be used at high pH. Quaternary ammonium compounds, 'quats' on the other hand, are not pH sensitive. Non-quaternary cations are also much more sensitive to polyvalent anions. Cationic surfactants are used in several different applications. One common use for cationic surfactants is in fabric softners. Cationic head groups are also added to laundry detergents in conjunction with anionic surfactants, because they help to improve the dirt removal properties of the anionic surfactants. Cationic head groups also increases the disinfecting properties of household cleaners. Among the many types of surfactants , cationic surfactants are very useful as corrosion inhibitors

due to their protective effectiveness in neutral and acidic media. e.g ; Cetyltrimethyl ammonium bromide (CTAB), Dodecyl ethyl dimethyl ammonium bromide (DDEAB).etc.

(iii) ***Zwitterionic***: Zwitterionic surfactants have both the charges on polar head group .While the positive charge is almost in availably ammonium, the source of negative charge may vary, although carboxylate is the most common one. Zwitterionics are often referred to as 'amphoterics'. Zwitterionic surfactants have excellent dermatological properties. They are frequently used in shampoos and other cosmetic products, and also in hand washing liquids because of their high foaming properties. Anamorphic surfactant is one that changes from net cationic via zwitterionics to net anionic on going from low to high pH. Neither the acidic nor the basic site is permanently charged, i,e. the compound is only zwitterionic over a certain pH range. The change in the charge with pH of the truly amorphic surfactants naturally affects properties such as foaming, wetting, detergency, etc. All these properties strongly depend on the solution pH. Surfactants containing perfluorinated hydrophobic moieties are used in a wide variety of applications, ranging from fire extinguishing media to electroplating additives and water-repellent fiber coatings [7].e.g. Dodecyl ammonio propane sulphonate (DDAPS) etc.

(iv) ***Nonionic***: Nonionic surfactants do not have any charge on polar head group and have either a polyether or a polyhydroxyl unit as polar group. In the vast of non-ionics, the polar group is a polyether consisting of oxyethylene units, prepared by the polymerization of ethylene oxide. Strictly speaking, the prefix 'poly' is a misnomer. The typical number of oxyethylene units in the polar chain is five to ten, although

some surfactants, e.g.; dispersants, often have much longer oxyethylene chains. Some common nonionic surfactant head groups include fatty acids and glycols. Nonionic surfactants function very well as grease removers. Nonionic surfactants are commonly used in detergents, soaps and household cleaners. e.g.; polyoxyethylene [4] lauryl ether (Brij30), polyoxyethylene [10] cetyl ether (Brij56)

1.1.2. Critical micelle concentration (cmc):

Surfactants or amphiphilic molecules contain both hydrophilic and hydrophobic parts. The hydrophilic part of the molecule prefers to interact with water while the hydrophobic part is repelled from water. Surface active molecules adsorb at the air/water interface, decreasing surface tension. As the interface becomes saturated, the molecules start to form aggregates or micelles in the bulk of the liquid resulting in consistency of surface tension .The amphiphile molecules exist in dilute solutions as individual species in the media with ideal physical and chemical properties. As the amphiphile concentration increases, these properties deviate gradually from ideality and at the concentration where aggregation of monomers into micelles occurs; an abrupt change is observed, (**Figure 1.2**). This concentration is called the critical micelle concentration (cmc). cmc is a key parameter for the optimization of surfactants in chemical formulations and variety of products.

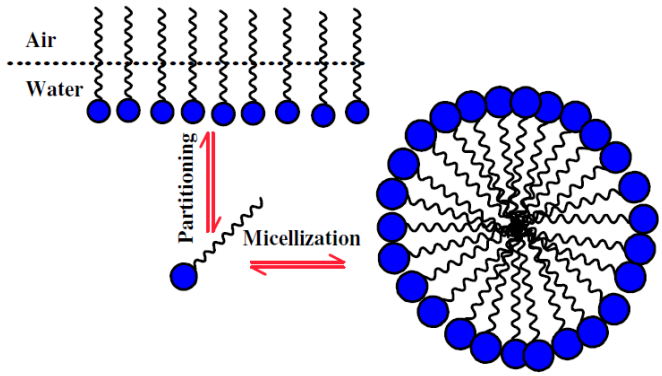


Figure 1.2: *Representation of changes observed at critical micelle concentration*

Various factors affects the cmc values e.g., temperature, the length of the hydrocarbon tail, the nature of the counterions and the existence of salts and organic additives, thus amphiphiles have characteristic cmc values under given conditions.[8,9] When micelle formation takes place, the head group repulsions are balanced by hydrophobic attractions and for ionic micelles, also by attractions between head groups and counter ions. Hydrogen bonds can also be formed between adjacent head groups, [10,11] contributing towards stabilization of micelles

1.1.3. Micellar structure and shapes:

In polar solvents such as water, amphiphilic surfactant monomers self assemble to form a micelle in such a way that their hydrocarbon tails huddle in the core of the micelle, and the polar head groups project outwards into the polar bulk solution. Micelles are often drawn as static structures of spherical aggregates of oriented surfactant molecules. However, micelles are in dynamic equilibrium with surfactant monomers in the bulk, which are frequently being exchanged with the surfactant molecule in the micelles. The equilibrium between monomer and aggregate is established within a few milliseconds. The micelles themselves have the property of constantly disintegrating and reforming. The surface layer of a micelle resembles a concentrated electrolyte solution with a dielectric constant lower than that of the bulk water. The micellar phase is less polar than water and the ionic micelles have polarity near to that of pure ethanol even at the stern layer.[12,13] The number of monomers in a micelle i.e. the aggregation number, determines the size and geometry of the micelle and hence is an important quantity.[14] In aqueous solutions, the aggregation numbers for surfactants generally range between 10 and 100. [15-17]

Figure 1.3(a). Represents that, the electric charge in ionic micelles is neutralized by counterions in the electrical double layer around it. The first layer immediately adjacent to its surface is called stern layer.[18] In this layer, the counterions are adsorbed so strongly that there is no thermal agitation and they migrate simultaneously with the colloidal micelle in an electrical field. According to the most widely accepted model, head groups of surfactant molecules are also located in this layer. The rest of the double layer is called the diffuse (Gouy-Chapman) layer since the ions are diffused into the bulk solution because of the thermal motion. The core radius is about the length of the fully extended alkyl chain of the amphiphile. The core is assumed to consist of two regions, namely the inner and outer core. The outer core contains approximately the first four methylene groups. There is also another defined region within micelles called palisade layer (mantle) which includes the head groups. Based on the Hartely model, the overall volume of a micelle is approximately twice that of the stern layer. [19]

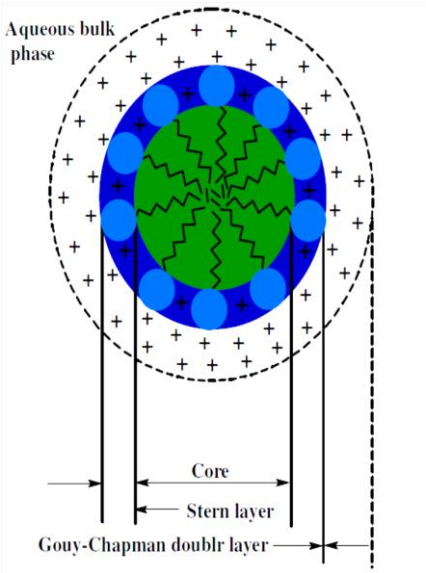


Figure 1.3(a): *Model of a typical ionic micelle showing the location of Head group( ) surfactant chain ( ) and counter ion (+)*

The shape and size of the micelle depends on the architecture of the surfactant molecules and the charge on the head group. There are different types of aggregates of surfactants that are formed depending upon the solution concentration and the molecular structure of the surfactant molecule. These consist of spherical micelle, cylindrical micelle, bilayers, vesicles, worm like micelle, rod shaped micelle, reverse micelle (also called inverse micelle) etc. (**Figure 1.3(b)).**

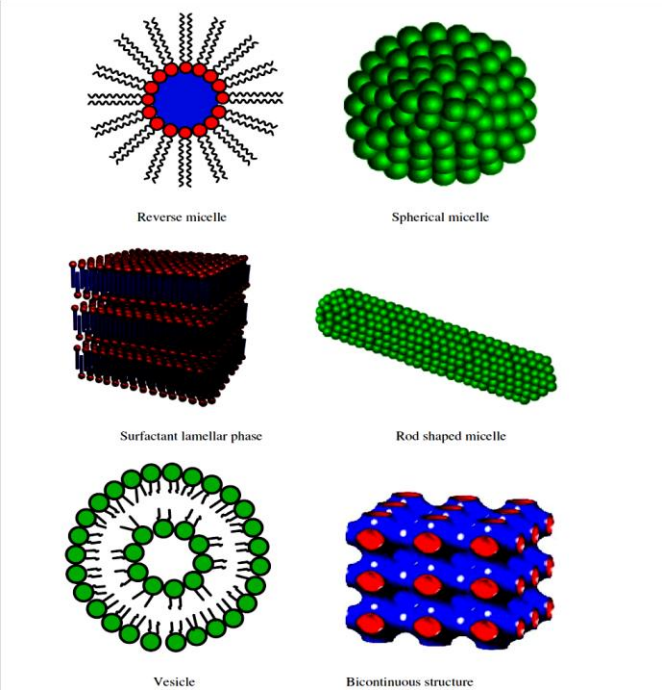


Figure 1.3(b): *Schematic representations of organized aggregates that may form in aqueous solution of surfactant depending on the concentration.*

1.1.4. Micellar solubilization and co-solubilization:

Surfactant micelles have received much attention because micelles are able to solubilize hydrophobic organic compounds, which have low water solubility, through incorporation of them into the hydrocarbon-like core of the micelle and hence partition such compounds between the micelle cores and aqueous phase.[20] This

phenomenon greatly enhances the total concentration of a compound in solution above its aqueous solubility, and is referred to as "solubilization".[21] Micellar solubilization can be further enhanced as the hydrophobic chain length increases, and hence the size of micelle [22] It also increases with reduction in the ionic charge of the hydrophilic end.[23] Solubility of PAHs has also been found to be affected by the interaction between polar head groups of surfactant monomers in a micelle. The stronger interactions results in reduced space available within the bulk of polar head groups and thus reduced solubilization, while weaker interactions results in larger space available and hence enhanced solubilization.[24] Studies have shown that application of surfactants result in a several-fold increase in the solubility of hydrocarbons. Many of the most persistent contaminants especially PAH exhibit low water solubility and hence, solubility of contaminants can often be improved by addition of surfactants, thereby facilitating transport across cell membranes and making them more available for degradation.[25, 26]

Much of the work on micellar solubilization of PAHs has focused on individual compounds, whereas at a contaminated site, PAHs mostly exist in mixtures. Only a limited number of studies have been reported where effects of multiple solutes on micellar solubilization of an individual component were examined. Chaiko et al.[27] and Nagarajan et al.[28] reported that when non-aqueous phase liquids (NAPLs) comprised of benzene, hexane and cyclohexane were mixed with solutions of various cationic and anionic surfactants, it was observed that extent of solubilization of benzene in the surfactants was not influenced by the presence of cyclohexane and hexane. They observed selective solubilization in some mixtures and a synergetic

effect on the solubilization of hexane in the presence of small amounts of benzene. It was concluded that benzene solubilized in the outer micellar layers caused an increase in the micellar core volume, which in turn increased the solubilization of hexane. Cosolubilization plays an important role in selective solubilization and separation of solubilizates from a mixture of different types of solubilizates, as is reflected from cosolubilization of multiple PAHs in surfactant micelles from NAPLs. [29-30] Till date, only a few studies have systematically investigated the co-solubilization and separation of different types of solubilizates using micelles. This demands extensive research in the field.

2. Hydrophobic organic contaminants:

Hydrophobic organic compounds (HOC) are ubiquitous soil pollutants and cause many environmental problems. Among HOCs, polycyclic aromatic hydrocarbons (PAHs) are major components of crude oil, creosote, coal tar and wastes from the combustion of fossil fuel, coal gasification, and incineration of industrial wastes.[31] PAHs are non-polar, neutral, and hydrophobic organic molecules comprised of two or more fused benzene rings. They have received much attention since they are known to be potentially mutagenic or carcinogenic to human being and other living organisms [32] Sixteen PAHs are listed by EPA as priority pollutants due to their toxicity. Even though PAHs have low solubility in water, their slow dissolution can contaminate large amounts of ground water for a long period.[33] Physical, chemical and biological methods have been used for the remediation of hydrophobic organic compounds contaminated sites. Among many treatment methods for hydrophobic organic

compounds contaminated soil, bioremediation has been used for the destruction of organic compounds in soil and has been considered as an economical option for contaminated soil and groundwater attenuation. However, conventional remediation methods, such as "pump and treat" and soil venting with nutrient solution, are often insufficient for PAHs contaminated soils because of their bioavailability in soils is often limited by their low solubility and strong sorption to the soil.[34, 35]

2.1 Polycyclic aromatic hydrocarbons (PAHs):

2.1.1. General properties

PAHs are nonpolar and hydrophobic organic chemicals composed of two or more benzene rings. They have low solubility in water and are strongly bound to soil. **Table 1.1** show properties of some PAHs. PAHs are major components of crude oil, creosote, coal tar and wastes from the combustion of fossil fuel, coal gasification and liquefaction, and incineration of industrial wastes.[32,34] These compounds are produced by industrial activities such as oil processing and storage, and largely by combustion. In urbanized areas, it has been reported that urban runoff also contains significant amounts of PAHs[36] Combustion products are the major sources of PAHs in storm water runoff from urbanized areas.[37] A benzene ring has six carbon atoms and a conjugated system of π-electrons .The π- electrons delocalization in the aromatic ring of cyclic $(4n+ 2)$ π-bond system causes cyclic compounds to be particularly stable compared to nonaromatic compounds.[38] From a remediation perspective, it is important to examine the environmental properties of these compounds. PAHs generally exist as solids in the environment, and some PAHs may exist as needles, plates, crystals, or prisms and range from colorless to golden yellow.

