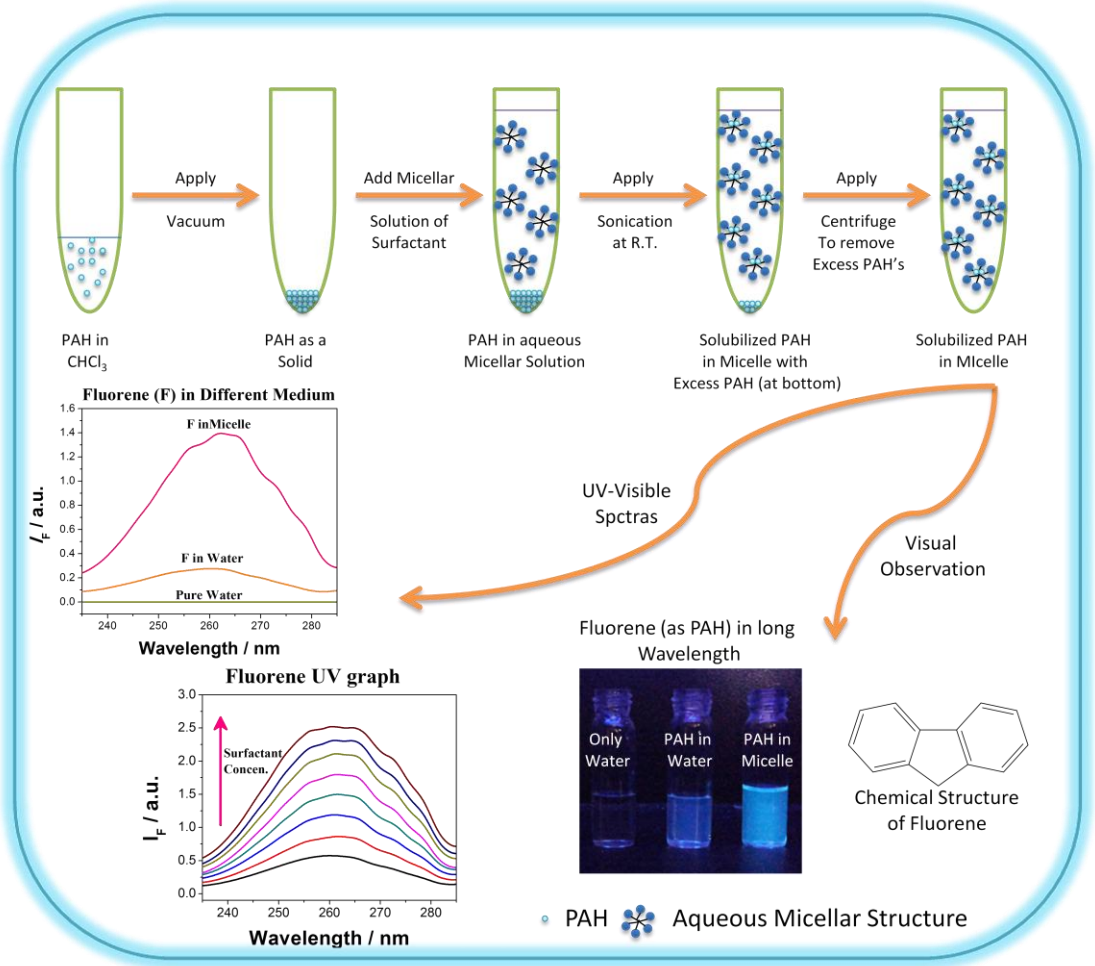
Chapter 5

Solubilization of Polycyclic Aromatic Hydrocarbons (PAHs) in Aqueous Gemini Micelle



