Summary of the Thesis Entitled

“Synthesis and Modification of Materials Using Various Surfactants”

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By

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Various organic compounds (polycyclic carcinogenic dyes, agro-chemicals etc.) are well known pollutants. They contaminate eco-system and pose a great threat to mankind. Various strategies are designed (e.g. solvent extraction, precipitation, adsorption and ion-exchange) to address above concerns. Bioremediation showed good promises as a safe and economic option. Poly aromatic hydrocarbon (PAHs) and dyes are two important class of pollutants which are produced due to incomplete combustion of fuel and color based industries (textile, dye manufacturing, pulp/paper), respectively. In order for bacteria to degrade any organic hydrophobic material, it must be made available for uptake by the bacteria [1-3]. Pollutants become bioavailable when they are in either the dissolved or the vapor phase. It has been known that surfactant aggregates can enhanced aqueous solubility and hence biodegradability due to the presence of hydrophobic environment inside the aggregate. Due to above facts, surfactant-enhanced remediation (SER) has been proved a promising technique in removing organic pollutants from water bodies.

Removal of soluble dyes from water is another big challenge. In physical methods, adsorption is one of the most popular technique to recycle contaminated water. In this process role of the adsorbent is of prime importance. However, single adsorbent (both natural and synthetic) cannot be used for every type (organic material, metal ions, organometallics etc) of water pollutants. There is always a need to increase the adsorbent efficacy by adopting physical (*e.g.*, ball-milling) and chemical methods (synthesis of hybrid adsorbent, surface modification, optimization of experimental conditions (pH, dose, temperature, co-adsorbents, *etc*)). Surfactant treated adsorbent has been found one of such effective modifications. Among them cationic surfactant has been used to modify amphiphilicity of the adsorbent surfaces in recent past [4]. Gemini surfactants have slowly replaced conventional surfactants from research arena due to their novel aqueous solution behaviour.

This thesis work was planned to adopt certain strategies: synthesis of adsorbent, modification of adsorbent, modification of solution behaviour of surface active ionic liquid in presence of anionic gemini surfactant, interaction behaviour of two oppositely charged gemini surfactants, internal morphological modification in aqueous mixed geminis. One (or more than one) or another strategy has been used to devise methods (adsorptive removal, extractive removal or micellar induced solubilisation/ co-solubilization) for the removal of dyes or PAHs from the background aqueous solution.

The present thesis comprises of eight chapters. **Chapter 1** contains general introduction related to the research problem together with relevant literature. Material and methods, involved there to acquire research data, are compiled in **Chapter 2**. This is followed by the subsequent chapters (**Chapter 3 - Chapter 7**) that include surface modification and application of adsorbents, clouding behavior of surface active ionic liquids, mixed micellization, morphological modifications and micellar morphology induced PAH solubilization, respectively. Over all conclusion of the work is given in **Chapter 8**

Chapter 1: General Introduction

Surfactants are amphiphilic in nature, containing water soluble (hydrophilic) group (their "heads") and water insoluble (hydrophobic) group (their "tails"). They possess the ability to radicalize alter the surface and interfacial properties and to self-associate themselves into aggregates called ‘micelles’. 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***. The *cmc* can be determined by various physico-chemical methods as shown in Figure 1.

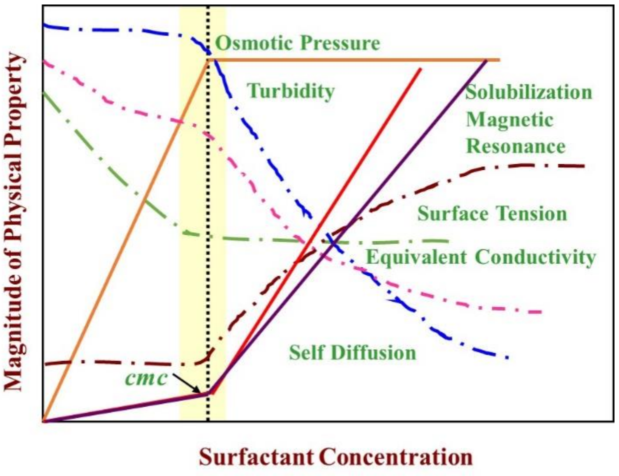


Figure 1. Variation of different physical properties with surfactant concentration (various techniques to find ***cmc***).

Mixing of two or more surfactants in an aqueous solution leads to the formation of mixed micelles. When more than one surfactants are added simultaneously in water, several physicochemical properties of the mixed system compared to those of the single surfactants, are changed. The negative and positive variations from *ideal* ***cmc*** (computed from regular solution theory [5]) indicate synergistic and antagonistic interactions in various surfactant mixtures.

Generally, the solution behaviour of two types of surfactant (ionic and non-ionic) is in sharp contrast with respect to influence of temperature. Non-ionic surfactant solutions (e.g. *CiEj* type, where *i* and *j* are number of carbon atoms in tail and number of oxyethylene group, respectively) cannot withstand elevated temperature and undergo clouding followed by phase separation into two isotropic liquids, surfactant lean and surfactant rich phases, at a well-defined temperature known as ***cloud point (CP)*** [6]. Application of CP has been explored for the extraction of various compounds. The extraction methodology is known as *cloud point extraction methodology* (**CPEM**). CPE has a potential to replace hazardous solvent extracting systems and, therefore, beneficial for green chemistry approaches. It also offers a simple, rapid, sensitive, and inexpensive alternative to other separation or pre -concentration techniques based on organic solvent extraction.