[39] Naphthalene is lowest molecular weight PAH with lowest melting point (80.6ºC) and largest aqueous solubility (31.2 mg/L).[38] The highest molecular weight PAH of environmental interest is coronene, and it has the lowest solubility in water, which is about 1.4×10^{-4} mg/L. [40]

Within the PAH family, many properties, such as solubility, melting and boiling point, vapor pressure, and octanol–water partition coefficient (K_{ow}), correspond to the molecular weight and structure of the compound. Octanol–water partition coefficient (K_{ow}) is a measure of solubility and defined as partition of the organic compound between octanol / water phase. [38] As shown in **Table 1.1**, the solubilities of PAHs decrease as the number of benzene rings increases. Even though PAHs have low solubility in water, their dissolution can contaminate large amounts of ground water for long periods. [33]

Table 1.1: ***Physio-chemical properties, solubility and cancer class of different PAH's (Wilson and Jones, 1993).***

PAH	No. of Rings	Mol. wt. g mole^{-1}	Boiling point °C	Aq. Sol. [a] (µ g/L)	Log K_{ow}	Cancer Class	
						U.S EPA [b]	IARC[c]
Naphthalene	2	128	218	31200	3.50	D	3
Phenanthrene	3	178	339	1300	4.45	D	3
Anthracene	3	178	340	70	4.46	D	3
Fluoranthene	4	202	375	260	4.90	D	3
Pyrene	4	202	393	133	4.90	D	3
Benz [a] anthracene	4	228	435	14	5.61	B2	2A
Chrysene	4	228	448	2	5.90	B2	3
Benzo [a] pyrene	5	252	496	4	6.04	B2	2B
Dibenz [a,h] anthracene	5	278	535	0.5	7.20	B2	N/A

[a] *Refrence [41]*

[b]*Cancer class from U.S. Environmental Protection Agency (U.S EPA) weight-of-evidence*

classifications. D-not classifiable; B2-probable human carcinogen.

[c]*Cancer class from International Agency for Research on Cancer (IARC). 3-not classifiable; 2A probabale human carcinogen; 2B-possible human carcinogen; N/A-not applicable. (U.S. Environmental Protection Agency, 2002. Integrated risk information system (IRIS). Office of Research and Development, National Center for Environmental Assessment, Washington, DC.)*

2.1.2. Fate of PAHs in the soil and groundwater environment:

As it is mentioned that PAHs have very low water solubility and high K_{ow} values, they tend to get sorbed preferably to the soil organic matter instead of being solubilized in the infiltrating water. The sorption process is, therefore, counteractive to efficient biodegradation process as it decreases bioavailability, and as these compounds are located in micro porous areas of the soil due to sorption which makes it inaccessible

to the bacteria and hence to biodegradation. The biodegradation will thus be controlled by the slow desorptive and diffusive mass transfer into the biologically active areas. [42] It has been claimed that a slow sorption following the initial rapid and reversible sorption lead to a chemical fraction that is very resistant to desorption. [43] This phenomenon is called aging, and the existence of such desorption-resistant residues may increase the time for their removal as the compound stay in the soil dramatically. PAHs have also been shown to be partitioned or incorporated more or less reversibly into the humic substances of the soil after partial degradation and thereby are even more immobilized in the soil.[44] At the same time they show very low aerobic degradability depending on the environmental conditions and the available concentration. Only two and three ringed compounds have been shown to be degraded under anaerobic conditions with nitrate or sulfate as the terminal electron acceptor.[45] Very low concentrations have a strong influence on the biodegradation of such hydrophobic compounds, and some studies have indicated that the process stops below a certain threshold concentration.[46] The low mobility and high persistence means that they can stay in the soil for decades and even at sites with contaminations dating at least 50 years back.

2.1.3. PAH Toxicity:

Research into the toxicology of HOCs is ongoing, but presently many of these pollutants are considered to be mutagenic and/or known carcinogens.[47,31,40,39] HOCs are found throughout a list of priority hazardous substances compiled by the U.S. EPA and the Agency for Toxic Substances and Disease Registry (ATSDR, 1999). In addition, in the 1997 report on carcinogens, the U.S. Department of Health and

Human Services cited evidence that 15 PAHs caused various types of cancer in experimental animals.[39] According to Lee et al., [48] PAHs are the largest class of chemical carcinogens, and both Clar [49] and Harvey [47] also reported in detail about the evidence of PAH carcinogenicity in animals. Harvey [32] reported that some PAH metabolites bind to protein, DNA, and RNA, and adducted compounds may cause damage to cells and cause carcinogenic effects. Some of the PAHs causing various types of cancers grouped under various classes are listed in **Table 1.1**

2.2 Bioavailability and Biodegradation of organic contaminants (PAH's):

Bioavailability and biodegradation are two important factors that affect the ultimate fate of any contaminant. Bioavailability is governed by (1) the substrate concentration that the cell membrane "sees," (i.e., the "directly bioavailable" pool) and (2) the rate of mass transfer from potentially bioavailable (e.g., nonaqueous) phases to the directly bioavailable (e.g., aqueous) phase. The biodegradation process consists of several steps (**Figure 1.4**). Consider a substrate that is initially present in soil or a porous matrix where it is inaccessible to microorganisms. The substrate may be adsorbed to the matrix or may be present in the liquid or solid phase. First, this substrate has to be transferred to sites where it can come in direct contact with microorganisms. This can occur by desorption, dissolution, or mobilization of the contaminant from the soil 'phase' to the aqueous phase, and eventually by transport, *i.e.* convection and dispersion (**Figure. 1.4**). Subsequently, the substrate has to be taken up by the cells. And hence converted into the product. Biodegradation of PAHs is restricted by their limited bioavailability, which is mainly associated with PAH hydrophobic nature and strong adsorptive capacity in soil.[50, 51] It has been reported that the mass transfer rate

of PAHs into the aqueous phase is the rate-limiting step in their degradation. [52, 53] The bioavailability of soil contaminants can be increased by stimulating the process that is limiting the rate of biodegradation.[54] Stimulation of desorption and dissolution rates can be accomplished by all kinds of physical and chemical means. For instance, the temperature can be raised, soil might be pulverized to increase access and decrease diffusional distances, soil may be agitated, acoustic techniques may increase bioavailability, or soil organic matter may be oxidized using chemical agents.[55] However, the most promising way to increase a contaminant's bioavailability is thought to be the addition of surface active agents such as surfactants that stimulate mass transfer rates.

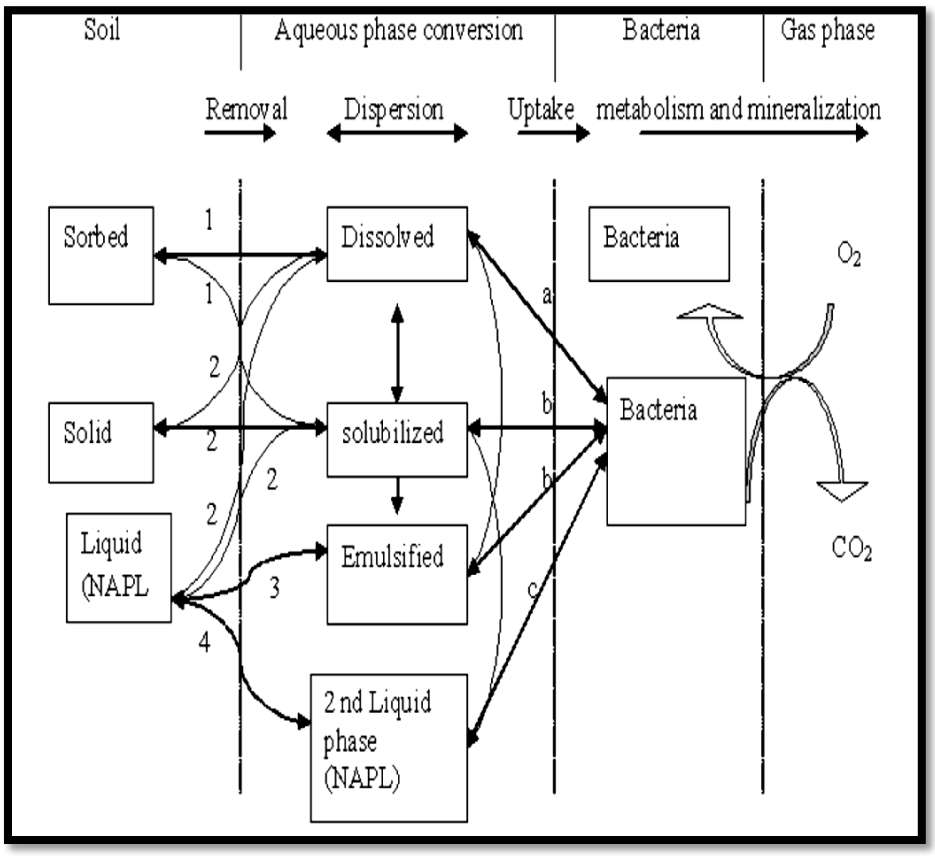


Figure 1.4: *Processes involved in the biodegradation of contaminants that are initially present in soil. Processes involved in the transfer of compounds between the soil phase and the bulk aqueous phase: 1: desorption 2: dissolution 3: detachment 4: mobilization. Processes involved in the uptake of contaminants by cells: a: uptake of dissolved substrate; b: uptake of 'pseudo solubilized' substrate; c: uptake of substrate by direct attachment of the organism to substrate droplets.*

2.3. Role of surfactants in remediation of PAH contaminated sites:

The bioavailability of polycyclic aromatic hydrocarbons in soils is often limited by their low solubility and strong sorption to soil. As a way to increase the bioavailability of PAH contaminated soil, surfactant aided soil flushing has been considered for dissolving and mobilizing the soil bound hydrophobic contaminants. [56-61] Beginning with petroleum industries for oil recovery, surfactants have been applied in the field of contaminated soil remediation applications.[51,62-64] Three types of surfactants viz.

cationic, anionic and nonionic surfactants have been considered for use in soil washing. Many researchers have reported that surfactants could increase the solubility and mass transfer of hydrophobic organic compounds.[51,65] The increased bioavailability with surfactant addition can be attributed to two main mechanisms based on the nature of contaminant. First, surfactants can reduce the interfacial tension between the aqueous phase and the non-aqueous phase liquid (NAPL). Therefore, the presence of the surfactant can disperse the NAPL and increase the contact area. Increased dispersion and contact area of the NAPL can give enhanced bioavailability for microorganisms. Second, the surfactant can increase the aqueous solubility of less soluble organic compounds significantly, providing more available substrate for microorganisms. Schippers et al.[66] proposed three possible mechanisms to explain the enhanced biodegradation of PAH by the surfactant addition. The first mechanism is that bacteria might be able to utilize micellar solubilized / micelle portioned PAHs directly through the cell membrane. The second mechanism is that surfactant can increase mass transfer to the aqueous phase, and bacteria might subsequently use the aqueous phase PAHs. The third mechanism is that the surfactant might change the hydrophobicity of the cell surface, and the changed hydrophobicity might enhance the direct cell attachment to PAHs or NAPL. In general, surfactants could enhance the apparent solubility of PAHs by micelle formation, which commences at the CMC and then solubility is proportional to surfactant concentration. [57] However, biodegradation of PAHs is not always correspondingly enhanced by surfactants. Some research groups have found that addition of surfactants stimulated PAH biodegradation,[67-71] whereas others reported no effect [32] or inhibition by

surfactants.[71,73] The contradictory results may be due to the varied interactions among PAH-degrading species, PAHs, and surfactants. Surfactants may be used as a growth substrate in preference to PAH compounds or toxic to some microorganisms, and hence PAH degradation would be reduced. If surfactants are neither toxic nor growth substrates, they can either enhance degradation of PAHs by solubilizing the PAHs inside the micelle that are accessible to microorganisms, or decrease degradation by preventing cells from directly contacting PAHs. [72, 74, 75] Numerous batch and column studies have indicated that surfactants enhance recoveries of non-aqueous phase lipids NAPL [76, 77] by solubility enhancement or desorption. There have also been indications that pretreatment of a soil with surfactant washing (Igepal CA-720) to solubilize PAHs enhances biodegradation of these contaminants. [78] Studies with nonionic and anionic surfactant additions have indicated that they can enhance/limit the biodegradation of soil xenobiotics and a range of other hydrocarbons (**Table1.2**). Nonionic surfactants have also shown to inhibit biodegradation at concentrations above their CMC. Indeed many synthetic surfactants are known to exert an inhibitory effect on PAH-degrading microorganisms. [63] However, the positive cases are counterbalanced by almost as many negative results. Anionics and nonionic surfactants are less likely to be adsorbed to the soil surface. Cationic surfactants have been used to lower aquifer permeabilities by sorption on to the aquifer materials. [79] These are effective solubilizers, good desorption agents, emulsifying agents, suspending agents etc. In spite of above advantages these are having some limitations for use as some are toxic to soil microorganisms, require more degradation time, adsorb more to the soil. [80]