5.1. Introduction

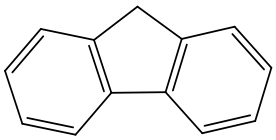
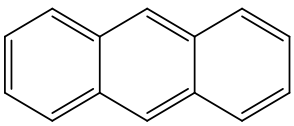
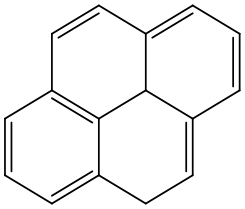
Environmental concerns are contamination of soil and sediment / ground water (mainly drinking) by some man-made organic pollutants / activities [1]. Polycyclic aromatic hydrocarbon (PAH) is one of the threatening organic pollutants which have many hazardous effects (carcinogenic and mutagenic) on mammalian (particularly on human) health [2]. PAHs, composed of fused aromatic rings of linear, cluster or angular arrangement, are generally formed by natural anthropogenic pyrolysis of organic matter during fossil fuel (oil and coal), forest fires, cooked meat (at high temperature) and chemical manufacturing [1, 3]. Once formed, PAHs can widely spread into environment and easily transfer through atmosphere or water, and in the end accumulate in soils / sediments (ultimately in food chain) for a long time which is hazardous to the ecosystem [1*a*, 4]. Due to low bioavailability, higher sorption with soil particle and lower aqueous solubility, researchers have used various physical, chemical and biological treatments for removal of PAHs from soil [5]. Among them, surfactant / micellar system is one of the most promising and cost effective method for improvement of PAHs aqueous solubility with a better remediation technique.

In last two decades, conventional surfactants (above their cmc) have been extensively used for PAHs solubilization in a number of studies [6]. A new class of surfactant, gemini surfactant, have also gained a lot of interest especially in PAHs solubilization due to their better physico-chemical properties [7]. Few research groups have studied solubilisation of PAHs by gemini surfactants and their binary mixtures with conventional cationic, anionic or non-ionic surfactants [6*h*, 8]. Study revealed that solubilization efficiency of gemini surfactants is much higher than their single chain counterparts [9]. Gemini surfactants (***m*-*s*-*m***) or their binary mixtures may improve the PAHs solubility but again contaminate the soil and sediments

significantly. This can be avoided by introduction of biocompatible group in the architecture of gemini surfactant. In this direction, Kabir-ud-Din and co-workers [8*j* and *l*] have used cleavable spacer based gemini surfactants and their binary mixtures with conventional (non-degradable) surfactants to improve the PAHs solubilization. As can be seen, very little work has been made in this direction of solubilization with biocompatible spacer based gemini micelles. This prompted to check PAHs solubilization in the synthesized biocompatible spacer based cationic gemini surfactants (Chapter 2).

In this Chapter, three most common PAHs (fluorene, anthracene and pyrene-see Table 1) have been used for solubilization in micellar solutions above their cmcs at 298 K. Both gemini and conventional surfactants are used to compared solubilization data.

Table 1. Structural formula and properties of polycyclic aromatic hydrocarbons (PAHs).

PAHs	**Chemical structure**	**M.W.**[a] **gm/mol**	**Solubility**[b] **mol/L**	**Log K_{ow}**[c]
Fluorene (fluo) $C_{13}H_{10}$		166.22	1.98×10^{-5}	4.18
Anthracene (anth) $C_{14}H_{10}$		178.23	2.53×10^{-7}	4.45
Pyrene (pyre) $C_{16}H_{12}$		204.27	6.57×10^{-7}	5.18

[a]Molecular weight
[b]Aqueous solubility at 25°C
[c]Octanol-water partition co-efficient