Key property of micelles is to enhance the solubility of organic substances in aqueous solutions by providing multiple sites (Figure 2) of interaction where solutes can partition depending upon the hydrophobic or polar character.

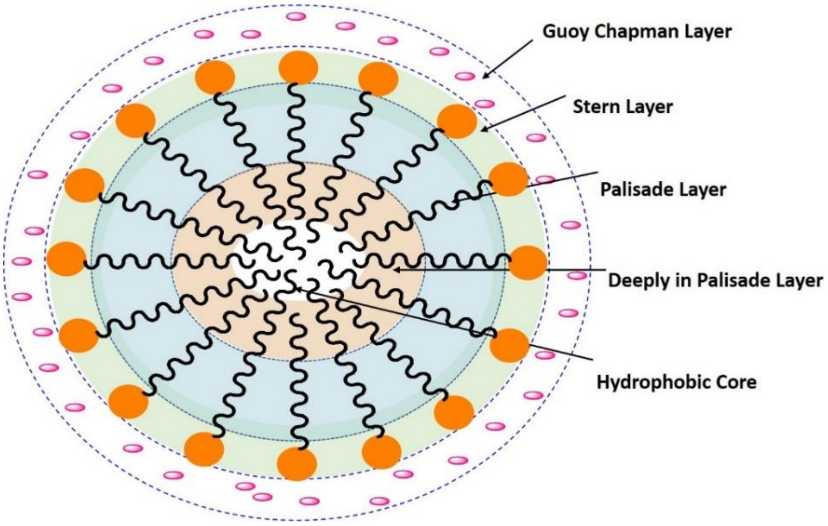


Figure 2. Various solubilization sites of the normal micelle.

The interior of the surfactant micelle acts as an organic pseudo phases of different polarities from head group to core regions. Incorporation of different hydrophobic compounds takes place into the micelles according to their polar / non-polar character. This phenomenon is known as micellar solubilization.

Now days, natural and synthetic adsorbents are modified by various surfactants to improve their performances in order to diminish contamination of hydrophobic material in soil and aqueous bodies [7, 8]. When surfactants are applied for the modification of adsorbent surfaces, they commonly arrange as monolayers or bilayer depending upon their solution concentration. This modification can potentially solubilized or immobilized hazardous hydrophobic materials into the three dimensional architecture formed due to surface modification. It has been reported that gemini surfactant treated clay is more efficient than their conventional counter-parts [9, 10]. Cationic gemini surfactant (CGS) has also been used for the modification of silica and it was observed that the adsorption amount of hydrophobic compound is related to the number of hydrophobic chains in a typical gemini surfactant [11, 12].

Chapter 2: Materials and Methods

Sources of the material are given in Chapter 2. A brief account, of different methods used and synthesis, modification and characterization of bio/ nano-adsorbents has also been given in this chapter. Structures of different compounds are also complied in the same chapter.

Chapter 3: Adsorbtion of anionic azo-dyes using Surfactant modified synthetic and natural adsorbents

This chapter deals with a comparative study of gemini and conventional surfactants modified adsorbents (both synthetic and natural). Two water soluble dyes are taken and adsorption was studied spectrophotometrically. The surface modified adsorbents (graphene-zirconium oxide nanocomposite, Gr@ZrO_2-NC or eggshell powder, EgSP) has been used for the adsorption studies (Figure.3). It has been found that synthetic adsorbent (with or without surfactant) is more efficient than eggshell (EgSP) based adsorbents.

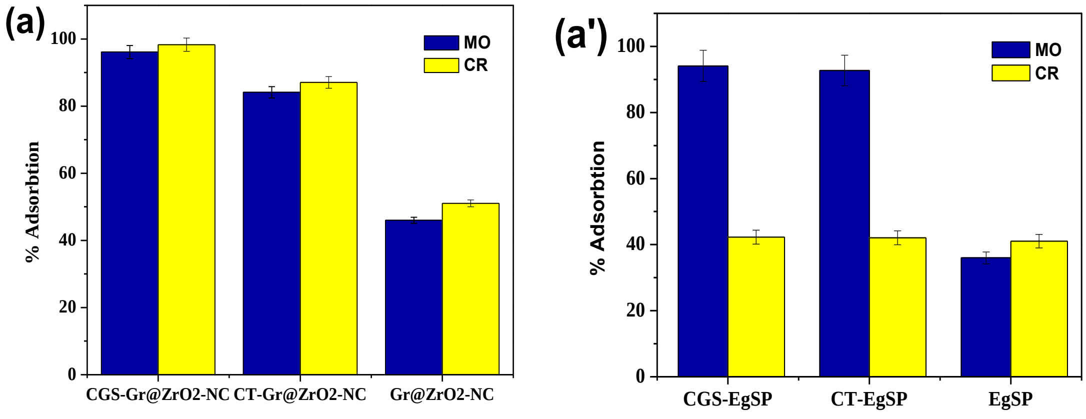
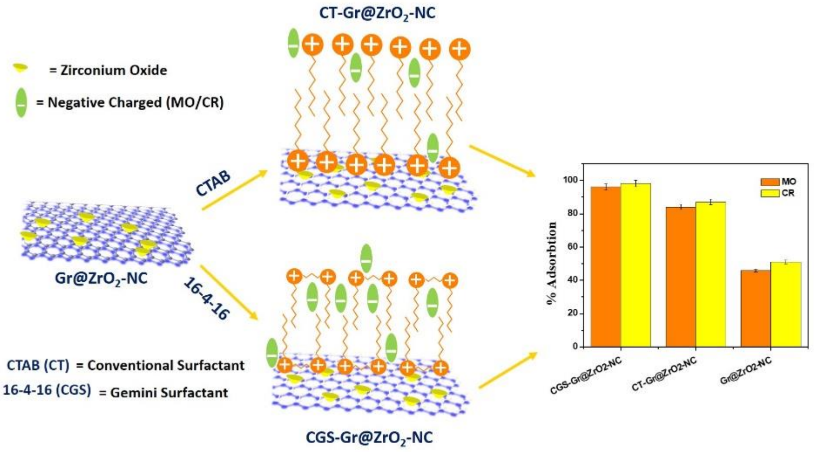


Figure 3 Percent adsorption of anionic azo dyes (MO and CR) on adsorbents with and without surfactant functionalization (a) Gr@ZrO_2-NC and (a') EgSP.