Table 1.2: ***Selected studies involving the use of synthetic surfactants to stimulate hydrophobic organic contaminant biodegradation (Makkar and Rockne, 2003).***

Compound	surfactant	Medium	Surfactant conc.	Effect on biodegradation kinetics	References
Phenanthrene	Nonioinc surfactant	Liquid	CMC	0	[72]
Phenanthrene	Nonioinc surfactant	Liquid	>CMC	-	[72,81]
Phenanthrene Pyrene,Fluoranthene Fluorene,anthracene	Nonionic sodium dodecyl sulfate	Liquid	>CMC	-	[69]
Napthalene and Phenanthrene	TritonX-100,Brij 35,Tergitol,NPX,legpal CA-720	Liquid	>CMC	+	[70]
Phenanthrene	Tween 80	Soil	>CMC	+	[82]
Naphthalene	Triton X-100, Brij 30	Liquid	>CMC	+	[83]
Phenanthrene	Triton X-100, Triton-102,Triton-CF21,Triton N-101,Brij30,Brij35, polyoxyethylene-10,	liquid	>CMC	+	[73,84]

	Laurylether,Tergitol 15-S-9				
Phenanthrene	**Tergitol-NP-10, Tergitol-15-S-20, Tergitol TMN-10**	**Liquid**	**>CMC**	**-**	**[73]**
Phenanthrene	**Tergitol NP-10**	**Liquid**	**>CMC**	**+**	**[85]**
Phenanthrene T 10 and T 15,Fluoranthene,fluorene,Anthracene and substituted Napthalene	**Arkopal-N-300,SapogenatT-300**	**Soil**	**>CMC**	**+**	**[64]**
Phenanthrene	**Tween 40, Triton X-114, Brij 35**	**Soil slurry**	**<CMC**	**+**	**[86,87]**
Napthalene,Phenanthrene and pyrene	**Triton X-100**	**Liquid**	**>.CMC**	**+**	**[84]**
Anthracene	**Triton-X-100, Dowfax8390**	**Liquid**	**<CMC**	**-**	**[74]**
Napthalene and Phenanthrene	**TritonX-100**	**Liquid**	**>CMC**	**+/-**	**[88]**
Total petroleum,hydrocarbons	**Legapal Co-630**	**Liquid**	**>CMC**	**+/-/0**	**[89]**
Pyrene	**T 10 and T 15**	**Soil slurry**	**>CMC**	**+**	**[90]**
Pyrene,chrysene, Benzo[a]pyrene	**Tween 80**	**Soil**	**>CMC**	**+**	**[91]**
Aroclor 1242	**L-carvone, sodium**	**Soil**	**100-180** μg/ml	**+**	**[92]**

	dodecyl,Sulfate, Sorbitan trioleate				
Phenanthrene, acenaphthene, anthracene, fluorene, and pyrene	**Triton X-100, Triton N-101, Brij-30, Brij-35**	**Liquid**	**>CMC**	**-**	**[93]**

+ = beneficial effect defined as a significant increase in biodegradation rate and/or extent
- = detrimental effect; 0 = no effect

Aims and Objectives

The main objective of this work was to investigate the solubilization and cosolubilization aspects of naphthalene and pyrene in single surfactant systems. The specific objectives of this research included.

(i) The effects of hydrophobic chain length and hydrophilic groups of two surfactant series with dodecyl (C_{12}) and hexadecyl (C_{16}) chain lengths having cationic , anionic and nonionic head groups on the solubilization of PAHs of increasing hydrophobic character. The experimental results of this study may be useful to understand and predict cosolubilization of a mixture of PAHs and selective solubilization of one PAH over another in a particular surfactant system and thus provides us a valuable information on the selection of surfactant systems for selective separation of PAHs from a mixture of PAHs for SER of contaminated soils

(ii) The influence of nonionic, cationic and anionic surfactant structures on the solubilization behavior of naphthalene and pyrene in single and mixed states of PAHs

(iii) The understanding of the effect of the presence of multiple PAHs on the micellar partitioning of individual PAHs

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Chapter 2
Review of literature

Review of literature

Polycyclic aromatic hydrocarbons (PAHs) constitutes a group of over 100 different chemicals that are formed during the incomplete burning of coal, oil and gas, garbage or other organic substances like tobacco or charbroiled meat. PAHs are usually found as a mixture containing two or more of these compounds, such as soot. PAHs are a class of organic compounds with two or more fused benzene rings in linear, angular, or cluster structural arrangements.[94] PAHs are ubiquitous in natural environment, including air,[94] water,[95] soil,[96] sediments[97] etc. These series of aromatic compounds are of major concern, since they are listed as priority pollutants by United States environmental protection agency due to their toxicity to various organisms and their mutagenic and carcinogenic potentials to humans through food chain. [98]

Due to low solubility, high hydrophobicity, and complex chemical structure, PAHs tend to accumulate in soil and sediment and have limited availability to biodegradation. However, biodegradation is still a major environmental process which affects the fate of PAHs in both terrestrial and aquatic ecosystems. It is well established that many individual polycyclic aromatic hydrocarbons are degraded by bacteria. [98-104] Recently there has been an increased interest in developing and understanding microbial degradation process when contaminants are present in complex mixtures. A mixture of contaminants in a bioremediation system may result in inhibition, co-metabolism, augmentation, or no effect at all. Laboratory studies using defined mixtures of PAHs have begun to address the problems raised by the presence of more than one contaminant. [63,104-109] In these studies, combinations of

individual effects have been observed. Because most studies utilizing sediments from contaminated sites are complicated by factors in addition to multiple contaminants (e.g. bioavailability, experimental protocols and environmental factors). Assuming that the biodegradation rates are proportional to the concentration of the dissolved contaminants, sorption to sediment organic matter or partioning to an oil phase may control biodegradation by maintaining low aqueous phase contaminant concentration. [110] Since PAH desorption (bioavailability) is a critical factor in the rate and extent of sediment bioremediation, surfactants may enhance the bioavailability of sorbed PAHs by decreasing the capillary forces in the sedimentation matrix [68] or by increasing the apparent aqueous solubility of contaminants at concentrations above their critical micelle concentration. [57]

A large number of studies[111-114] are reported in literature which have extensively dealt with the aqueous solubility enhancement of individual PAH or hydrophobic model organic compounds by a variety of single and mixed surfactant systems. However, since PAHs occur in mixtures at the contaminated sites, it is highly relevant to study the simultaneous solubilization of hydrophobic organic compounds in water by different surfactant systems of varied architectures. Inspite of being important from environmental as well as technological point of view, only limited studies are reported in literature which deal with the cosolubilization of different hydrophobic organic compounds like PAHs in aqueous surfactant solutions. A brief overview of such studies is given below:

- R. Nagaraian and E.Ruckenstein (1981) have reported a selective solubilization of benzene in micelles from a binary mixture of benzene and

hexane as solubilizates and attributed to its smaller molecular volume and lower interfacial tension against water.[115]

- M.A. Chaiko et al.(1984) and R.Nagarajan et al.(1984) reported that when NAPLs comprised of benzene, hexane and cyclohexane were contacted with solutions of various cationic and anionic surfactants, it was observed that extent of solubilization of benzene in the surfactants was not influenced by the presence of cyclohexane and hexane. They observed selective solubilization in some mixtures and a synergetic effect on the solubilization of hexane in the presence of small amounts of benzene. It was concluded that benzene solubilized in the outer micellar layers caused an increase in the micellar core volume, which inturn increased the solubilization of hexane.[23,24]

- S. Guha et al (1998) reported the partitioning of aqueous–phase naphthalene, phenanthrene, and pyrene into micelles of the nonionic surfactant Triton X-100. They found an increase in the solubilization capacity of Triton X-100 for phenanthrene in the presence of naphthalene and concluded that naphthalene solubilized at the micelle water interface or in the shell region of the micelles likely increased the solubilization of the other more hydrophobic PAHs. The inverse trend in competitive solubilization was observed by Hill and Ghoshal in systems containing micellar solutions of Brij35 contacted with NAPLs comprised of hexadecane and naphthalene, and/or phenanthrene. The micellar partitioning of phenanthrene was decreased in systems containing three component NAPL in comparison to the systems containing a two component

NAPL comprised of hexadecane and phenanthrene. However the micellar partitioning of naphthalene from the three component NAPLs was similar to the two component NAPL. Furthermore, from a limited investigation of solubilization of naphthalene and phenanthrene from the three component NAPLs, selective solubilization of naphthalene was observed. The striking differences in PAH partitioning patterns in the two studies, suggests that selective solubilization of PAHs may be strongly influenced by the micellar characteristics of the nonionic surfactant employed.[84,116,117]

- S. Nagadome et al. (2001) reported lowering of plasma cholesterol level caused by dietary intake of phytosterol/phytostanols during their investigation on the solubilization of cholesterol (ch), cholestanol (chsta) and stigmasterol (stig) in their single and 1:1 mixed form within two kinds of free bile salts viz. sodium cholate (NaC) and sodium deoxycholate (NaDC). Their findings show that ch is selectively solubilized by bile salts and its solubilization is decreased in presence of chsta and stig.[118]
- J.E. McCray et al (2001) reported solubilization of toluene, ethylbenzene, and butylbenzene in solutions of a rhamnolipid biosurfactant and found that in the presence of multiple solutes the relatively hydrophobic compounds experienced solubility enhancements greater than those compared to single solute systems. The authors attributed aqueous phase interactions between the co-solutes and the biosurfactant micelles as being responsible for competitive

solubilization but concluded that partitioning of solutes into the micellar shell did not play a role in the competitive solubilization. [117]

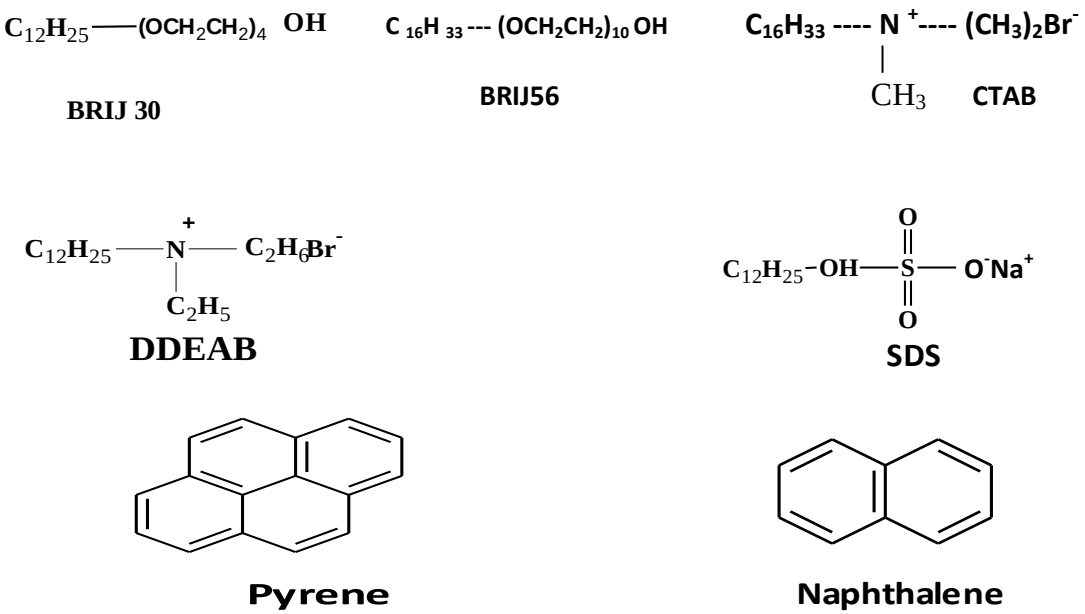
- Ping Li and Luwei Zhao (2002) reported cosolubilization of three non-polar drugs (hydrocortisone , β-estradiol and ethynylestradiol) in polysorbate 80 solution and found that solubility of any drug decreased in presence of other steroidal compounds.[119]
- Venkatramana M. Rao et al. (2006) reported the use of combined approach of surfactants and cyclodextrins in solubilization of poorly soluble drugs. Theoretical simulations show that the combined solubility is less than the sum of the individual solubility values in cyclodextrins and surfactants[120]

In view of such a limited number of studies on the cosolubilization of hydrophobic organic compounds like PAHs in aqueous micellar solutions, it is of high relevance to study in detail the effect of cationic, anionic and nonionic surfactants on the cosolubilization of PAHs. Such studies would be a step towards studying details of the factors like (a) effect of chain length (b) nature of head group (c) concentration of surfactants on the aqueous solubilization and co-solubilization of PAHs of different hydrophobicities and hence aqueous solubilities .This piece of work is an attempt to address some of such problems as described in aims and objectives of this work in chapter 1

Chapter 3
Experimental

Materials:

The nonionic surfactants used were polyoxyethylene [4] lauryl ether (Brij30) and polyoxyethylene [10] cetyl ether (Brij56). These were obtained from sigma Aldrich chemical co. (>98% purity) and were used as received. The cationic surfactants used were hexadecyltrimethyl ammonium bromide (CTAB) and dodecylethyldimethyl ammonium bromide (DDEAB) (Aldrich products). While anionic surfactant employed was sodium dodecyl sulfate (SDS) (Aldrich product). The PAHs; naphthalene (Nap, > 98%) and pyrene (Py, > 98%) Aldrich products, and were used as hydrophobic moieties in present study. The structures of surfactants, and PAHs used are presented in **scheme 3.** Surfactant solutions were prepared in triple distilled water.