5.2. Materials and Method

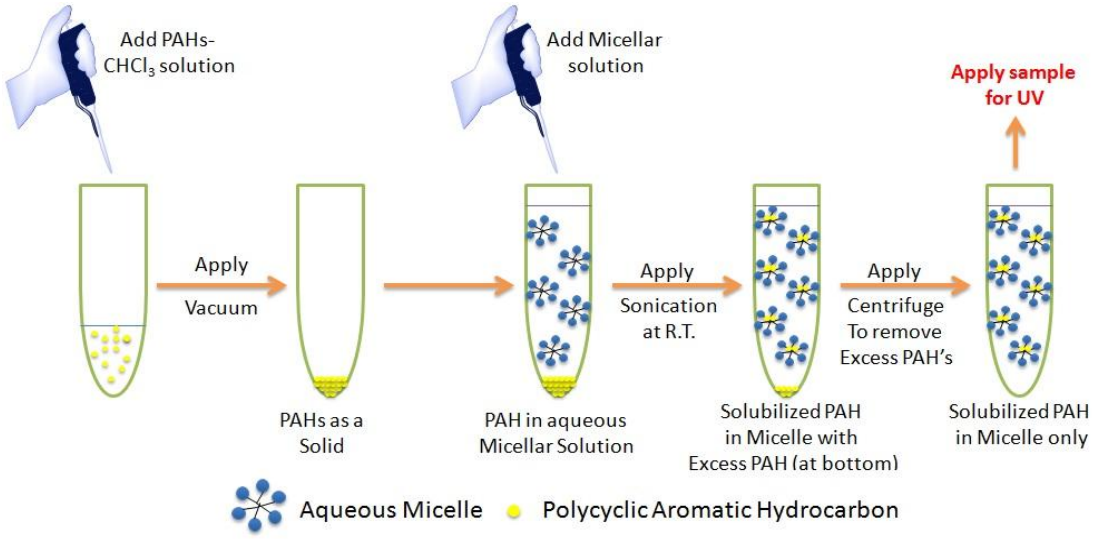
5.2.1. Materials

Rectified spirit (95% ethanol), polycyclic aromatic hydrocarbons (fluo, anth and pyre) were purchased from Sigma-Aldrich and TCI chemicals and used as received. PAHs structures along with their physical properties are compiled in Table 1. $CHCl_3$ and de-ionized double distilled water were the same as used in Chapter 4.

5.2.2. Methods

5.2.2.1. UV-Visible Spectroscopy

Aqueous solubility of PAH has been checked by using conventional as well as gemini surfactants at different concentrations (above their cmcs) using excess amount of PAH. After preparation of the sample solution, it was sonicated (Toshniwal instruments, India) for 5-10 minutes (several times with an interval of 30 minutes) at 298 K followed by centrifuging (4000 rpm) to remove excess PAHs (Scheme 1).



Scheme 1. Schematic representation of solubilization of polycyclic aromatic hydrocarbons (PAHs) in aqueous micellar solution through sonication.

The solubilized PAHs in micellar solution were analyzed at a maximum wavelength by UV-visible spectrophotometer (Perkin Elmer spectrometer, Lambda 35) using a quartz cell of path length 1 cm. The concentration of surfactant was kept the same in both the reference and measurement cell to eliminate its effect on the UV-absorbance. The uncertainty of the measurements was within 2-5%. Concentrations of PAHs were calculated using Lambert-Beer law ($A = \varepsilon cl$, where, A - abosbance, c - concentration, l – cell path length, ε - molar extinction coefficients used as such for all PAHs reported earlier [6*d*, 10]).