Surfactant based modification of adsorbent and its effect on dye adsorption process is shown in Scheme 1.



Scheme 1. Role of surfactants on percent adsorption of Dyes

The adsorption process follows Langmuir isotherm and kinetic data can be treated by pseudo-second order model. The re-usability of the adsorbent was demonstrated by desorbing the adsorbed dye. Maximum desorption was achieved by using ethylene glycol. It has been seen that adsorbent, when gently hold on a cotton pad (of thickness < 0.5 cm), shows nearly complete removal of each dye without interacting or leaving any colored spot on the pad (Figure 4). This information can be utilized in designing prototype filters to remove aqueous organic pollutants (dyes in particular) from the outlets of various industries.

Figure 4. Proto type pictorial diagram for the auto- removal of dye (MO or CR) using CGS-Gr@ZrO_2-NC (< 0.5 cm) placed on cotton pad.

Chapter 4: Solution behavior of anionic Gemini modified surface active ionic liquid: interaction; clouding and solubilization

Micellization and CP behaviors of a SAIL (tetra-n-pentyl ammonium bromide, TPeAB) have been studied in the presence of an anionic gemini surfactant, 12-4-12A in aqueous solution. Cmc and NMR data (Figures 5 and 6) suggest about the degree of non-ideality of the interaction in the mixed micelle using Rubingh's Non-ideal solution theory [5]. Various quaternary bromides were added to the 12-4-12A solution, only TPeAB have shown clouding phenomenon at certain specific compositions. This composition was further optimized with the help of biomolecules (amino acids and cyclodextrin).

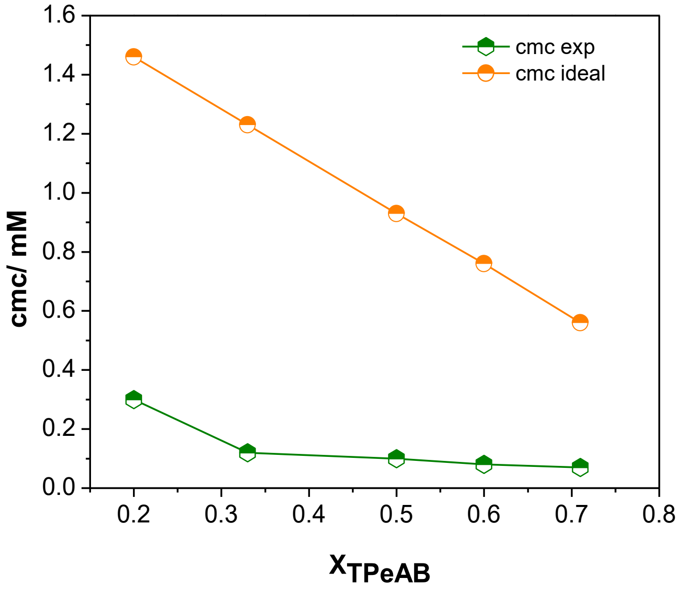


Figure 5. Critical micelle concentration (*cmc*, by conductometrically) variation of mixed system (12-4-12A + TPeAB) with mole fraction of TPeAB (x_{TPeAB}) in aqueous solution at 30 °C. The plot represents experimental and ideal values (calculated from Clint model).