Scheme 3: *Structures of surfactants, Naphthalene and pyrene used in this study*

Methods:
Determination of cmc

The cmc values of all the surfactants were determined from the plot of surface tension (γ) vs logarithm of surfactant concentration (log C_t) shown in **Figure 3.1**. Surface tension measurements were made with a Kruss-9(Germany) tensiometer, equipped with thermostatable vessel holder, by the platinum ring detachment method. Surfactant concentration was varied by adding solution of known surfactant concentration in small installments using a Hamilton microsyringe to 30 cm^3 of water in the sample vessel placed in the thermostatable vessel holder. Measurements were made after thorough mixing and temperature equilibration. Temperature was maintained at 25 ^{0}C (within ± 0.1 ^{0}C) by circulating water from a HAAKE GH thermostat through the thermostatable vessel holder. The accuracy of the measurements was within ± 0.1 dyne cm^{-1} .The readings were taken in triplicate to ensure reproducibility.

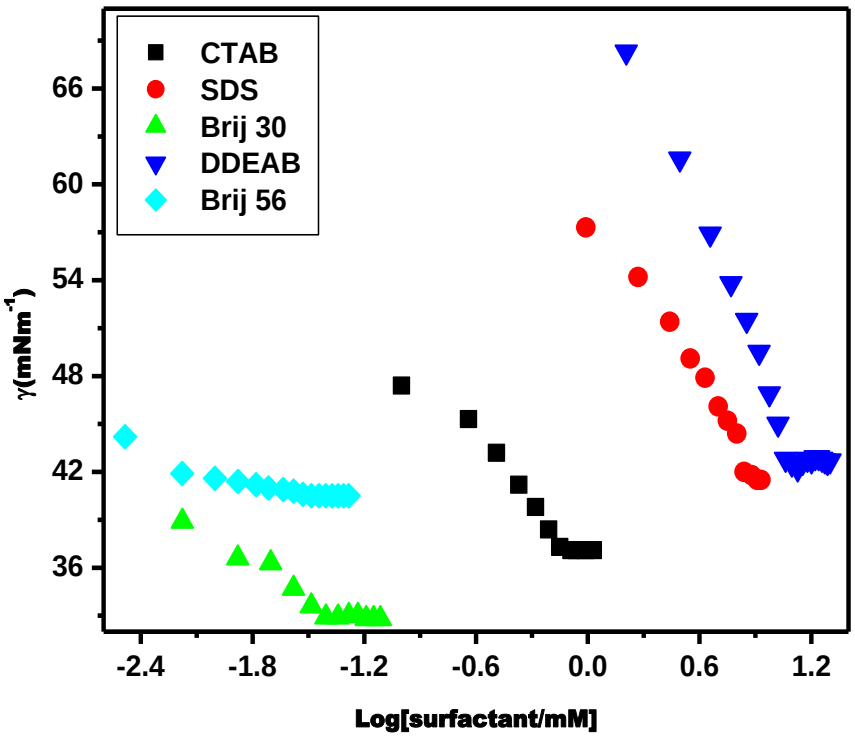


Figure 3.1: Plots *of surface tension vs logarithm of surfactant concentration of various surfactants at 25* ^{0}*C.*

Determination of solubility:

Batch tests for solubilization and cosolubilization of various PAHs in surfactant solutions were performed using two surfactant series viz, C_{12} series involving one cationic (DDEAB), one nonionic (Brij30) and one anionic (SDS) with 12 carbon alkyl chain as hydrophobic groups and a C_{16} series containing one cationic (CTAB) and one nonionic (Brij56) with 16 carbon alkyl chain as hydrophobic groups. Five or

more concentrations of each surfactant in the concentration range above their cmc values cmc were placed in 5 borosilicate glass vials of 5ml capacity. PAHs in single and in mixed states (1:1 molar ratio) were separately added to each vial in amounts slightly more than required to saturate the solution. The sample vials were then sealed with screw caps. The samples were then agitated for a period of 12 h on a magnetic stirrer maintained at a temperature 25 ± 0.5 ^{0}C using magnetic Teflon pieces placed in the vials. These sample vials were then left for sedimentation for a period of 2-3 h and then decanted. The decanted samples were subjected to centrifugation at 13400 rpm for 15 min so as to remove the undissolved solid PAH. The concentration of dissolved solute was determined spectrophotometrically with Shimadzu spectrophotometer (model UV -1650 PC) following appropriate dilution of an aliquot of the supernatant with the respective concentrations of the surfactants. The surfactant concentration was kept the same in both reference and the measurement cells to eliminate the effects of surfactant on UV absorbance. Duplicate tests were performed for each surfactant concentration. The solubilities of naphthalene and pyrene at each surfactant concentrations were determined at their characteristic wavelengths, 221.8 nm and 337 nm respectively at which their calculated molar extinction coefficients were 49.023 $mM^{-1}cm^{-1}$ and 49.081 $mM^{-1}cm^{-1}$ respectively, calculated from the slope of absorbance versus concentration of the PAH in methanol. The solubility of naphthalene and pyrene in 1:1 mixture was determined at their respective wavelengths using their respective extinction coefficients.

Naphthalene shows no absorption peak at 337 nm and pyrene also do not show any absorption peak at 221.8 nm, as depicted from their spectrum in methanol in **Figure 3.2** ensuring that two PAHs are non-interfering and thus their cosolubilization can be studied. **Figure 3.3** shows the absorption spectra of naphthalene, pyrene and their 1:1 mixture in solubilized form in 19mM DDEAB surfactant solution. The solubilization characteristics of such PAHs in various surfactant solutions were obtained from their UV-visible spectra at varied surfactant concentrations as discussed in next section.

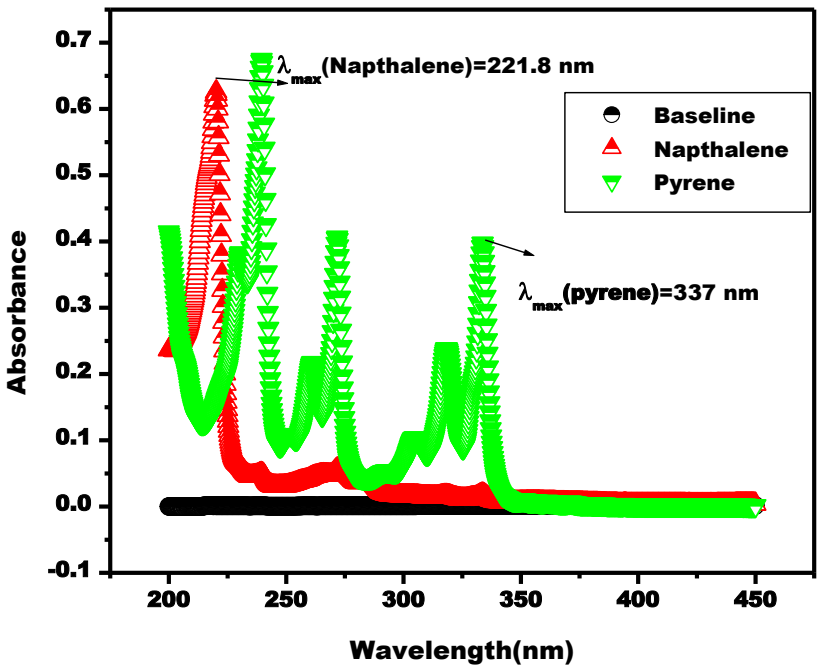


Figure 3.2: *Absorption spectrum of naphthalene and pyrene in methanol*

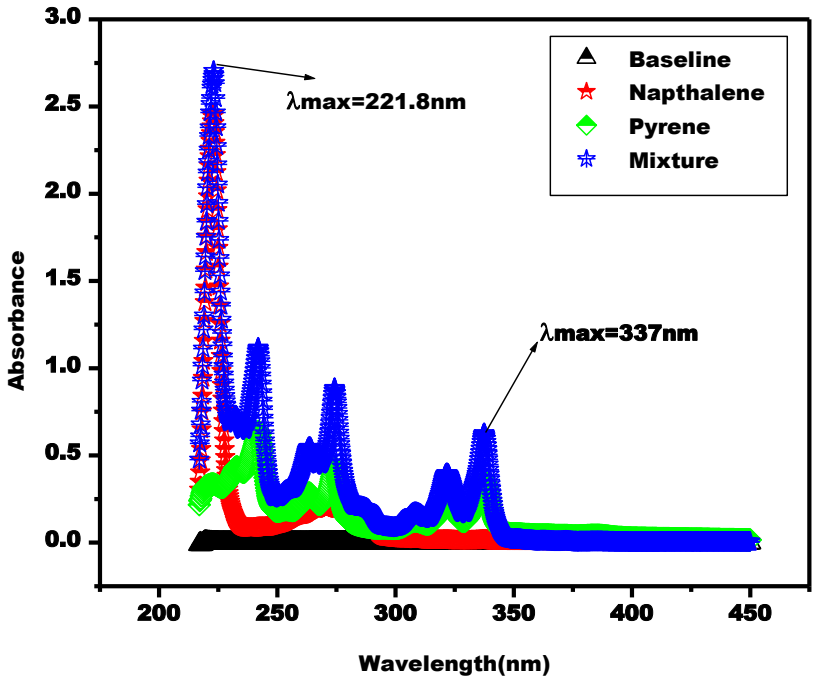


Figure 3.3: *Absorbance vs wavelength of naphthalene, pyrene and their 1:1 mixture for 19mM DDEAB*

Chapter 4
Results and Discussions

The *cmc* values of the surfactants obtained experimentally (cmc^{exp}) from the plots of surface tension (γ) vs logarithm of surfactant concentration (log C_t) as presented in **Figure 3.1** and those reported in literature (cmc^{lit}), along with the reported Hydrophilic-Lipophilic Balance (HLB) value, ϑ_{alkyl} and Aggregation Numbers (N) are presented in **Table 4.1**

Table 4.1: **Experimental and Reported Critical Micelle Concentration (cmc^{exp} and cmc^{lit}) values, HLB number, ϑ_{alkyl} and Reported Aggregation Number (N) of the Various Surfactants Used in This Study**

Surfactant system	cmc^{expt} ($mmoldm^{-3}$)	cmc^{lit} ($mmoldm^{-3}$)	HLB	N	ϑ_{alkyl} ($Lmol^{-1}$)
Brij30	0.033	(0.035)[a]	10.48	(101)[c]	0.0914
Brij56	0.036	(0.04) [b]	13.38	(141)[b]	0.154
CTAB	0.764	(0.815) [c]	23.87	(61)[c]	0.355
DDEAB	14.02	(14.0) [d]	23.7	(53)[c]	0.193
SDS	7.59	(8.1)[e]	24.69	(62)[f]	0.149

critical micelle concentration, [a] reference [121]. [b] reference [122]. [c] reference [111], [d] reference [123]. [e] reference [124]. [f] reference [125].
HLB -------- hydrophilic - lyophilic balance [calculated from chemSW software]

ϑ_{alkyl} *------ volume of alkyl chain per mole of surfactant*

As observed from the table, the *cmc* values of the surfactants are in good agreement with the reported values. Smaller values of *cmc* indicate high propensity of nonionic surfactants to form micelles. The literature values of *N* show that Brij surfactants form non-spherical rod like micelles while others form spherical micelles.

4.1. Molar Solubilization Ratio (MSR) and Micelle-phase/Aqueous-phase partitioning of PAHs in different micelles:

Molar solubilization ratio (MSR) is defined as the number of moles of organic compound solubilized per mole of surfactant added to the solution. [126] It is the measure of degree of effectiveness of a surfactant in solubilizing a given solubilizate.

It is equivalent to increase in solubilizate concentration per unit increase in micellar surfactant concentration. In the presence of excess of the hydrophobic organic compound MSR, given by the equation. [114,127-128]

$$\boldsymbol{MSR} = ([\boldsymbol{S_t}] - [\boldsymbol{S_{cmc}}])/(\boldsymbol{C_t} - \boldsymbol{cmc}) \qquad (4.1)$$

is obtained from the slope of the linear fit that results when solubilizate concentration is plotted against surfactant concentration. $[S_t]$ is the total apparent solubility of PAHs in surfactant solutions at a particular total surfactant concentration, C_t, above *cmc* and $[S_{cmc}]$ is the apparent solubility of PAHs at *cmc*, which is taken as their water solubility because it changes only very slightly up to the *cmc* of the surfactant. All the concentrations are expressed in mmol/L. Concentrations of naphthalene and pyrene in their single and mixed states at different surfactant concentrations were determined spectrophotometrically as described in experimental section. **Figures 4.1A** and **4.1B** show variation of solubilities of naphthalene/pyrene in their single and mixed states respectively with total surfactant concentration in various surfactant systems. The solubilities of PAHs increase linearly over the range of surfactant concentrations above *cmc* indicating their solubility enhancement in water. This phenomena is due to solubilization of organic solutes within the surfactant micelles. The values of MSR calculated from the above plots using **eq 4.1** for all systems studied herein are given in **Table 4.2** alongwith the regression coefficient for linear line fit for the C_{12} and C_{16} series of surfactants.