5.3. Results and Discussion

5.3.1. Solubilization of PAHs

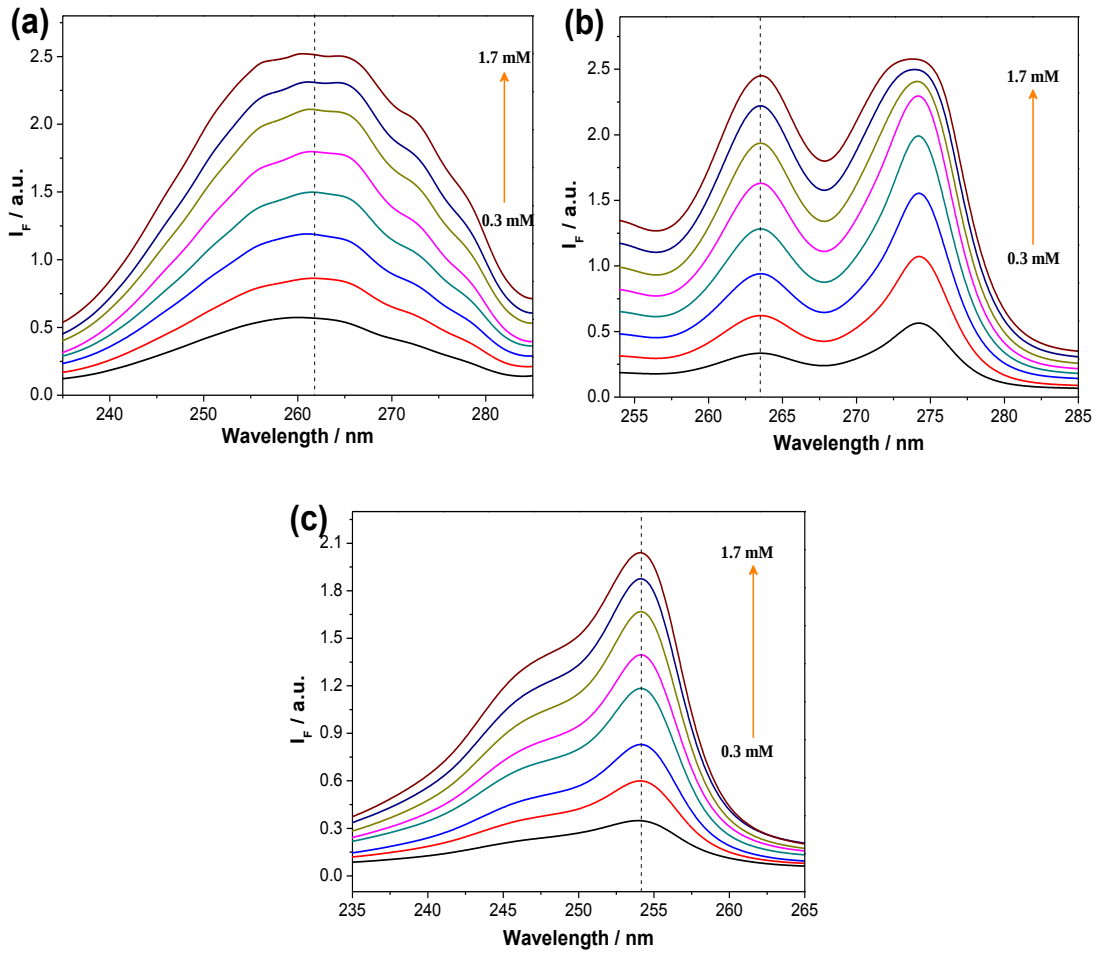


Figure 1. UV-Visible spectra at 298 K of (*a*) fluorene (λ_{max} = 261-262 nm, ε = 2.15 x 10^4 $M^{-1}cm^{-1}$), (*b*) pyrene (λ_{max} = 264 nm, ε = 4.71 x 10^4 $M^{-1}cm^{-1}$), (*c*) anthracene (λ_{max} = 254, ε = 1.82 x 10^5 $M^{-1}cm^{-1}$) nm in aqueous micellar solution of [14-Isb-14].

PAHs / organic compounds (fluorene, fluo; anthracene, anth; pyrene, pyre) are having very less solubility in pure water (Table 1). It can be improved via their incorporation into micelles (above their cmcs) in surfactant solution. This phenomenon is called micellar solubilization [11]. Absorbance of PAH has been found to increase with increase of 14-Isb-14 concentration (Figure 1). Similar solubilization experiments are also performed with other gemini / conventional surfactants to obtain the absorbance data.

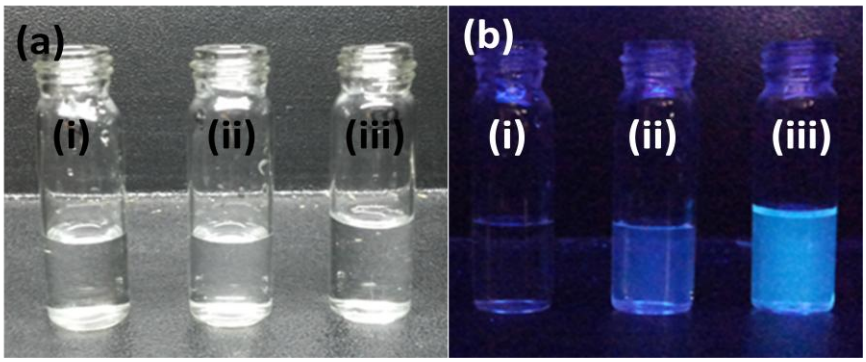


Figure 2. Visual observation of fluorene (fluo) solubilization, pure water (i), fluo in water (ii), fluo in micelle (iii): (*a*) visible light; (*b*) long UV wavelength (365 nm).

Visual appearances of the PAH (fluorene) aqueous solution with and without surfactant are shown in Figure 2. This visual appearance clearly shows the enhancement of amount of PAH (qualitatively) in a typical micellar solution.