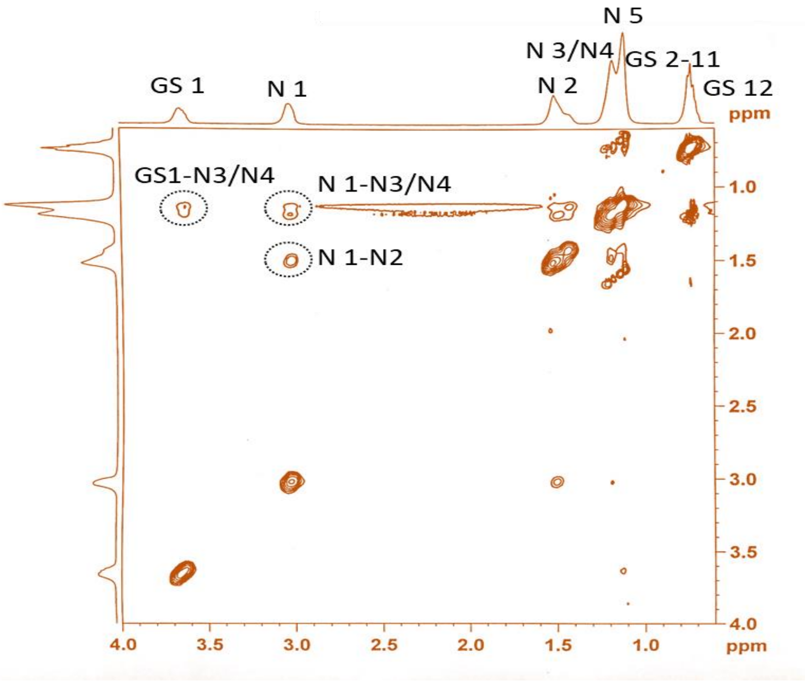
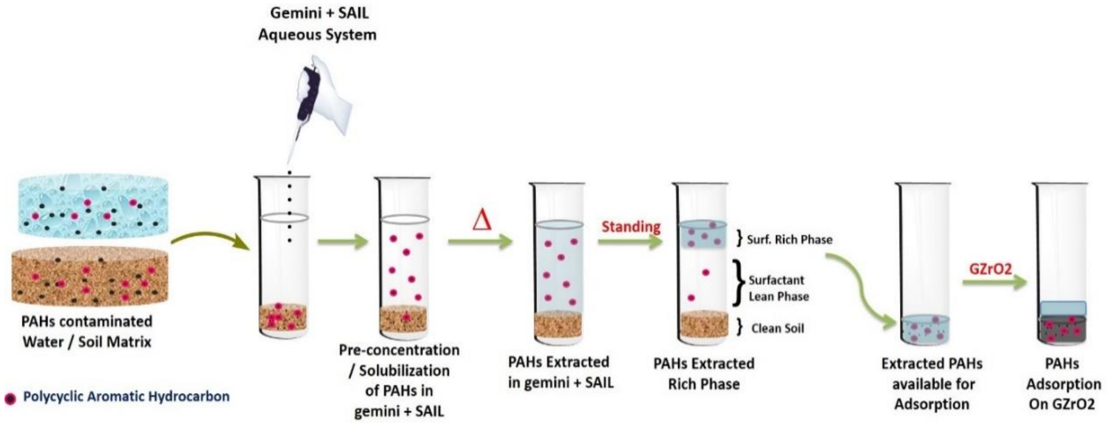


Figure .6 2D NOESY ^{1}H NMR spectra of the mixed system (2 mM 12-4-12 A + 2 mM TPeAB) in D_2O.

DLS, POM and TEM data were acquired to gain information related to the morphology of the mixed system at ambient temperature and near the cloud point. A few such optimized systems were used for solubilization/ co-solubilization studies with various PAHs. These solubilized systems were used for cloud point extraction of above PAH in the surfactant-rich phase (SRP). Gr@ZrO_2-NC has shown good adsorption capacity for PAH. The solubilized/adsorptive removal of nearly water insoluble PAHs may find application for recharging of aquatic/ solid soil matrices (Scheme 2).



Scheme 2. Representation of extraction and degradation of PAHs.

Chapter 5: Mixed Micellization and Interaction of oppositely charged Gemini surfactants

cmc measurements (Figure 7) have been performed in the mixed aqueous system (12-4-12A + Cationic geminis) at various mole fractions and data are compiled in Table 1. A pseudo phase separation model has been applied to evaluate how the *cmc*s of binary mixtures (12-4-12A + cationic gemini) deviate from the ideal mixing [5]. The *cmc* values of the mixture (cmc_{exp}) are found lower than the individual components of the mixture (cmc_1) or (cmc_2) (Figure 8).

The higher the negative magnitude of β^m, stronger is the synergistic interaction between the two gemini components. The perusal of data of Table 1. indicates that β^m shows a dependency on the nature of the spacer present in the cationic gemini surfactant and hints toward stronger attractive interactions with cationic gemini surfactant.

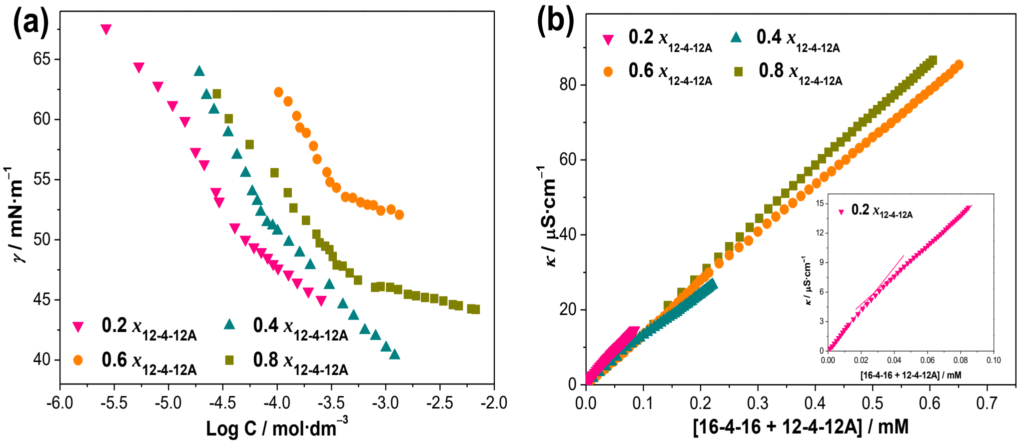


Figure 7. (*a*) Representative plot of surface tension (γ) *vs* log C (logarithm of concentration) and (*b*) Plot of specific conductance (κ)) *vs* [surfactants], of mixed gemini surfactants (16-4-16 + 12-4-12A) at different mole fractions (x) of anionic gemini (12-4-12A) in aqueous solution at 303 K

