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Water/soil pollution by organic compounds (Poly aromatic hydrocarbons, dyes and pesticides, etc), many of which are known to be toxic or carcinogenic, has caused considerable and worldwide concern. Contaminated soil and water pose a serious threat to human health and ecosystem. Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants generated primarily during the incomplete combustion of organic materials (e.g. coal, oil, petrol and wood)[1-3]. Several different remediation technologies (e.g. solvent extraction, precipitation, adsorption and ion-exchange) have been tested in efforts to remove these environmental contaminants. Among them, bioremediation is showing particular promise as a safe and costeffective option. In spite of their xenobiotic properties, a variety of genera of gram-positive and negative bacteria, fungi and algae have been isolated and characterized for their ability to utilize PAHs. The general characteristics of PAHs are high melting point and boiling points (therefore they are solid), low vapor pressure, and very low aqueous solubility [4]. Aqueous solubility of PAHs decreases for each additional ring [5]. In order for bacteria to degrade any given PAH, it must be made available for uptake by the bacteria [6-8]. PAHs become bioavailable when they are in either the dissolved or the vapor phase. Photolysis reactions involving PAHs are similar to biodegradation reaction (i.e. the PAHs degrade more effectively when they are in the vapor or aqueous phase) [9]. The aqueous solubility and biodegradability of PAHs can be enhanced using surfactants, which comes under surfactant-enhanced remediation (SER). Surfactant micelles have a hydrophobic core, which helps to accumulate PAHs and increase the aqueous solubility. Therefore, SER is becoming a promising technique in removing PAHs from various media (e.g. soil and aqueous) and numerous studies have been conducted.

Dye pollution is also one of the most difficult problem faced by the textile finishing, dye manufacturing and pulp and paper industries. The discharge of harmful dyes to rivers without proper treatment causes damage to the environment, including biota, both aquatic and terrestrial. Removal of water soluble dyes from water is a big challenge. There are many techniques to remove dyes from the wastewater including physical, biological and chemical methods. Although chemical and biological methods provide high dye removal efficacy, they generates material which requires further treatment.[10] In physical methods adsorption is one of the most popular technique to recycle contaminated water. Moreover, modification of the adsorbents improves potential efficacy towards several pollutants. Surfactant treated adsorbent has been found one of such effective modifications. Cationic surfactant has been used to modify amphiphilicity of the adsorbent surfaces in recent past [11].



Figure 1. Natural and anthropogenic sources of polycyclic aromatic hydrocarbon

The thesis consists of seven chapters including: i) General Introduction; ii) Material and Methods; iii) Mixed Micellization and Interaction of amphiphiles; iv) Internal Structural modification in Self-assembly of Aqueous Mixed gemini surfactant systems; v) Solubilization of poly aromatic hydrocarbons in various gemini surfactant systems; vi) Adsorbtion /extraction of various organic compounds using Surfactant modified adsorbents and vii) General Conclusion.

Chapter 1: GENERAL INTRODUCTION

This chapter contains general literature survey related to solution behavior of surfactant (aggregation, clouding and solubilization), modification of adsorbents (conventional or nanocomposite) and extraction behavior of surfactant modified materials.

The term surfactant is a blend of surface active agent. They are usually organic compounds and their unique molecular structure contains two opposite groups. One is hydrophobic group/part ("tail") usually a straight hydrocarbon chain while the other is a hydrophilic group ("head"), ionic/polar in nature. On the basis of charge on the polar head group, surfactant can be classified into different groups namely,

Cationic surfactant: Cetyl trimethylammonium bromide (CTAB) CH3(CH2)15N⁺(CH3)3 Br⁻ Anionic surfactant: Sodium dodecyl sulfate (SDS)

CH3(CH2)11SO4⁻Na⁺

Zwitterionic surfactant: Dodecyl betaine

C12H25N⁺(CH3)2CH2COO⁻

Nonionic surfactant: Polyoxyethylene alcohol

$C_nH_{2n+1}(OCH2CH2)_mOH$

Based on molecular structures surfactants are also divided into various classes such as gemini surfactants, bolaform amphiphiles, block copolymers, biosurfactants among others.