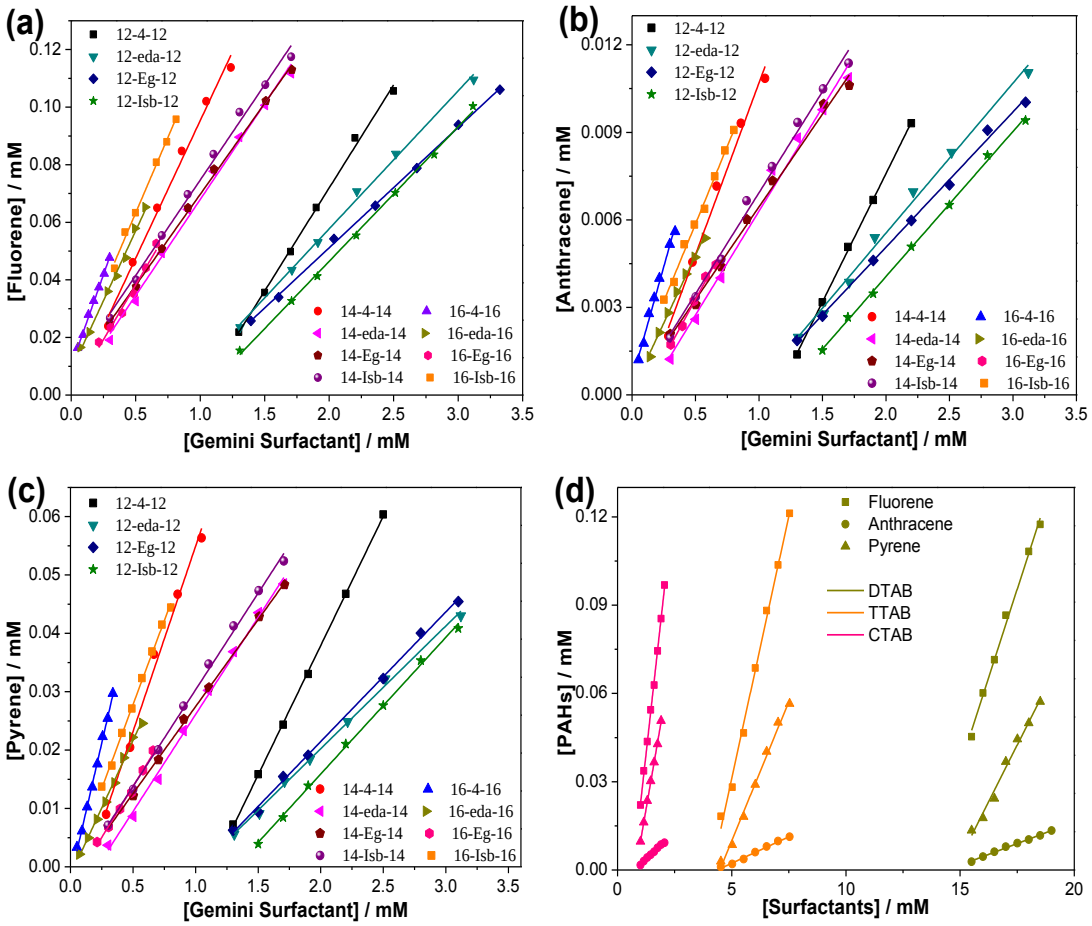


Figure 3. Variation of solubility of (*a*) fluorene, (*b*) anthracene and (*c*) pyrene with cationic gemini surfactant concentrations; (*d*) PAHs with conventional cationic surfactants (C_mTAB) concentrations, in aqueous solution above their cmc at 298 K.

Concentrations of PAHs were calculated by the absorbance of solutes in micellar solution (Figure 1), which was evaluated using respective ε (using Lambert-Beer law). Solubility data of PAHs are plotted against [surfactant] (Figure 3). Solubility increases linearly with [surfactant] which suggest good enhancement of solubility in surfactant solutions. The increased solubilization is due to the incorporation / partitioning of PAH within the surfactant micelle.