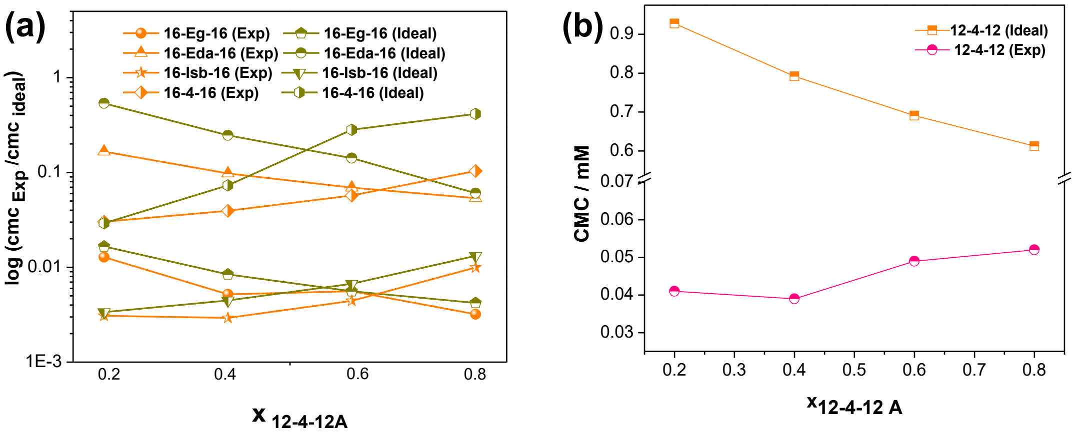


Figure 8. Critical micelle concentration (CMC) by conductometry with a variation of mixed surfactant systems (cationic-anionic) with a mole fraction of anionic gemini surfactant ($x_{12\text{-}4\text{-}12A}$) in aqueous solution at 303 K. The plot represents experimental and ideal values (calculated from ideal mixing model).

Table 1. Micellization parameters (cmc_{exp} and cmc_{ideal}) and interaction parameter (**β^{m}**, by Rubingh's method) of mixed gemini surfactant systems in aqueous solution at 303 K.

	16-4-16			**16-Isb-16**			**16-Eda-16**			**16-Eg-16**		
$x_{12\text{-}4\text{-}12A}$	**cmc_{exp}**	**cmc_{ideal}**	**β^{m}**	**cmc_{exp}**	**cmc_{ideal}**	**β^{m}**	**cmc_{exp}**	**cmc_{ideal}**	**β^{m}**	**cmc_{exp}**	**cmc_{ideal}**	**β^{m}**
	(mM)			**(mM)**			**(mM)**			**(mM)**		
0.0	0.0244	-	-	0.0027	-	-	0.044	-	-	0.0034		
0.2	0.0292	0.0306	-11.87	0.0031	0.0034	-12.96	0.059	0.0538	-	0.0128	0.0042	-
0.4	0.0734	0.0395	-	0.0037	0.0045	-7.90	0.141	0.0695	-	0.0052	0.0056	-0.08
0.6	0.2822	0.0570	-	0.0046	0.0067	-8.05	0.265	0.0978	-	0.0056	0.0084	-0.42
0.8	0.4159	0.1036	-	0.0099	0.0132	-9.80	0.518	0.165	-	0.003	0.0165	-7.13
1.0	0.5310	-		0.5310	-	-	0.531	-	-	0.531		

Elucidation of the nature of self-assembly and its modification has been studied by various techniques, TEM, 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 (Figure 9). Vesicles are formed for various compositions (of the mixtures) having nearly equal mole fractions (0.4 or 0.6) and relevant spacer(s) (Figure 10). However, similar compositions gave nearly rod-shaped morphologies for hydrophilic spacers (Isb/Eg). The data was corroborated by DLS (Figure 10) and TEM micrographs (Figure 11). The information related to neutralization of aggregate charge has been acquired by zeta potential data (Figure 12).