A gemini surfactant consists of two conventional surfactant molecules chemically bonded together by a spacer (Figure 2). The two terminal hydrocarbon tails can be short or long; the two polar head groups can be cationic, anionic or nonionic; the spacer can be short or long, flexible or rigid. Gemini surfactants can self-assemble at much lower concentrations and are superior in surface activity as compared to conventional surfactants.



Figure 2: Representative structure of conventional and gemini surfactant

Surfactants when present in solution show different phenomena viz micellization, clouding, adsorption, spreading, wetting, solubilisation, micro-emulsion etc. The minimum concentration at which surfactants begin to form micelles and are in dynamic equilibrium with the monomers in the bulk aqueous solution is known as the *critical micelle concentration* or *cmc*. This *cmc* can be determined by various physico-chemical methods as shown in Figure 3.



Figure 3: Different available methods to find cmc.

Mixing of two or more surfactants in an aqueous solution leads to the formation of mixed micelles (Figure 4). When more than one surfactant is added simultaneously in water, several physicochemical properties of the mixed system compared to those of the single surfactant, are changed. The negative and positive variations from ideal cmc (computed from regular solution theory [12]) indicate synergistic and antagonistic interactions in various surfactant components.



Figure 4: Representative structure of mixed micelle.

Key property of micelles or mixed micelle is to enhance the solubility of organic substances in aqueous solutions by providing multiple sites (Figure 5) of interaction where solutes can partition depending upon the hydrophobic or polar character.



Figure 5: Various micelle solubilization sites

Clouding is another phenomenon generally shown by nonionic surfactant solutions on heating. The system becomes cloudy and phase separates, at well-defined temperature known as *cloud point (CP)*, into two phases: one is surfactant rich and another surfactant lean phase [13]. The clouding behavior has not been observed frequently in aqueous ionic surfactants. However, clouding in ionic surfactant solutions has been observed in presence of quaternary bromides [14]. A renewed interest in clouding phenomenon has been found in recent time due to its utility as an alternative extraction method in place of conventional liquid-liquid extraction methodologies [15].

Chapter 2 MATERIALS AND METHODS

2.1. Materials

Gemini surfactants are synthesized and characterized using reported methods [16]. PAHs (anthracene, fluorine, phenanthrene and pyrene) were of highest purity grade available. Chemical structures of geminis and PAHs (with abbreviations) are given in Scheme 1. Freshly prepared deionized double distilled water (0.5- 1.5μ S·cm⁻¹) was used to prepare the solution for all measurements except SANS and NMR. D₂O has been used in the sample preparation for SANS and NMR experiments (99.9 atom % D, purchased from Sigma, St Louis, USA). TPeAB (\geq 99%, Sigma-Aldrich, St. Louis, MO, USA), Glycine (\geq 99%, Sigma-Aldrich, St. Louis, MO, USA), L-leucine (\geq 98%, Sigma-Aldrich, St. Louis, MO, USA), L-phenylalanine (\geq 99%, Sigma-Aldrich, St. Louis, MO, USA), α -cyclodextrin (98%, Spectrochem, Mumbai, India) and β -cyclodextrin (99%, Spectrochem, Mumbai, India). Graphite powder (extra pure) and Zirconium acetate [Zr (CH₃COO)₂] were purchased from., SD fine. Methyl Orange and Congo Red dyes were purchased from Loba Chemie Pvt. Ltd Mumbai, India,



Scheme 1. Schematic representative chemical structures of anionic and cationic gemini surfactants and PAHs with abbreviations

2.2 Synthesis and Modification of conventional/ nanocomposite adsorbents

Graphene oxide (GO) was prepared according to the method described by Hummers and Offeman (1953) [17] from graphite fine powder. The synthesis of GZrO2@ SFM (gemini or conventional) was carried out in two steps. In the first step, ~3 g of zirconium acetate and 200 mg of GO were dispersed into 200 mL of water and sonicated for 30 min. In the second step, sodium borohydride 20 mL (1% w/v) solution [18] was added drop-wise into the solution mixture. The surface modification of the adsorbents is done with surfactants as reported [19]. The structural, functional, morphological, optical and thermal properties of synthesized adsorbent were performed using XRD, FTIR, electron microscopy, UV-visible spectroscopy and TGA techniques respectively. Figure 5 shows various technique to characterize the synthesized nanocomposite. Surface modification of the synthesized nanocomposite is confirmed by the FTIR and EDAX analysis.