Molar solubilization ratio (MSR) [12], number of moles of PAH solubilized per mole of surfactant, can be obtained from the slope of the linear plot (Figure 3, least square linear correlation, R^2 = ~ 0.9900-0.9990). The MSR can also be represented by the following equation,

$$MSR = (S_a - S_{CMC}) / (C_s - CMC) \quad (1)$$

Where, S_a is the apparent solubility of a typical PAH at the particular surfactant concentration (C_s). S_{CMC} is the apparent solubility of the compound at the cmc (which can be taken equivalent to aqueous solubility, Table 1). Solubilization can also be described in terms of micelle-aqueous phase partition coefficient (K_m). Micellar interior (non-polar core) is responsible for the solubilization and K_m should be approximately proportional to the non-polar contents of the surfactant. K_m is the ratio of the mole fractions of the solubilizate in the micellar phase (X_m) to the aqueous phase (X_a) [13].

$$K_m = \frac{X_m}{X_a} \quad (2)$$

The value of the X_m and X_a can be obtained from MSR/(1+MSR) and $S_{CMC}V_m$, respectively, where V_m is the molar volume of water equal to 0.01805 l/mol at 298 K. Therefore, K_m can be written as,

$$K_m = \frac{MSR}{S_{CMC}V_m(1 + MSR)} \quad (3)$$

The calculated values of MSR and K_m for all the PAHs are listed in Table 2. From the MSR and ln K_m values (Table 2), it can clearly be seen that more effective solubilization of PAHs has been found in single gemini (dimeric) surfactants compared to their identical chain length monomeric counterparts. This may be due to more non-polar environment produced by gemini micelle (friendly atmosphere for PAHs) and their lower cmcs (than the conventional surfactants) [8*j* and *l*, 14].

Table 2. Solubilization parameters (molar solubilisation ratio, MSR; micelle-aqueous phase partition coefficient, ln K_m; Gibbs free energy, ΔG^o_s) of cationic conventional (C_mTAB) and gemini surfactants (***m*-*s*-*m***) at 298 K.