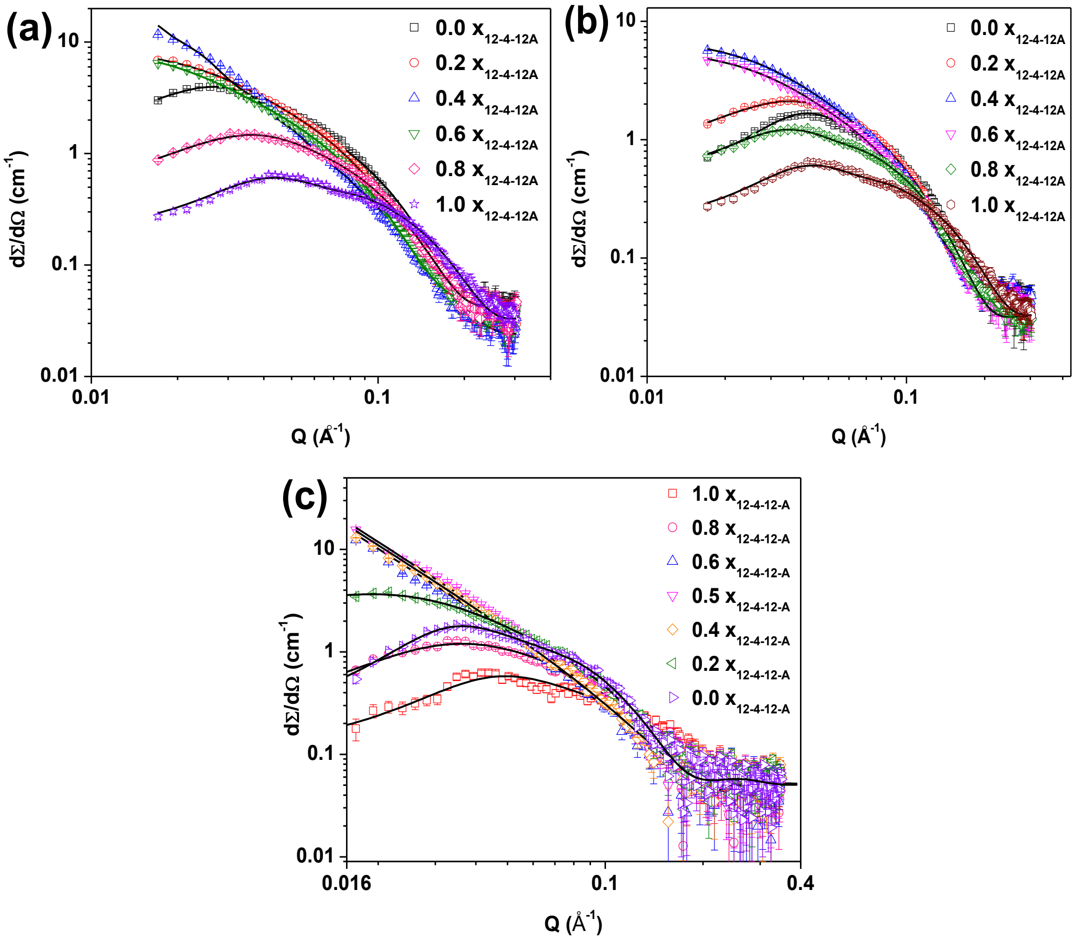


Figure 9. SANS spectra of 10 mM mixed aqueous gemini surfactant systems at different mole fraction of anionic gemini surfactant ($x_{\mathbf{12\text{-}4\text{-}12A}}$) system at 303 K: (*a*) 16-4-16; (*b*) 16-Isb-16 and (c) 16-Eda-16.

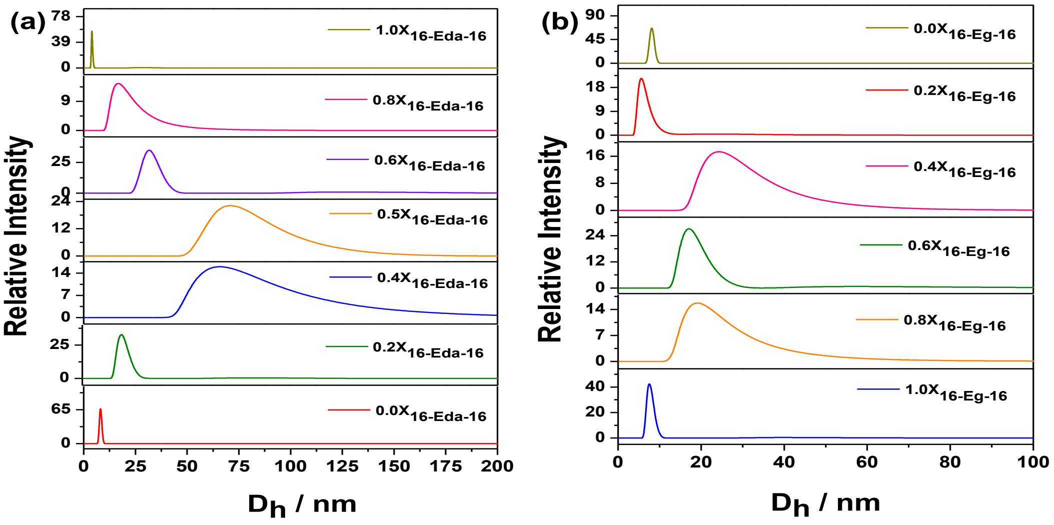


Figure 10. DLS spectra of 10 mM mixed aqueous gemini surfactant systems at different mole fraction of anionic gemini surfactant ($x_{12\text{-}4\text{-}12A}$) system at 303 K (a) 16-Eda-16 (b) 16-Eg-16.

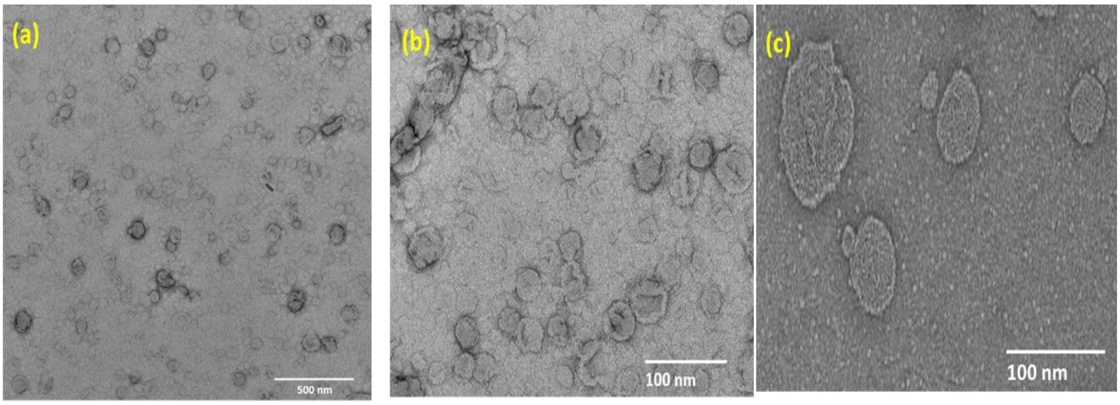


Figure 11. Negative stained TEM images of aggregates of $X_{12\text{-}4\text{-}12\text{-}A}$ with: (*a*) 0.4 $X_{16\text{-}eda\text{-}16}$ (*b*) 0.6 $X_{16\text{-}eda\text{-}16}$ (c) 0.6 $X_{16\text{-}4\text{-}16}$