2.3 Methodology

2.3.1 Electric Conductivity measurements

Conductivity of the aqueous gemini mixture (of different mole fractions) was measured as a function of [surfactant or mixture] using a conductivity meter (EUTECH Cyberscan CON510, cell constant 1 cm⁻¹) with an inbuilt temperature sensor. A pre-calibrated cell has been used to measure specific conductance (κ) at each concentration (thermo-stated at 303 \pm 0.1 K using SCHOTT CT1650 bath). The CMC value was obtained from the intersection point of two straight lines in a plot of κ *vs* [surfactant or mixture].

2.3.2. Surface Tension measurements

CMC values are also determined from surface tension measurements using a Du-Nouy detachment tensiometer (Win – Son & Co., Kolkata) with a platinum (gold joint) ring. The tensiometer was calibrated using double distilled water.

2.3.5 Viscosity measurements

The viscosity measurements were carried out using an Ubbelohde suspended level capillary viscometer thermostatted at 303 ± 0.1 K.

2.3.3 Dynamic light scattering (DLS) / Zeta (ζ)-Potential measurements

Average hydrodynamic diameter (D_h) and Zeta (ζ) - potential measurements were performed on a SZ-100 nanoparticle size analyzer (HORIBA, Japan). This instrument is equipped with a green (5320Å) laser and photomultiplier tube detectors. The measurement is based on the time dependent fluctuation in the intensity of scattered light through a dispersion of particles under random motion. Analysis allows to compute diffusion coefficients which are used in Stokes-Einstein equation for the determination of D_h .

2.3.4. SANS measurements

SANS measurements were carried out using a SANS spectrometer at Dhruva Reactor, Bhabha Atomic Research Centre, Trombay, India [20]. The samples were placed in a quartz cuvette having a thickness of 2 mm and measurements were performed at various mole fractions / temperatures. SANS data were corrected and normalized to an absolute scale using a standard procedure. In SANS measurements, coherent differential scattering cross-section per unit volume ($d\Sigma/d\Omega$) as a function of scattering vector (Q = $4\pi \sin\theta/\lambda$, where 2 θ is the scattering angle and λ is the wavelength of the incoming neutrons), is measured. [21]

2.3.5Transmission Electron Microscopy

Transmission electron microscope (TEM) image was obtained with a JEOL JEM 2100 transmission electron microscope accelerating at a working voltage of 120kV. A drop of mixed gemini solution was placed on the carbon-coated copper grid (200 mesh) followed by drying for a few minutes (~298 K).

2.3.6 NMR Measurement

¹H NMR spectra were obtained with Bruker NMR spectrometer with a proton resonance frequency of 400.15 MHz at 298 K.

2.3.7. Cloud Point (CP) Measurement

Cloud point (CP) data are acquired by placing samples containing anionic gemini surfactant (12-4-12A) solutions, with a fixed concentration of SAIL, into a temperature-controlling thermostat (SCHOTT CT 1650). The temperature of the sample solution was precisely controlled with an accuracy of ± 0.1 °C.

2.3.8. Solubilization experiment

Solubility of PAH has been determined in aqueous gemini systems (single or mixed), at different mole fractions (x = 0 - 1, total [gemini] = 10mM) by adding an excess amount of PAH (fluorene, anthracene, phenanthrene or pyrene). Aqueous gemini(s) + PAH mixture has been equilibrated for 48h before centrifugation to remove excess PAH. The solubilization of PAH in micellar solutions, containing different morphologies, has been analysed, at respective λ_{max} , by UV-visible spectrophotometer (Shimadzu, UV-2450) having a quartz cell (path length 1 cm) at 303 K. The composition of gemini mixture was same in both reference and measurement cuvettes to eliminate its effect on the UV-absorbance.