The effectiveness of solubilization can also be expressed in terms of the partition coefficient, K_m, of the organic compound between the micelle and aqueous phases and

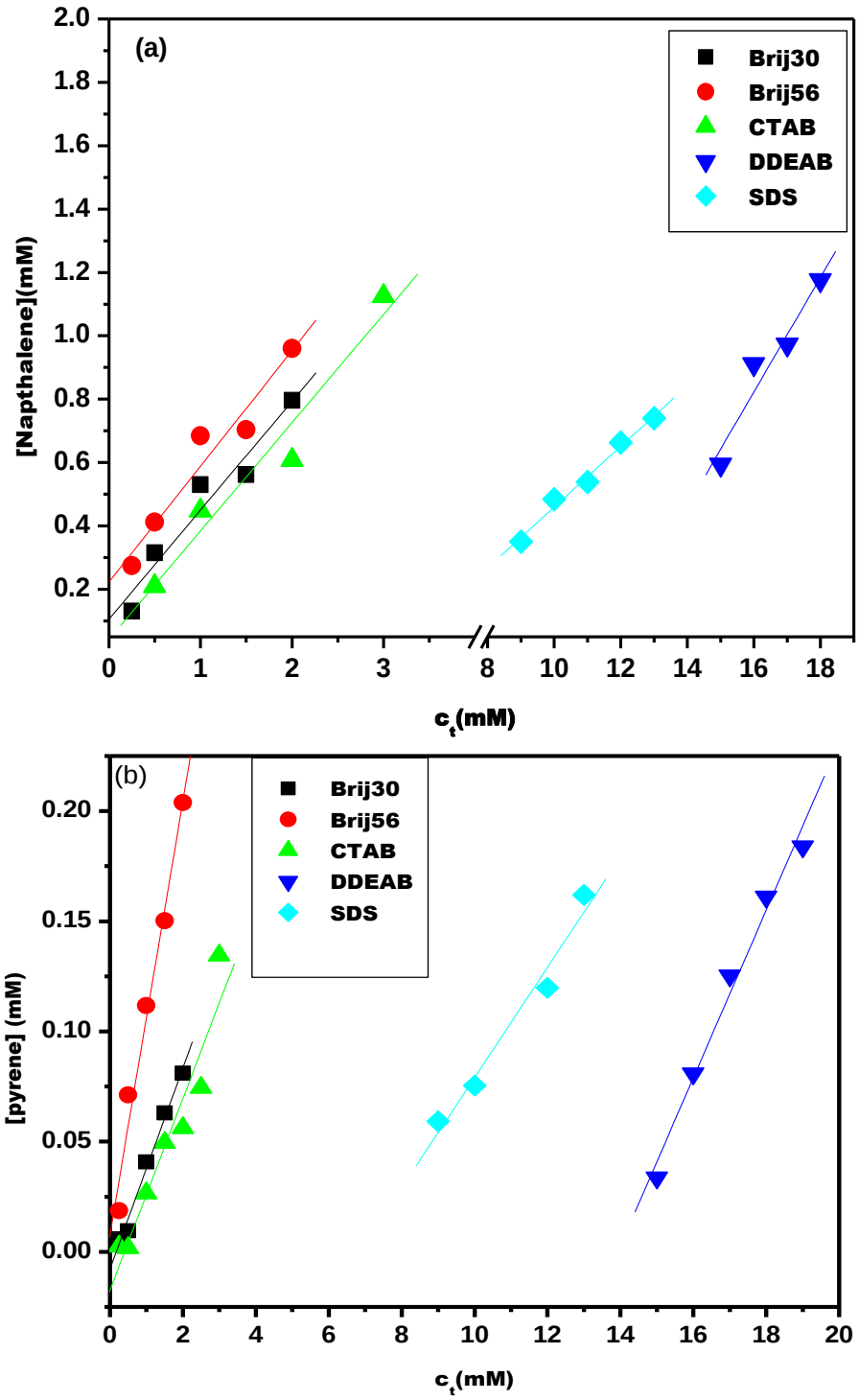


Figure 4.1A: *Variation of solubility of (a) naphthalene, and (b) pyrene in their single state with total surfactant concentration in various surfactant systems at 25 ^{o}C.*

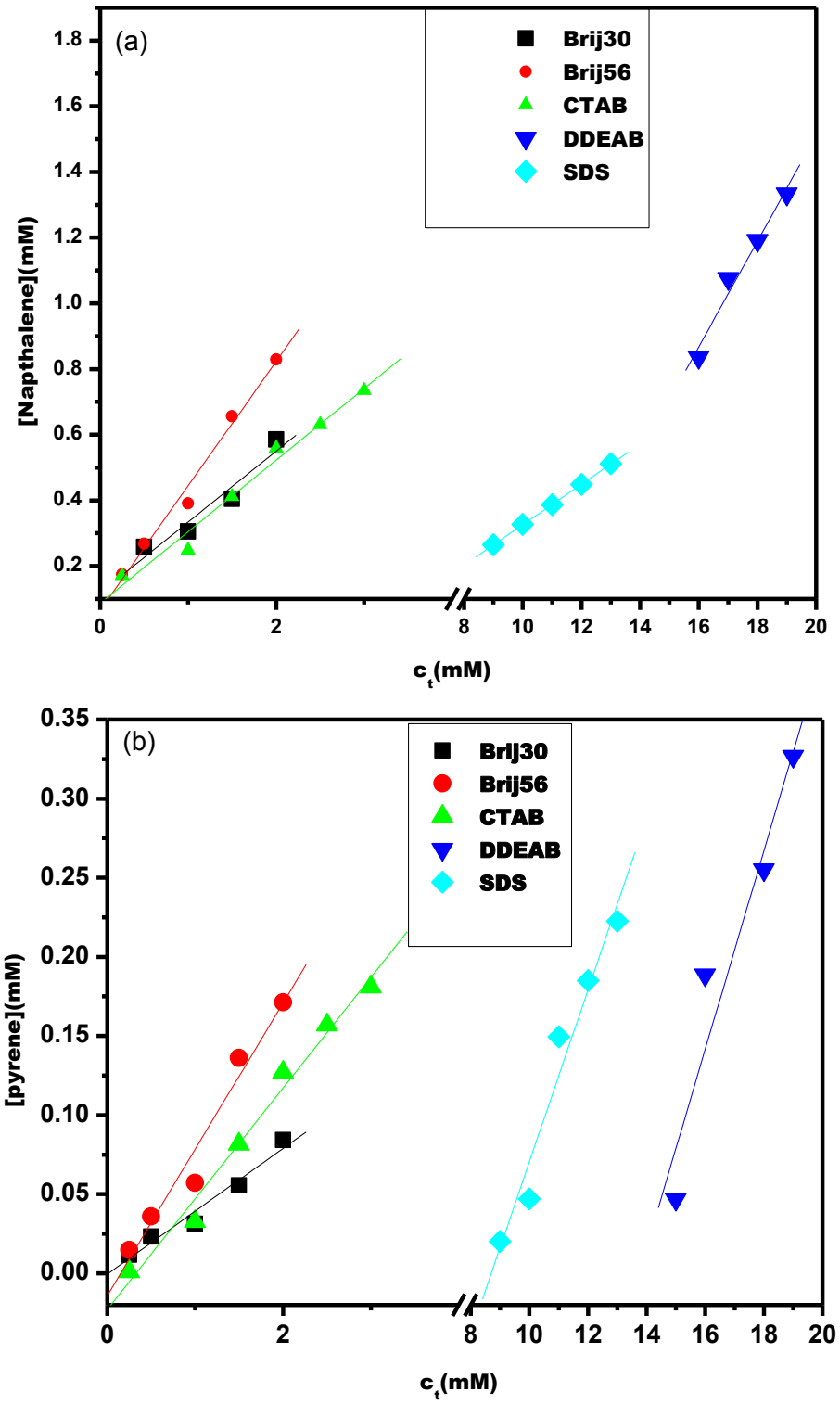


Figure 4.1B: *Variation of solubility of (a) naphthalene, and (b) pyrene in their mixed 1:1 state with total surfactant concentration in various surfactant systems at 25 ^{o}C.*

is defined as $K_m = X_m/X_a$, the ratio of mole fraction of organic compound in the micellar phase, X_m, to that in the aqueous phase, X_a. The value of K_m is a function of temperature and the nature of surfactant/solubilizate. The value of X_m in terms of MSR can be written as [57, 84]

$$\left.\begin{aligned} \boldsymbol{X_{m(i)} = \frac{MSR_{(i)}}{1+MSR_{(i)}}} \quad \textbf{(for single PAH systems)} \\ \boldsymbol{X_{m(i)} = MSR_{(i)}/(1+\sum_{i=1}^{n} MSR_{(i)})} \quad \textbf{(for mixed PAH systems)} \end{aligned}\right\} \qquad (4.2)$$

Values of X_m calculated from the **eqs. 4.2** for naphthalene and pyrene in their single and mixed states in various surfactant systems are compared in **Figure 4.2.** X_a can be expressed as $X_a = [S_{cmc}]\, V_m$. V_m is the molar volume of water equal to 0.01805 L/mol at 25 ^{0}C. With these expressions, K_m becomes [57]

$$\left.\begin{aligned} \boldsymbol{K_m = MSR/\{[S_{cmc}]V_m(\ 1+MSR)\}} \quad \textbf{(for single PAH systems)} \\ \boldsymbol{K_m = MSR/\{[S_{cmc}]V_m(1+\sum_{i=1}^{n} MSR)\}} \quad \textbf{(for mixed PAH systems)} \end{aligned}\right\} \quad \textbf{(}4.3\textbf{)}$$

The K_m values of various PAHs in different surfactant solutions are also presented in **Table 4.2** for the C_{12} and C_{16} series of surfactants.

Table 4.2: **Molar Solubilization Ratio (MSR), Logk$_m$, Association Constant(K$_1$), Average Number of PAH Molecules per Micelle (S^M), Multi-Component Relative Solubilization Ratio (S^i), Mole fraction in (1:1) mixture (X^i_{mix}) and regression coefficient (R^2) in MSR of Naphthalene and Pyrene in Their Single and Mixed States in Various Surfactant Systems At 25 ^{0}C.**

Surfactant system	MSR		LogK$_m$		K$_1$(mol^{-1}dm^3) ($x10^3$)		S^M	S^i	X$^i_{mix}$	R^2
	Single	mixed	Single	mixed	Single	mixed	Single/ Mixed			Single/ Mixed
Naphthalene										
Brij30	0.264	0.136	4.67	4.42	1.07	0.56	26.2/ 13.6	1.07	0.12	0.966/ 0.979
Brij56	0.380	0.264	4.79	4.64	2.19	1.51	53.5/ 36.9	1.26	0.20	0.984/ 0.994
CTAB	0.420	0.250	4.82	4.62	1.02	0.63	24.9/ 15.2	0.84	0.19	0.976/ 0.989
DDEAB	0.251	0.235	4.66	4.62	0.55	0.51	13.5/ 12.5	3.49	0.18	0.968/ 0.985
SDS	0.098	0.050	4.32	4.02	0.26	0.13	6.5/ 3.1	2.37	0.05	0.973/ 0.979
Pyrene										
Brij30	0.043	0.039	6.52	6.46	66.24	6.09	4.1/ 4.0	1.88	0.03	0.994/ 0.981
Brij56	0.106	0.085	6.91	6.72	22.79	18.17	14.9/ 11.9	1.15	0.06	0.989/ 0.982
CTAB	0.055	0.094	6.64	6.77	5.10	8.78	3.4/ 5.7	2.88	0.07	0.960/ 0.992
DDEAB	0.038	0.067	6.50	6.64	3.14	5.41	2.1/ 3.5	1.83	0.05	0.992/ 0.965
SDS	0.032	0.044	6.42	6 .53	3.08	4.13	2.1/ 2.7	2.74	0.04	0.985/ 0.978

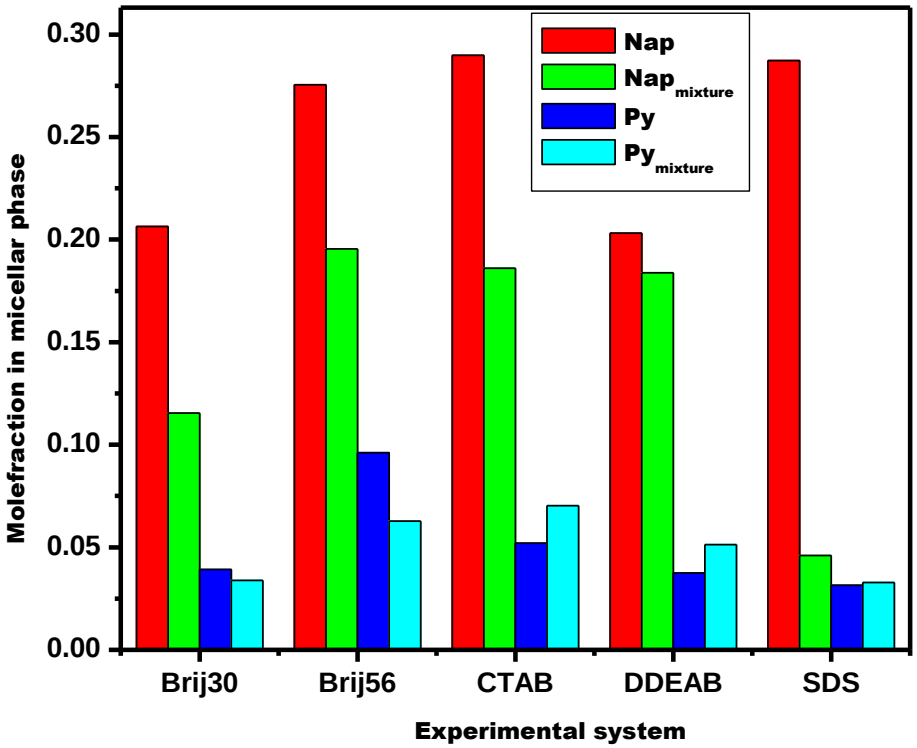


Figure 4.2: *Mole fraction of naphthalene and pyrene in micellar phase during their solubilization/cosolubilization in different surfactant systems at 25 ^{o}C.*