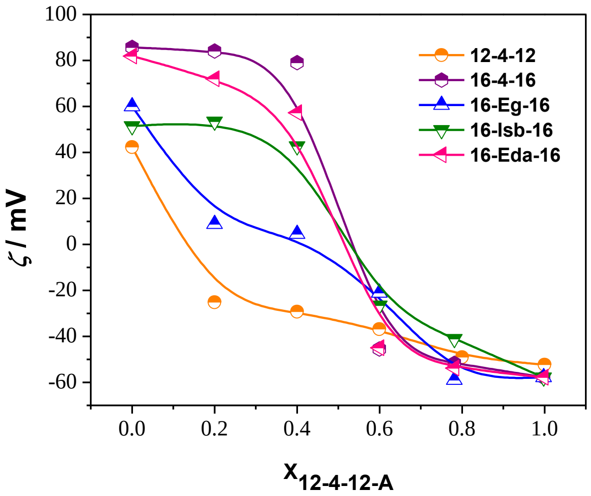


Figure 12. Zeta (ζ) – potential data of 10 mM mixed gemini surfactant aqueous systems at a different mole fraction of anionic gemini surfactant ($x_{\mathbf{12\text{-}4\text{-}12A}}$) in aqueous solution at 303 K.

Mixing increases the surfactant packing parameter (*P*), of the so-called *single surfactant* (cationic + anionic geminis). Zeta potential data show the formation of aggregates of lower charge together with charge reversal. Variations in *P*, spacer nature, chain-length and |charge| decide the type of the aggregates to be formed. However, composition between 0.4 to 0.6 (mole-fraction) shows moderate charge together with the formation of higher order aggregates e.g., vesicles, as observed by SANS, DLS and TEM. Influence of heating has been found to be dependent on the hydrophobic/ hydrophilic nature of the spacer. The morphologies so formed, by mixing different combinations, are exploited for the enhancement of aqueous solubility of, other-wise very less soluble organic compounds (e.g., PAHs, **Chapter 7**).

Chapter 7: Solubilization of poly aromatic hydrocarbons in various morphologies based on mixed gemini surfactants

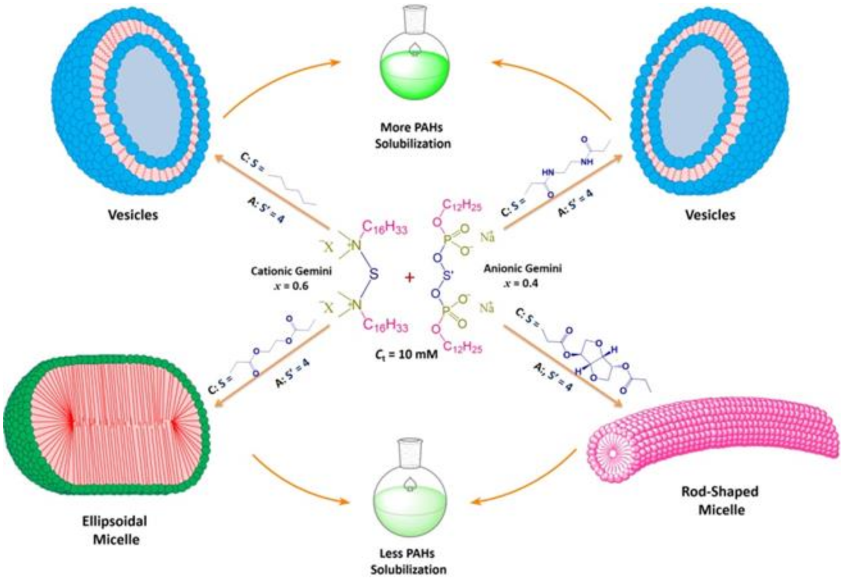
It has been found that mixing of cationic gemini, with oppositely charged anionic gemini surfactant, shows increased solubilization of polycyclic aromatic hydrocarbons (PAHs). Further, gemini mixtures shown better solubilization potential (higher MSR value, Table.2) over constituting individual components.

Table 2. Solubilization parameters (molar solubilization ratio, MSR; micelle-aqueous phase partition coefficient, ln K_m; Gibbs free energy, ΔG^o_s) of 10 mM single and mixed gemini surfactants in aqueous solution at 303 K.

$x_{12\text{-}4\text{-}12\text{-}A}$	**Morphology**	***Anthracene***			***Pyrene***			***Fluorene***			***Phenanthrene***		
		MSR	**ln K_m**	**$-\Delta G_s$ KJmol^{-1}**	**MSR**	**ln K_m**	**$-\Delta G_s$ KJmol^{-1}**	**MSR**	**ln K_m**	**$--\Delta G_s$ KJmol^{-1}**	**MSR**	**lnK_m**	**$--\Delta G_s$ KJmol^{-1}**
						16-4-16							
1.0	Ellipsoidal	0.026	8.86	22.33	0.038	10.15	25.58	0.091	10.36	26.09	0.049	9.49	23.92
0.8	Rod	0.028	8.94	22.52	0.058	15.07	37.98	0.071	9.82	24.74	0.152	10.63	26.78
0.6	Rod	0.028	8.91	22.46	0.086	21.84	55.05	0.108	10.20	25.71	0.223	11.05	27.85
0.4	Vesicle	**0.032**	9.06	22.83	**0.171**	40.32	101.62	**0.254**	10.94	27.56	**0.233**	11.01	27.74
0.2	Rod	0.026	8.84	22.29	0.143	34.53	87.03	0.149	10.49	26.42	0.081	9.99	25.19
0.0	Rod	0.026	8.84	22.29	0.109	27.22	68.60	0.159	10.54	26.57	0.190	10.84	27.33
						16-Isb-16							
0.8	Ellipsoidal	0.013	8.18	20.62	0.064	16.64	41.94	0.189	10.69	26.91	0.045	9.39	23.67
0.6	Rod	**0.028**	8.91	22.46	0.065	16.96	42.75	**0.195**	10.72	27.01	**0.142**	10.55	26.59
0.4	Rod	0.026	8.86	22.32	**0.084**	21.44	54.04	0.168	10.59	26.69	0.096	10.16	25.60
0.2	Ellipsoidal	0.027	8.87	22.37	0.060	15.56	39.22	0.113	10.24	25.80	0.072	9.87	24.88
0.0	Ellipsoidal	0.014	8.21	20.69	0.075	19.45	49.02	0.128	10.35	26.09	0.079	9.97	25.11