2.3.9 Adsorption studies

Adsorption studies were carried out by batch process. Solutions of dyes (20 mL) of desired concentrations (10–100 mg L^{-1}) were equilibrated with 0.2 g of adsorbent in 50mL capped glass bottle. The mixtures were kept at room temperature for 24 h. Samples after equilibration were taken for UV-VIS analysis. The samples were analyzed in triplicates and adsorption capacities were calculated.

Chapter 3 MIXED MICELLIZATION AND INTERACTION OF AMPHIPHILES

cmc measurements (Figure 6) have been performed in the mixed aqueous system (12-4-12A + Cationic gemini shown in (scheme. 1) at various mole fractions and data are compiled in Table 1. A pseudo phase separation model has been applied to evaluate how the *cmcs* of binary mixtures (12-4-12A + cationic gemini) deviate from the ideal mixing [22]. The *cmc* values of the mixture (cmc_{exp}) are found lower than the individual components of the mixture (12-4-12A(cmc₁) or (cmc₂).



Figure 6. (*a*) Representative plot of surface tension (γ) vs log C (logarithm of concentration) and (*b*) Plot of specific conductance (κ)) vs [surfactants], of mixed gemini surfactants (16-4-16 + 12-4-12A) at different mole fractions (*x*) of anionic gemini (12-4-12A) in aqueous solution at 303 K

Table 1 Micellization Parameters (Critical Micelle Concentration, CMC) and Interaction Parameters (by Using Rubingh's Method) of Single (Pure) and Mixed (Binary) Gemini Surfactant Systems in Aqueous Solution at 303 K

<i>x</i> _{12-4-12A}	CMC exp	CMC ideal	βm				
	(mM)	(mM)	-				
16-4-16							
0.0	0.0244						
0.2	0.0292	0.0306	-11.87				
0.4	0.0734	0.0395	-				
0.6	0.2822	0.0570	-				
0.8	0.4159	0.1036	-				
1.0	0.5310						
16-Isb-16							
0.0	0.0027						
0.2	0.0031	0.0034	-12.96				
0.4	0.0037	0.0045	-7.90				
0.6	0.0046	0.0067	-8.05				
0.8	0.0099	0.0132	-9.80				
1.0	0.5310						
16-Eda-16							
0.0	0.044						
0.2	0.059	0.0538	-				
0.4	0.141	0.0695	-				
0.6	0.265	0.0978	-				
0.8	0.518	0.165	-				
1.0	0.531						
16-Eg-16							
0.0	0.0034						
0.2	0.0128	0.0042	-				
0.4	0.0052	0.0056	-0.08				
0.6	0.0056	0.0084	-0.42				
0.8	0.003	0.0165	-7.13				
1.0	0.531						

For a mixture of oppositely charged surfactants or surface-active ionic liquid (TPeAB), similar cmc measurements were performed to study interactions. NOSEY experiment has also been performed to established interaction/ intercalation of TPeAB pentyl chain with / into dodecyl chain of 12-4-12A.

Chapter 4. INTERNAL STRUCTURAL MODIFICATION IN SELF-ASSEMBLY OF AQUEOUS MIXED GEMINI SURFACTANT SYSTEMS

Elucidation of the nature of self-assembly and its modification has been studied by various optical (POM and TEM) and scattering methods (SANS and DLS). The analyzed SANS data show the morphological transition on increasing the mole fraction of 12-4-12 A in the mixtures keeping [gemini(s)] (10 mM) constant. Vesicles are formed for various compositions (of the mixtures) having nearly equal mole fractions (0.4 or 0.6) and relevant spacer(s). However, similar

compositions gave nearly rod-shaped morphologies for hydrophilic spacers (Isb/Eg). The data was corroborated by DLS and TEM/ POM micrographs. The information related to neutralization of aggregate charge has been acquired by zeta potential data.



Figure 7. SANS spectra of 10 mM mixed aqueous gemini surfactant systems at different mole fraction of anionic gemini surfactant ($x_{12-4-12A}$) system at 303 K: (*a*) 16-4-16; (*b*) 16-Isb-16



Figure 8. DLS spectra of 10 mM mixed aqueous gemini surfactant systems at different mole fraction of anionic gemini surfactant ($x_{12-4-12A}$) system at 303 K (a) 16-Eda-16 (b) 16-Eg-16.