4.2. Solubilization of PAHs in various surfactant systems:

In conformity with early findings, [129,130] in each surfactant series, MSR and K_m values are found to be higher for nonionic than for cationic surfactants which in turn are having higher values than anionic indicating that for the same hydrophobic chain length nonionics have higher solubilizing power for the PAHs. The solubilization of PAHs in nonionic surfactant micelles may occur in the core due to their hydrophobic nature and the shell region of the micelles as well because of their slight polarity owing to the presence of resonating π - electrons in the aromatic rings.[131-132] However, as per the results reported by Bernardez and Ghosal,[133] the resonating π-

electrons in the PAHs form weak bonds with the oxygen of POEs present in the head groups of nonionic surfactants leading to the predominant micellar core solubilization than the solubilization in the shell region of the micelle.[133] Therefore owing to the large core volume in the Brij surfactants due to their high aggregation numbers (**Table 4.1**), the micellar core solubilization would be higher than in their respective ionic surfactant counterpart explaining their relatively larger values of MSR and K_m. In cationic micelles, in addition to micellar core solubilization, naphthalene and pyrene get adsorbed at the cationic micelle–water interface due to electrostatic interaction between π- electrons of PAHs and the positive charges of surfactant head groups. Therefore balance between the micellar aggregation number and extent of interfacial adsorption would decide the solubilization of PAHs within such self assemblies. Since cationics have lower aggregation number and hence smaller core volume in addition to having smaller electrostatic interaction with PAHs (atleast with pyrene), the MSR and K_m values come to have lower values. This is supported by our data wherein the MSR and K_m values for Brij30 are higher than DDEAB which in turn is having much higher value than SDS for both the PAHs. This is also the case within C_{16} series of surfactants except for the case of naphthalene solubilization within CTAB and Brij56 micelles. In this case the trend is not followed. Herein MSR and K_m values of Brij56 towards naphthalene are lower than CTAB, although the aggregation number of Brij56 (141) is much higher compared to aggregation number (61) of CTAB, but the HLB value of CTAB is (23.87) much higher than that of Brij56 (13.38) calculated by molecular modeling software (ChemSW). We are of the opinion that in this case naphthalene molecules, being more polar than pyrene, not

only resides in micellar core but adsorbs appreciably at the interface of the cationic micelles as well due to electrostatic interaction between π-electrons of naphthalene and the positive charges outweighing the hydrogen bonding interactions observed in nonionic micelles. This results in appreciable interfacial solubilization of naphthalene within the CTAB micelles in addition to micellar core solubilization leading to higher values of MSR and K_m than the nonionic counterpart. This would not be the case with the pyrene since it is more hydrophobic and thus prefers to be predominantly in core of micelle. Perhaps the presence of ethyl group in the head group of DDEAB increases the hydrophobicity of the micelle-water interface compared to CTAB resulting in slightly lesser naphthalene solubilization than in Brij30 micelles. In case of SDS micelles, the PAH molecules would prefer only the interior because of repulsive interaction between the π- electrons of the PAHs and the negative charge of the micellar head group. As such PAHs solubilize less in these micelles resulting in lowest MSR and K_m values among the studied systems. The MSR and K_m values are, in general, higher in the C_{16} series than in the C_{12} series of compounds for both PAHs. With the assumption that the inner nonpolar core of the micelle is responsible predominantly for solute solubilization and that the hydration of the outer polar zone of the micelle is localized, K_m should be approximately proportional to the non polar content of the surfactant. This has been experimentally observed by Kile et al [129] for solubilization of DDT in nonionic surfactants where the main contributor to solubilization was the non polar content of surfactant independent of the oxyethylene chain length. Moreover, their solubilization data for nonionic, cationic and anionic surfactants revealed that the values of K_m could be better related with non polar

content of the surfactant rather than with the micelle size, leading to the conclusion that micellar size may not be a major factor for observed differences in K_m of ionic and nonionic surfactants. This is supported by our data as well, wherein MSR and K_m values for Brij30/DDEAB micelles are much lower than for Brij56/CTAB micelles for both the PAHs.

4.3. Cosolubilization of PAHs in various surfactant systems:

The relative efficiency of different solubilization sites within the micelles towards solubilizing different solutes determines the extent and position of their solubilization during co-solubilization. Naphthalene and pyrene compete with each other for a location in the interior of the micelle which leads to decrease in the solubility of one solute in presence of other in accordance with reported studies. [23] Three phenomena might occur during cosolubilization of naphthalene and pyrene within micelles:

1. Naphthalene would successfully compete for the interfacial region/palisade layer and thus replace pyrene from the palisade layer because of its polar nature and lower molecular volume as also observed in earlier studies. [133]

2. The more hydrophobic pyrene may displace less hydrophobic naphthalene from micellar core thereby reducing its solubility within the micelle in accordance with literature. [23, 24,134]

3. Naphthalene solubilized in the outer micellar layers (palisade layer) may decrease the interfacial tension enabling the core volume to increase and thereby resulting in increase in solubilization of pyrene as reported earlier.[23,24,134]

During co-solubilization of naphthalene, the order of solubilization efficiency (MSR values) in different surfactant systems is: (a) in nonionic: Brij56> Brij30 (b) in cationics: CTAB> DDEAB. This can be easily explained as solubilization in C_{16} series of surfactants is more than C_{12} series of surfactants and by taking the above three points in consideration. The outer hydrophilic corona of micelles has much more efficiency for solubilizing polar naphthalene, having smaller molecular volume, from equimolar binary mixture of naphthalene and pyrene. Naphthalene successfully competes for the palisade layer as is quite evident from the data presented in **Table 4.2**. Less significant decrease in MSR values of naphthalene for DDEAB during cosolubilization with the simultaneous increase in MSR of pyrene indicates replacement of naphthalene from the core of micelles by pyrene and its occupancy in the micellar palisade layer resulting in increase micellar core volume. This effect, however, is of smaller magnitude due to the lesser palisade layer solubilization of naphthalene within the DDEAB micelles. In case of CTAB, in contrast, naphthalene would prefer the palisade layer due to the greater charge density on the surface, larger aggregation number and less hydrophobicity (due to presence of only methyl groups) of the micelle-water interface. This results in large replacement of core solubilized naphthalene within the CTAB micelles by pyrene resulting in its drastic decrease in MSR value with simultaneous increase for pyrene. In case of nonionic surfactant systems, Brij30 and Brij56, naphthalene and pyrene get predominantly solubilized in the micelle core due to less significant effect of hydrogen bonding interactions between OE groups present in the palisade layer of the micelles and the π- electrons of the PAHs. This results in competitive solubilization of the two for the same

solubilization sites leading to decrease in the MSR value for both the PAHs compared to that during single solute solubilization. For the SDS surfactant system, naphthalene is mainly solubilized in the core of the micelle which therefore shows drastic decrease in MSR value due to the displacement of naphthalene by more hydrophobic pyrene from the core of the micelle.

For cosolubilization of pyrene, the order of solubilization efficiency in different surfactant systems is same as that for naphthalene: (a) in nonionics: Brij56 > Brij30 and (b) in cationics: CTAB > DDEAB showing importance of core volume for solubilization of pyrene within the micelles. Naphthalene, being more polar than pyrene, has strong ability to displace pyrene from the outer hydrophilic shell of the micelle. Therefore, naphthalene competes with pyrene for solubilization in micellar palisade layer resulting in decrease in the solubilization of pyrene in palisade layer. However, at the same time it increases the micellar core volume due to decrease in interfacial tension and hence facilitates increase in solubilization of pyrene in the micellar core. A balance between these two processes explains the experimental order obtained for MSR values of pyrene in the selected surfactant systems during co-solubilization. In case of Brij30 and Brij56 systems wherein the hydrogen bonding effect is less (explained earlier), the displacement of pyrene by naphthalene from the outer hydrophilic shell is of lesser magnitude and hence associated increase in the micellar core volume. This leads to the option that only competition of two solubilizates within the core of micelles is of significance. Therefore due to cosolubilization of naphthalene in the micellar core, there is the net decrease in the solubilization of pyrene. This decrease is more prominent in Brij56 because of its

larger aggregation number (141) and hence larger micellar core volume. However, for CTAB and DDEAB due to solubilization of naphthalene in palisade layer, there would be an increase in the micellar core volume which results in drastic increase in MSR of pyrene. For surfactant system of SDS their occurs an increase in MSR value of pyrene, suggesting an increase in solubilization on account of displacement of naphthalene by pyrene from micellar core.

4.4. PAH-PAH interaction in the micellar pseudophase:

Solubilized amounts of naphthalene (NAP) and pyrene (PY) during solubilization and cosolubilization as well as total solubilized amount of both the PAHs during cosolubilization are plotted against surfactant concentration in representative **Figure 4.3**. The total solubilized amount of PAHs (NAP+PY) solubilized during co-solubilization is less than the amount of NAP and greater than the amount of PY solubilized during single solute solubilization in all surfactant systems indicating that the solubilization of NAP is suppressed in presence of pyrene during cosolubilization, while as the solubilization of pyrene is synergistically favoured in presence of naphthalene during cosolubilization. To reveal the nature of interaction between PAHS inside the micelles, the formulation proposed by Nagadome et al. [118] has been adopted:

The solubilization equilibrium when PAHs is used in excess can be written as

$$\boldsymbol{solid\ PAH(crystal)} \overset{K_d}{\leftrightarrow} \boldsymbol{singly\ dispersed\ PAH\ in\ bulk} \overset{K_m}{\leftrightarrow} \boldsymbol{solubilized\ species\ in\ Micelle}$$

$$\downarrow \qquad\qquad \downarrow$$

$$\boldsymbol{\Delta G_d^o = -RT\ lnK_d} \qquad\qquad \boldsymbol{\Delta G_m^o = -RT\ lnK_m}$$

where, K_d = activity of singly dispersed PAH/ activity of solid PAH and is equal to activity of singly dispersed PAH because activity of solid PAH is unity. Since the PAH solubility is very low K_d approximates to molarity of PAH solubilized below *cmc*, which is taken equal to its water solubility, S_{cmc}. The equilibrium constant of

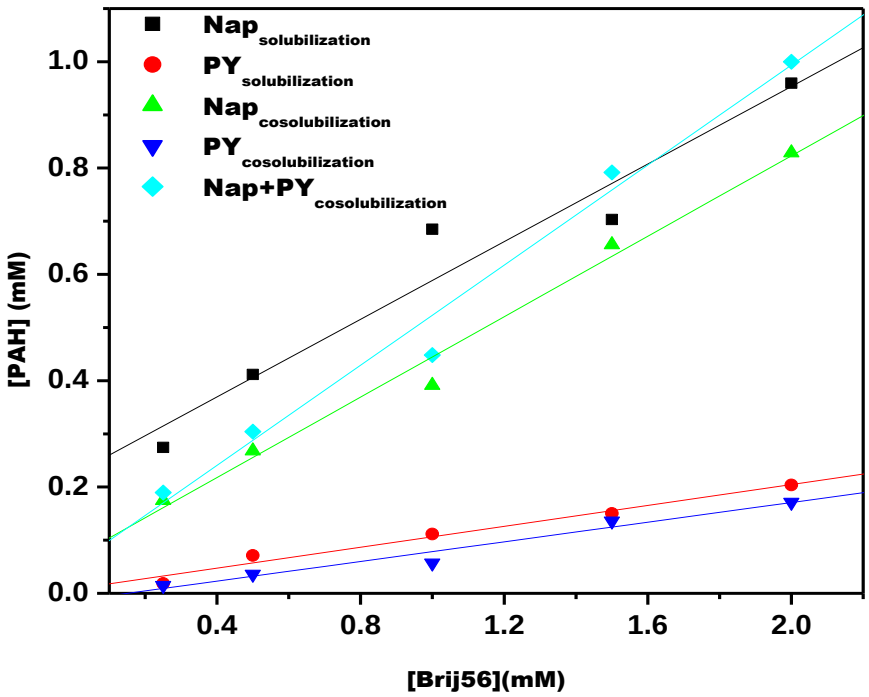


Figure 4.3*: Plot showing comparison between solubilized amounts of naphthalene and pyrene during solubilization and cosolubilization in addition to total amount of the two PAHs solubilized in Brij56 surfactant system at 25 °C.*

solubilization for conversion from solid phase to solubilized state in micelles is, therefore, given by

$$\boldsymbol{K_{eq} = K_d \times K_m} \qquad (4.4)$$

where K_m is the partition coefficient of the PAH between aqueous phase and micellar phase. Values of K_m were calculated from **eq 4.3(a)** for single solubilizate system.