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 (Chapter 6).

All PAHs show enhanced aqueous solubility in micellar or mixed micellar systems (solubility follow the order: water < micellar solution < mixed micellar solution). Analysis of MSR data clarify that mixed systems, with vesicle morphology, solubilized PAH preferentially over rod-shaped or ellipsoidal (spherical) micelle. Since morphologies are dependent on spacer nature (or chain length of the alkyl tail), magnitude of solubility enhancement (**Scheme 2**) can directly be correlated with molecular architecture of cationic gemini surfactant (as other component, 12-4-12A, is common for all the combinations). Among PAHs, solubilization efficacy of the surfactant systems is dependent on the polarity and site of solubilization (of the PAH). MSR (of co-solubilized PAHs) also gives an idea about the variation of solubility of a PAH in the presence of other one.



Scheme 2. Morphology dependent PAH solubilization

Chapter 8: Overall Conclusion

Based on the studies performed in the whole thesis, it can be said that surfactant is a good candidate to modify various types of material. Surfactant, not only enhances the material efficacy, also changes solution behavior of a typical surface active ionic liquid. Presence of surfactant at the surface or in the solution provides hydrophobicity which works behind transporting or mobilization of water soluble or insoluble materials towards adsorbent surface or aggregate interior. Mixing of geminis totally changes the internal micellar morphologies with a concomitant change in interaction pattern as well as aggregate structure. These changes can judiciously tuned with the help of variations in composition, spacer nature, alkyl tail-length or experimental conditions. Overall data embodied in the thesis can be utilized for various water remediation process by adopting different methodologies such as cloud-point extraction, micellar induced solubilization and surface modified adsorptive removal of various contaiminants.

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List of Publications from the Thesis:

1. **S. Singh**, A. Bhadoria, K.Parikh, S. K. Yadav, S. Kumar, V. K. Aswal, and S. Kumar, Self-Assembly in Aqueous Oppositely Charged Gemini Surfactants: A Correlation between Morphology and Solubilization Efficacy. *J. Phys. Chem. B* 2017, 121, 8756−8766.
2. **S. Singh**, S. K. Yadav, K. Parikh, A. Desai, S. Dixit and S. Kumar, Mixed Micellization / Clouding Assisted Solubilization of Polycyclic Aromatic Hydrocarbon: Potential in Environmental Remediation. *J. Mol. Liq.* 2018, 272, 413-422.
3. **S.Singh**, K.Parikh, S.Kumar, V.K. Aswal and S. Kumar, Spacer nature and composition as key factor for structural tailoring of anionic/cationic mixed Gemini micelles: Interaction and solubilization studies, *J. Mol. Liq.* 2019, 279, 108-119.
4. **S.Singh,** K. Parikh, S.Kumar, Gemini Functionalized Graphene Zirconium Oxide Nanocomposite: Implication in Adsorptive Removal of Anionic Azo Dyes (manuscript under preparation)
5. **S.Singh,** Debes Ray, V.K. Aswal, S.Kumar, Role of Chain-length Compatibility in the Self Assembly Formation of Anionic-Cationic Gemini Surfactant. (manuscript under preparation)

List of Publications not included in Thesis:

6. K. Parikh, **S. Singh** and S. Kumar, An interplay between spacer nature and alkyl chain length on aqueous micellar properties of cationic Gemini surfactants: A multi-technique approach, *J. Mol. Liq.* 2019, 278, 290-298.
7. K. Parikh, **S. Singh** and S. Kumar, Self-assembly in an aqueous gemini surfactant containing sugar based (isosorbide) spacer, *Arab. J. Chem.* 2018 DOI: http://doi.org/10.1016/j.arabc.2018.020.
8. **S. Singh**, B. R. Singh, W. Khan, A. H. Naqvi. Synthesis andcharacterization of carbon nanotubes/titanium molybdate nanocomposite andassessment of its photocatalytic activity. *J. Mol. Struct*. 2014, 1056–1057 , 194–201
9. R. A. K. Rao , **S. Singh** , B. R. Singh , W. Khan , A.H. Naqvi, Synthesis and characterization of surface modified graphene–zirconium oxide nanocomposite and its possible use for the removal of chlorophenol from aqueous solution. *Journal of Environmental Chemical Engineering*, 2014, 2, 199–210.
10. J. A. Khan, Md. Qasim, B. R. Singh, **S. Singh**, Md. Shoeb, W. Khan, D. Das, A. H. Naqvi. Synthesis and characterization of structural, optical, thermal and dielectric properties of polyaniline/CoFe2O4 nanocomposites with special reference to photocatalytic activity. *Spectrochim Acta. A*, 2013, 109, 313–321.