Figure 9. POM images of 10 mM mixed aqueous gemini surfactant systems at different mole fraction of anionic gemini surfactant ($x_{12-4-12A}$) system at 303 K (a) 0.6 X 12-4-12 (b) 0.6 X 16-4-16.



Figure 10. Negative stained TEM images of aggregates of $X_{12-4-12-A}$ with: (*a*) 0.4 $X_{16-eda-16}(b)$ 0.6 $X_{16-eda-16}(c)$ 0.6 $X_{16-4-16}$

Chapter 5 SOLUBILIZATION OF POLY AROMATIC HYDROCARBONS IN VARIOUS GEMINI SURFACTANT SYSTEMS

Recently, cationic gemini surfactant has been regularly used as one of the components of mixed micelle to achieve the enhanced potential in solubilization, pollutant removal or surface activity. In aqueous surfactant aggregates (micelles or vesicles, solubilization of organic solutes (*e.g.*, higher chain length alcohol or alkane) increases many folds and responsible for a number of surfactant -based applications. In the previous chapter (Chapter 4), various surfactant assemblies are observed depending upon the composition of oppositely charged gemini mixtures (surfactant+ surfactant or surfactant + TPeAB).

It has been found that mixing of cationic gemini, with oppositely charged anionic gemini surfactant, shows increased solubilization of polycyclic aromatic hydrocarbons (PAHs). Further, gemini mixtures shown better solubilization potential over constituting individual components. It was also observed internal modification of aggregates takes place as the composition of each surfactant changed keeping overall total concentration of the mixture constant. Solubilization of PAHs was found more with vesicular aggregates over rod-shaped/ ellipsoidal micellar systems (Table 2).

		MSR						
<i>X</i> 12-4-12-A	Morphology	Anthracene	Fluorene	Pyrene	Phenanthrene			
16-Eda-16								
1.0	Ellipsoidal							
0.8	Ellipsoidal	0.012	0.131	0.041	0.076			
0.6	Vesicles	0.022	0.180	0.096	0.236			
0.5	Vesicles	0.031	0.316	0.170	0.334			
0.4	Vesicles	0.016	0.200	0.102	0.261			
0.2	Ellipsoidal	0.011	0.060	0.062	0.088			
0.0	Ellipsoidal	0.009	0.099	0.057	0.179			
16-Eg-16								
0.8	Ellipsoidal	0.0012	0.106	0.011	0.260			
0.6	Rod	0.0154	0.089	0.008	0.125			
0.4	Rod	0.0051	0.121	0.032	0.109			
0.2	Ellipsoidal	0.0038	0.050	0.007	0.114			
0.0	Ellipsoidal	0.0032	0.101	0.016	0.176			
16-4-16								
0.8	Rod	0.0282	0.0711	0.0576	-			
0.6	Rod	0.0276	0.1078	0.0857	-			
0.4	Vesicle	0.0321	0.2544	0.1706	-			
0.2	Rod	0.0261	0.1486	0.1426	-			
0.0	Rod	0.0257	0.1587	0.1091	-			
16-Isb-16								
0.8	Ellipsoidal	0.0132	0.1889	0.064	-			
0.6	Rod	0.0276	0.1947	0.0653	-			
0.4	Rod	0.0260	0.1683	0.0840	-			
0.2	Ellipsoidal	0.0265	0.1125	0.0596				
0.0	Ellipsoidal	0.0136	0.1281	0.0756				

Table 2. Solubilization Parameter (Molar Solubilization Ratio, MSR of 10 mM Single andMixed Gemini Surfactants in Aqueous Solution at 303 K



Figure 11. Representative UV-Visible spectra of anthracene (a) and Fluorene (b) in 10 mM aqueous mixed gemini surfactant (16-4-16 + 12-4-12A) solution at different mole fractions of anionic gemini ($x_{12-4-12A}$)