The molar Gibbs free energy change upon solubilization, ΔG°, will therefore be given as

$$\boldsymbol{\Delta G^{\circ} = -RTlnK_{eq}} \qquad (4.5)$$

For cosolubilization of two solid solubilizates, A and B, the total equilibrium constant of cosolubilization for conversion from solid phase to solubilized state in micelles will be given by

$$\boldsymbol{K_{eq}^{mix} = (K^{A}{}_{d} \times K^{A}{}_{m}) \times (K^{B}{}_{d} \times K^{B}{}_{m})} \qquad (4.6)$$

where K_d^A and K_d^B are the respective activities of the two PAHs A and B dispersed in bulk and $K^A{}_m$ and $K^B{}_m$ are their respective partition coefficients in mixed solubilization systems. Taking the $K^A{}_m$ and $K^B{}_m$ from **eq 4.3(b)** the Gibbs energy change, $\Delta G^{\circ}{}_{mix}$ accompanying the conversion of two solubilizates from bulk phase to micellar phase would be given by:

$$\boldsymbol{\Delta G^{\circ}_{mix} = -RTlnK_{eq}^{mix}} \qquad (4.7)$$

If the mixture is ideally formed, the molar Gibbs energy of ideal mixing $\Delta G^{s}_{mix}(ideal)$ should satisfy the additive rule as

$$\boldsymbol{\Delta G^{s}_{mix}(ideal) = \chi^{A}\Delta G^{\circ}_{A} + \chi^{B}\Delta G^{\circ}_{B}} \qquad (4.8)$$

Where χ^A and χ^B are the mole fractions of the two species 'A' and 'B' within the micelles on the solubilizate only basis and were calculated from the equation

$$\boldsymbol{\chi^{A} = MSR_{A}/(MSR_{A} + MSR_{B})} \qquad (4.9)$$

where the MSR_i were taken as their MSR values during cosolubilization. The difference between the real value of the free energy change ΔG°_{mix} and $\Delta G^{s}_{mix}(ideal)$ gives the excess Gibbs energy

$$\Delta \boldsymbol{G^{s}_{excess}} = \boldsymbol{\Delta G^{o}_{mix}} - (\boldsymbol{\chi^{A} \Delta G^{\circ}_{A}} + \boldsymbol{\chi^{B} \Delta G^{\circ}_{B}}) \qquad (4.10)$$

Since the total amount of two PAHs solubilized during cosolubilization is more than the amount of NAP and PY solubilized during single solute solubilization ΔG^{S}_{excess} is negative for all surfactant systems.

The interaction parameter 'ω/RT', activity coefficients of the two PAHs in 1:1 mixture inside the micelles 'γ_{nap}' and 'γ_{py}' are calculated from the excess Gibbs energy, (Nagadome et al., 2001)[118] ΔG^{S}_{excess} as,

$$\boldsymbol{\omega} = \Delta \boldsymbol{G^{S}_{excess}} / (\boldsymbol{\chi^{A}\ \chi^{B}})\boldsymbol{RT} \qquad (4.11)$$

$$\boldsymbol{ln\, \gamma_{i}} = \boldsymbol{\omega}(\mathbf{1} - \boldsymbol{\chi^{A}})^{2}/\boldsymbol{RT} \qquad (4.12)$$

The values of ΔG^{S}_{excess}, ω/RT and $\gamma_{i's}$ calculated in different surfactant systems for the PAHs are presented in **Table 4.3**. The interaction parameter 'ω/RT' gives the cohesive forces between the unlike solubilizates. The negative values of 'ω/RT' obtained signify that the interaction between NAP and PY were enhanced and the two PAHs are spontaneously miscible in all surfactant systems studied. Two factors seem to influence the intermolecular interactions between the two PAHs within the micelle viz. solubilization site of the PAHs and steric fitness of the two PAHs within the micelle. Since NAP and PY have hydrophobic character, their interaction within the non polar environment will be more i.e. interaction will be more when both of them are solubilized in hydrophobic core than when both are solubilized in palisade layer.

Also a higher packing parameter and larger micellar size decreases the steric hindrance between the PAHs and makes their solubilization more favourable and hence increases the interaction between them.

Table 4.3: Excess Gibbs free energy changes (ΔG^{s}_{excess}), interaction parameter (ω/RT) and activity coefficients (γ_i) of naphthalene and pyrene at 25 ^{0}C in different surfactant systems

Surfactant system	ΔG^{s}_{excess} (kJ/mol)	ω/RT (x 10^{-3})	γ_{Nap}	γ_{Py}
Brij30	-7.89	-7.32	1.00	1.00
Brij56	-8.68	-7.96	1.00	0.99
CTAB	-8.91	-2.73	1.00	0.99
DDEAB	-8.85	-8.45	1.00	1.00
SDS	-8.08	-5.29	1.00	1.00

In case of Brij30 and Brij56 micelles, an appreciable amount of both the PAH is solubilized in close proximity within the hydrophobic micellar core. Also owing to their higher packing parameter and larger micellar size, the solubilization is sterically favoured which explains the appreciable interaction between the two PAHS as reflected by their higher 'ω/RT' values. In case of CTAB and DDEAB surfactant systems, an appreciable amount of naphthalene is solubilized at the interface leading to reduced interaction between them due to reduction of interfacial tension which in turn leads the increase in core volume of the micelle and thus favours core solubilization of pyrene. Also since their packing parameter and micellar size is small so that the steric fitness of the two PAHs solubilised accounts for the lower values of 'ω/RT' when compared with Brij30 and Brij56 surfactant systems. But the value of 'ω/RT' for DDEAB is more than either of Brij30 or Brij56 because here interfacial presence of naphthalene molecules increases the core volume to such an extent that

naphthalene molecules not only resides at the interface but an appreciable amount of it is also solubilized into the core of the micelle which results in an increased interaction between the PAHs in the core than either of the two. These values are lowest for SDS micelles owing to its highest HLB value and smallest micellar size among all surfactant systems studied.

The results of our study suggests that behavior of PAH mixtures in surfactant solutions involves complex interactions among the PAHs and between the PAHs and the surfactant monomers. The behavior, for example, deviates significantly from the dilute and the ideal solution theory. The mole fraction of the solvent molecules (micelle phase) (based on **Eq.4.2**) for one PAH system ranges from 0.93 to 0.97 while that for two PAH system(1:1 mixture) ranges from 0.74 to 0.92 , leading to the conclusion that while one PAH systems may behave somewhat like dilute solutions (solvent mole fraction closer to 1; e.g. [135]) the two PAH systems do not. If we assume that the micelle phase behaves as a liquid phase, the mole fractions of the solutes are also less than predicted by ideal solution theory as

$$\boldsymbol{Xm_{(i)}^{ideal}} = \frac{\boldsymbol{MSR_{(i)}^{pure}}}{(\mathbf{1}+\sum_{\boldsymbol{i=1}}^{\boldsymbol{n}} \boldsymbol{MSR_{(i)}^{pure}})} \textbf{ (for mixed PAH systems)} \qquad (4.13)$$

And is shown in **Figure 4.4**, but the relative degree of solute solubilization, NAP > PY, is the same. Such results suggest that the interactions of the PAHs within the surfactant hydrophobic tails are different from their interaction with themselves. Researchers have shown that the interaction of individual PAHs with surfactants are similar to their interactions with octanol. The experimental log K_m values of PAHs in

various surfactant systems are correlated to the logarithm of their corresponding octanol- water coefficient, log K_{ow}, according to the linear free energy relationship as already observed in our earlier studies, [38]

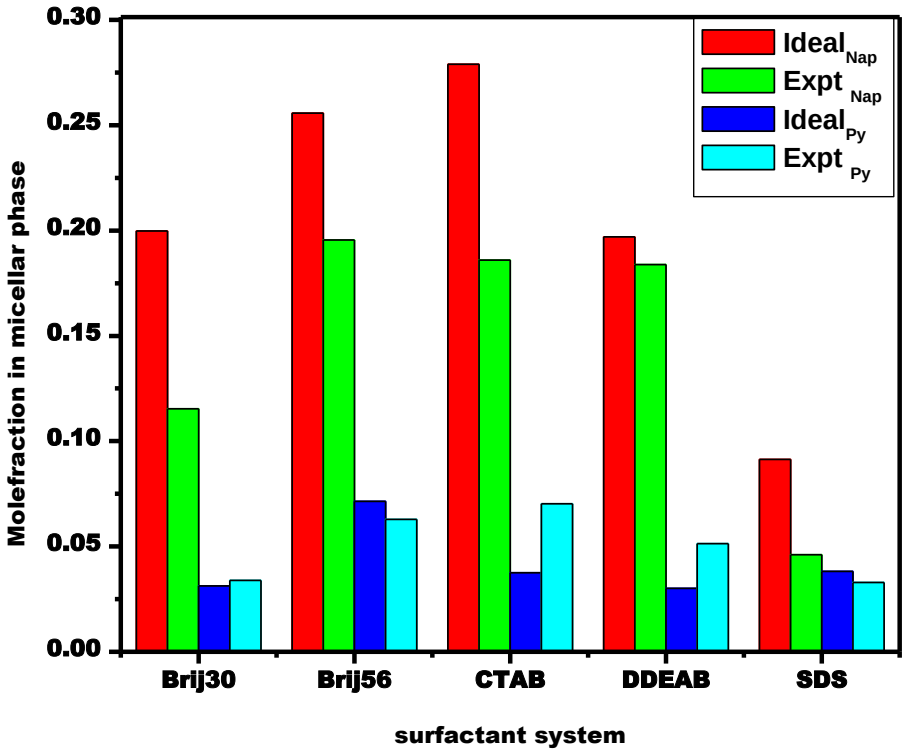


Figure 4.4: *Plot of ideal verses experimental mole fractions of Naphthalene and pyrene in mixture (1:1 molar ratio)*

$$Logk_m = a\,Logk_{ow} + b \qquad (4.14)$$

where *a* and *b* are correlation constants, relying on the lipophilicity of the solvent. The slope 'a' is a measure of the sensitivity of the solvent system to the changes in lipophilicity of solutes.[38] a < 1 means lower sensitivity of a nonaqueous system to hydrophobicity of hydrophobic solute than in the octanol-water system.The interaction of the solutes with the surfactant monomers can cause the micelles to change their structure. Attwood and Florence [126] summarize several studies that

showed that for certain solutes, the micelle reorganized to include both the solute and a large number of monomers. It follows then that the presence of two solutes could lead to further reorganization thereby not allowing two PAH to be packed into the micelle to the same extent as they were in single PAH systems. They are no longer solubilized independently of each other, thereby suggesting that other factors such as aqueous solubility and packing are important

4.5. Estimation of Binding Constants of PAHs with surfactant systems:

Moroi et al. [136,137] have demonstrated the evaluation of the first stepwise association constant, K_1, of a solubilizate incorporated into micelles in the case of solubilization to which Poisson distribution can be applied. As per this formulation, K_1, which serves as interaction parameter between them, is related to the total surfactant concentration, C_t , total micelle concentration [M_t] , cmc, and aggregation number, N, of micelles through the equation

$$\{[\boldsymbol{S_t}] - [\boldsymbol{S_{cmc}}]\}/[\boldsymbol{S_{cmc}}] = \frac{\boldsymbol{K_1}}{\boldsymbol{N}}(\boldsymbol{C_t} - \boldsymbol{Cmc}) \qquad (4.15)$$

The binding constant K_1 of the PAHs with the surfactant system is also related with the MSR, aggregation number N, and the solubility of the PAHs below *cmc*, S_{cmc} through the equation [138-140]

$$\left(\frac{\boldsymbol{MSR}}{\boldsymbol{S_{cmc}}}\right)\boldsymbol{N} \;=\; \boldsymbol{K_1} \qquad (4.16)$$

The value of K_1/N can be evaluated from the slope of ([St] - $[S_{cmc}]$)/ $[S_{cmc}]$ against (C_t –cmc). If the aggregation number is known, then the value of K_1 can be evaluated. Further, assuming a Poisson distribution of solubilizate molecules among micelles,

the formulation can also be used to evaluate average number of solubilizate molecules per micelle, S^M, according to the equation [23,126]

$$S^M = \frac{([S_t]-[S_{cmc}])}{[M_t]} = K_1\,[S_{cmc}] \qquad (4.17)$$

The value of $[S_{cmc}]$ can be taken as water solubility of PAHs, which changes only very slightly up to *cmc* of the surfactant.[137] **Figure 4.5** shows the representative plots of ([St] - $[S_{cmc}]$)/$[S_{cmc}]$ against (C_t-*cmc*) for a combination of C_{12} and C_{16} series of surfactants, where all the concentrations are expressed in mmol/L. The values of the aggregation number taken from literature for surfactant systems (**Table 4.1**) were used with the value of slope (K_1/N) to evaluate K_1 and hence S^M. The calculated values of K_1 and S^M are presented in **Table 4.2** for the C_{12} and C_{16} surfactant series. All the PAHs in each type of micelle satisfy the assumption of Poisson distribution, [141] because their S^M values are sufficiently low. The S^M values for naphthalene are the largest and those for pyrene the smallest in each of the single surfactant systems. Although S^M values of 6.5-26.25 and 24.9 -53.5 for naphthalene in the C_{12} and C_{16} surfactant series, respectively, seem to be quite large, the amount in mole fraction units is less than 0.21 in the case of the former and less than 0.30 in the latter.