Scheme 2. Schematic Representative PAH Solubilization Site in Vesicle Bilayer

Chapter 6. ADSORBTION /EXTRACTION OF VARIOUS ORGANIC COMPOUNDS USING SURFACTANT MODIFIED ADSORBENTS

Water pollution emanates from natural and anthropogenic sources of polycyclic aromatic hydrocarbons, textile finishing, dyeing industries among others. Several types of treatment methods have been proposed in order to address this problem. Among them, adsorption is still the most studied and utilized due to effectiveness, simplicity of design and from the ease of operation point of view. More recently, application of both conventional and engineered materials has received considerable attention to allow the pollutant (e.g., dye or PAHs) adsorption process. To increase the potential of above material, surfactant functionalized adsorbents are used for the adsorption of said pollutants. Mostly, a cationic surfactant is used to get modified adsorbing material. However, the potential of cationic gemini surfactant has not been exploited to achieve pollutant adsorption. Present chapter deals with a comparative study of gemini and conventional surfactants modified adsorbents. Two water soluble dyes are taken and adsorption studies and effect of modification on adsorption by gemini or conventional surfactant is measured (Figure.12)

In another set of experiment gemini+ TPeAB + β -CD system, containing solubilized PAH, is used to study extraction of PAH using liquid-liquid phase separation approach. The PAH, so extracted, concentrates in the surfactant rich phase (scheme 3). The rich phase was treated with GZrO2-NC and data are shown in figure 13.



Scheme 3. Representation of extraction and degradation of PAHs.



Figure 12. Effect of surface modification on adsorption of dyes (a), Effect of [dyes] on % adsorption (b), and adsorption capacity of the adsorbent as a function of [dyes]



Figure 13. UV spectra of Anthracene solubilization in:(*a*, *b*) 2mM 12-4-12 A + 80 mM TPeAB and (*c*,*d*) 2mM 12-4-12 A + 38 mM TPeAB + 7.3 mM β - CD; before (—), after phase separation in surfactant lean phase (—) and after adsorption on GZrO₂ nanocomposite from surfactant rich phase (------).

Chapter 7. OVERALL CONCLUSION

The work embodied in the present thesis allowed to conclude following points:

Gemini surfactant when mixed with oppositely charged amphiphilic molecules can produce mixed micelles due to synergistic interaction (based on cmc measurements and NOSEY NMR data). This mixed micellization causes modification of aggregates assemblies on varying the composition of the two components in the mixture. The mixing of certain composition may cause mixed micellization as well as clouding phenomenon followed by phase separation. These information's have been utilized to enhance the solubilization of various organic compounds with special impetus on PAHs solubilization. Solubilization data allow to conclude that solubility of PAH is dependent on morphology with a particular composition of the mixture. Extraction and possible degradation have been realized using certain surfactant modified natural and synthetic adsorbents.

List of Publications from the work

- Self-Assembly in Aqueous Oppositely Charged Gemini Surfactants: A Correlation between Morphology and Solubilization Efficacy.
 <u>Sneha Singh</u>, Arti Bhadoria, Kushan Parikh, Sanjay Kumar Yadav, Sugam Kumar, V. K. Aswal, and Sanjeev Kumar. J. Phys. Chem. B 2017, 121, 8756–8766
- Mixed Micellization / Clouding Assisted Solubilization of Polycyclic Aromatic Hydrocarbon: Potential in Environmental Remediation.
 <u>Sneha Singh</u>, Sanjay Kumar Yadav, Kushan Parikh, Arpita Desai, Sandhya Dixit and Sanjeev Kumar. Journal of Molecular Liquids 2018 DOI: <u>http://doi.org/10.1016/j.molliq.2018.09.022</u>
- Self-assembly in an aqueous gemini surfactant containing sugar based (isosorbide) spacer. Kushan Parikh, <u>Sneha Singh</u> and Sanjeev Kumar. Arabian Journal of Chemistry 2018 DOI: <u>http://doi.org/10.1016/j.arabc.2018.020</u>
- **4.** Morphology Induced Solubilization Efficacy in Aqueous Oppositely Charged Gemini Surfactants: Role of Spacer/ Composition (Manuscript under preparation).
- **5.** Role of chain length compatibility towards solubilization efficacy of hydrophobic molecules: A case of mixed oppositely charged gemini surfactant. (Manuscript under preparation).

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