If the solutes competes with each other for the location in the interior of the micelle, it will lead to decrease in the solubility of one solute in presence of the others.[23] The values obtained follows the trend observed for MSR and K_m values and explained through same arguments.

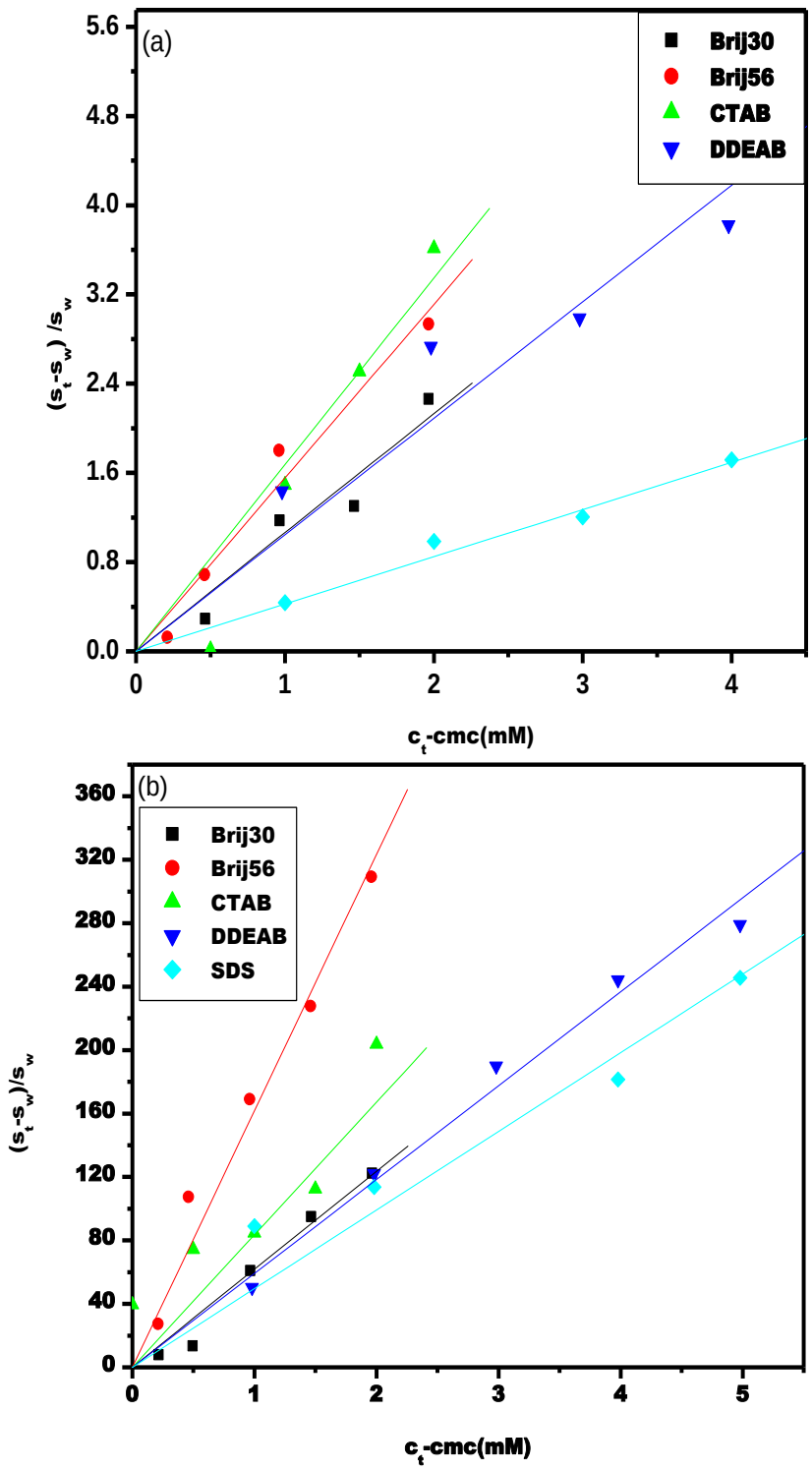


Figure 4.5A: *Plots of [St]-[Sw]/ [Sw] of (a) Naphthalene, (b) pyrene against surfactant concentration in micellar form (C_t-cmc) for C_{12} and C_{16} surfactant systems at 25 ^oC.*

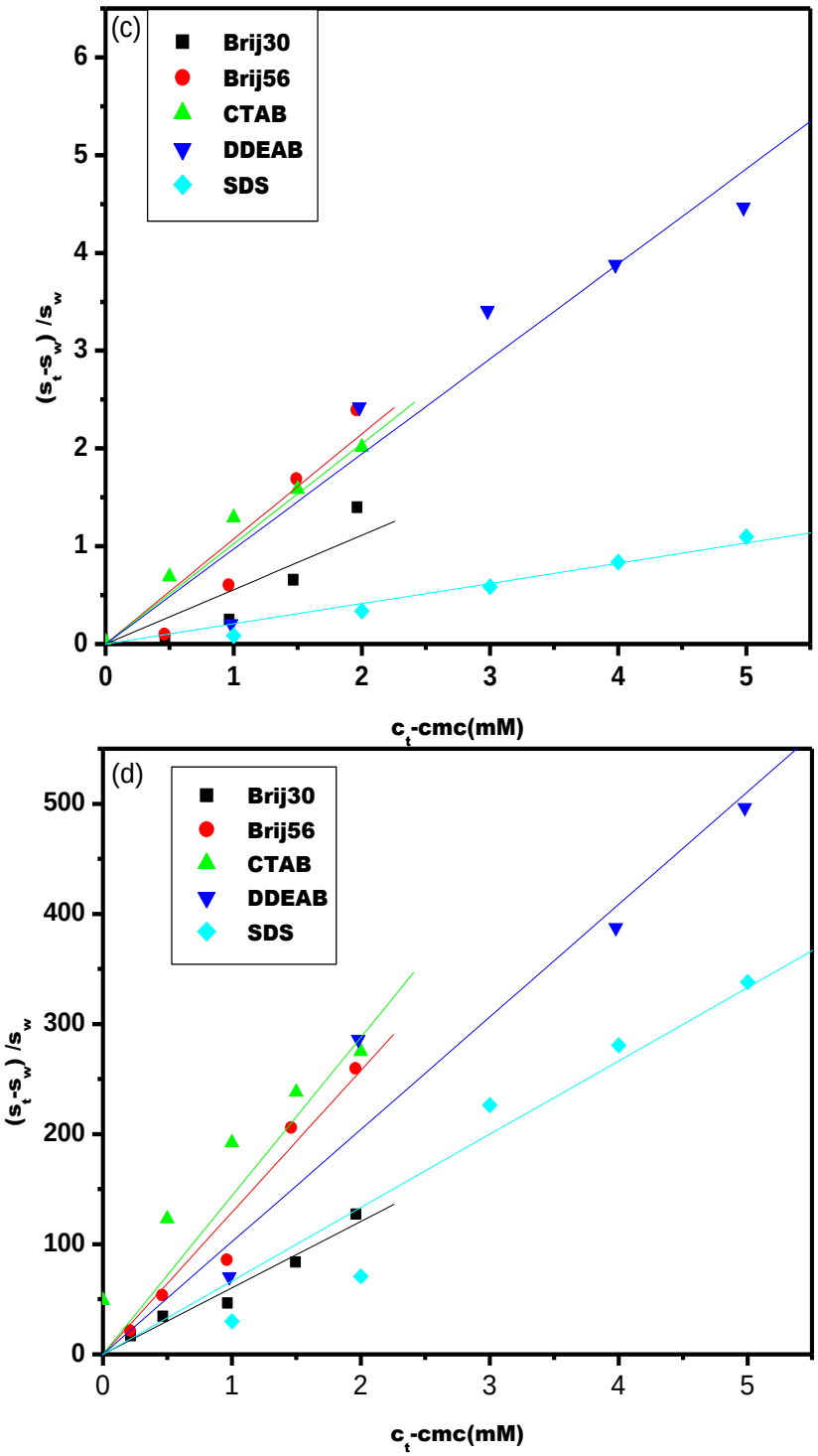


Figure 4.5B: *Plots of [St]-[Sw]/ [Sw] of (c) naphthalene in mixture and (d) pyrene in mixture against surfactant concentration in micellar form (C_t-cmc) for C_{12} and C_{16} surfactant systems at 25 ^oC.*

4.6. Multi-component relative solubilization ratio:

The multi-component relative solubilization ratio S^i can be used to quantify the degree to which one component is solubilized relative to the others. [116] The multi-component relative solubilization ratio is defined as the ratio of the MSR values of the solutes in the multiple solute system divided by the ratio of the MSR values of the two components of interest in single solute systems. The multi-component relative solubilization of naphthalene over pyrene in a 1:1 binary system of NAP/PY is calculated by

$$\boldsymbol{S(NAP)} = \frac{\left(\frac{\boldsymbol{MSR_{(NAP)}}}{\boldsymbol{MSR_{(PY)}}}\right)\boldsymbol{in\ mixture}}{\left(\frac{\boldsymbol{MSR_{(NAP)}}}{\boldsymbol{MSR_{(PY)}}}\right)\boldsymbol{in\ pure}} \qquad (4.18)$$

S^i values calculated for NAP and PY during co-solubilisation are given in **Table 4.2.** S^{NAP} value greater than unity indicates situations where naphthalene is selectively solubilized over pyrene, and conversely, S^{NAP} values less than one represent situations where pyrene is selectively solubilized over naphthalene. If value of S^i is close to unity, the solubilization is said to be ideal indicating that the two PAHs get solubilized independently of each other. However, large deviation of S^i from unity would indicate the competition for solubilization. We calculated the mole fraction of each solubilizate using **eq. 4.13** taking their MSR values as obtained experimentally for single solute system and termed it as ideal mole fraction. The experimental mole fraction of NAP and PY present in the micelle in binary solute system calculated from their MSR values during cosolubilization are compared with their ideal mole

fractions. These results suggest that the two PAHs compete for the location within the micelle for solubilization. The extent of which depends on the structure, interaction and solution behavior of the selected surfactant system

The values of mole fraction of the solute 'i', X^i_m calculated in the micelle confirms that polar interactions determine the solubilization of NAP when cosolubilized with PY as indicated by its higher solubilization in all surfactant systems viz. Brij30, Brij56, CTAB, DDEAB and SDS.

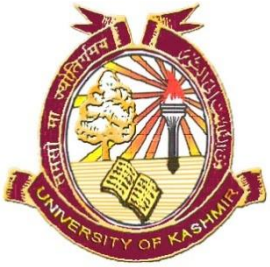
Chapter 5
Main Highlights of the work

The main highlights of the present studies are:

1. The present study deals with the investigation of solubilization and cosolubilization aspects of naphthalene and pyrene in single surfactant systems.
2. The main focus of the study had been on understanding: (i) the effects of hydrophobic chain length and hydrophilic groups of two surfactant series with dodecyl (C_{12}) and hexadecyl (C_{16}) chain lengths having cationic, anionic and non-ionic head groups on the solubilization of PAHs of increasing hydrophobic character, and (ii) the effect of nonionic, cationic and anionic surfactants on the simultaneous solubilization behavior of naphthalene and pyrene with their self assemblies.
3. Quantification of solubilization capacity was done in terms of the molar solubilization ratio, the micelle water partition coefficient and the average number of solubilizate molecules per micelle determined by employing spectrophotometric and tensiometric techniques. The extent of solubilization of naphthalene in all surfactant systems studied was much greater than that of pyrene. Anionic surfactants exhibits lesser solubilization capacity than cationics which in turn exhibits lesser solubilization capacity than nonionics in each series of surfactants, with higher efficiency in C_{16} series compared to C_{12} series, except in case of solubilization of naphthalene in CTAB and Brij56. In this case CTAB exhibits higher solubilization than Brij56 and thus shows discrepancy from normal trend.
4. Competitive solubilization of PAHs was observed during cosolubilization, which has been quantified in terms of multicomponent solubilization ratio. The solubility enhancement of naphthalene was reduced in the presence of pyrene. A synergetic

effect on the solubilization of pyrene was observed in the presence of naphthalene in CTAB, DDEAB and SDS surfactant systems, while in the rest of the studied surfactant systems the solubility of pyrene was reduced. Based on the regular solution theory, the interaction between two PAHs within the micelles was evaluated in terms of Gibbs energy change of mixing, 'ΔG^{s}_{excess}', activity coefficients and interaction parameter 'ω'. The ω and ΔG^{s}_{excess} values were negative indicating enhancement of interaction between the PAHs within the micelles leading to their spontaneous solubilization.

5. The present study finds its application in understanding the effect of the structure of PAHs on the solubilization in single PAH systems. The results of this study are also useful to understand and predict cosolubilization of a mixture of PAHs and selective solubilization of one PAH over other another in a particular surfactant system and thus provides valuable information on the selection of surfactant systems for selective separation of PAHs from a mixture of PAHs for SER of contaminated sites.



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