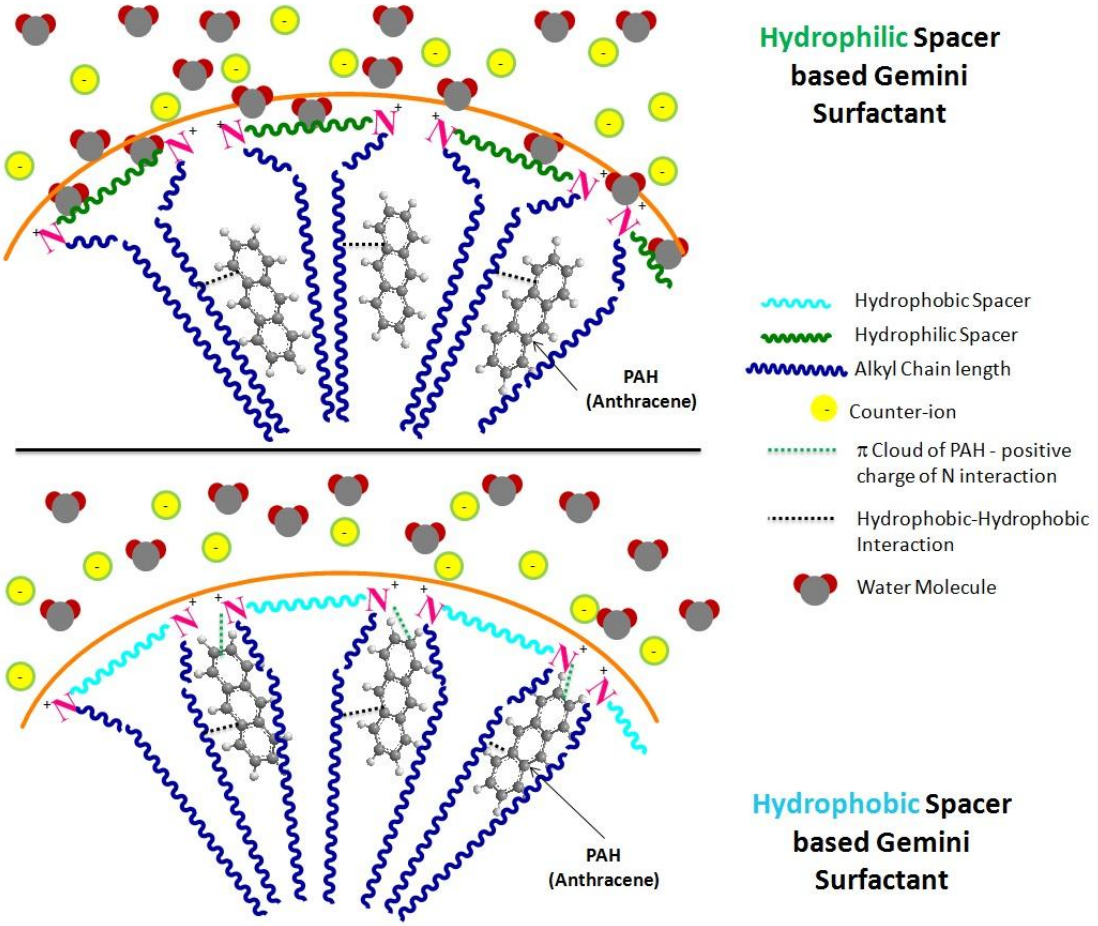
Surfactant	**Fluorene**			**Anthracene**			**Pyrene**		
	MSR	ln K_m	$-\Delta G^o_s$ kJ·mol^{-1}	MSR	ln K_m	$-\Delta G^o_s$ kJ·mol^{-1}	MSR	ln K_m	$-\Delta G^o_s$ kJ·mol^{-1}
DTAB	0.0241	10.27	25.44	0.0030	10.97	27.18	0.0154	11.04	27.35
TTAB	0.0357	11.66	28.89	0.0036 0.0005[c]	12.16	30.13	0.0189	12.76	31.62
CTAB	0.0698	12.01	29.75	0.0073 0.0043[e]	12.40	30.71	0.0450 0.0139[e]	12.41	30.76
12-4-12	0.0716 0.049[a]	12.04	29.83	0.0088	12.76	31.63	0.0443	12.69	31.44
14-4-14	0.0955	12.21	30.26	0.0118	12.68	31.41	0.0635	12.82	31.75
16-4-16	0.1271	12.85	31.84	0.0155 0.013[e]	13.46	33.35	0.0932 0.035[e]	14.16	35.09
12-Eda-12	0.0479	11.59	28.71	0.0051	11.87	29.42	0.0210	12.23	30.30
14-Eda-14	0.0666	12.11	30.00	0.0071	12.68	31.40	0.0333	13.09	32.42
16-Eda-16	0.0972	12.60	31.22	0.0093	12.88	31.90	0.0463	13.94	34.53
12-Eg-12	0.0418	11.37	28.16	0.0046 0.0067[b]	11.83	29.30	0.0222 0.0183[b]	12.17	30.14
14-Eg-14	0.0633	11.80	29.23	0.0064	12.04	29.83	0.0298	12.36	30.62
16-Eg-16	0.0760	12.58	31.16	0.0080 0.0014[d]	13.04	32.31	0.0349 0.0408[d]	13.75	34.07
12-Isb-12	0.0467	11.98	29.69	0.0050	12.40	30.73	0.0234	13.22	32.75
14-Isb-14	0.0662	11.77	29.15	0.0069	12.18	30.18	0.0331	12.43	30.79
16-Isb-16	0.1049	11.77	29.17	0.0106	12.09	29.96	0.0575	12.30	30.47

[a,b, c, d and e] data taken as such from [15*a*], [8*l*], [6*h*], [8*j*] and [15*b*], respectively.

The MSR values of conventional (C_mTAB) and gemini surfactants for all PAHs have been found 2-3 times lower when compared with the literature values [6*h*, 8*j* and *l*, 15] except 12-Eg-12 (anth) and 16-Eg-16 (pyre) combinations. This may be due to the difference of solubilization technique (sonication) indicating the superiority of the method.

5.3.2. Effect of Nature of Spacer

From Table 2, lower MSR (or ln K_m) values of hydrophilic spacer based geminis can be attributed to the limited solubilization of PAHs (*almost half*) than the hydrophobic spacer based geminis in all cases. PAH, being a hydrophobic material, is solubilize in micellar structure by two ways: (a) solubilized at the cationic micelle-water interface due to interactions between π electrons of arenes and the positive charge and (b) solubilized in the core due to hydrophobic-hydrophobic interactions (see Scheme 2). With hydrophilic spacer based gemini micelles, one can expect slightly more polar environment near and even just below the head group region then the polymethylene (hydrophobic) spacer based geminis. Therefore, effective hydrophobic volume with biodegradable spacers may decrease (Chapter 3) and responsible for decrease in MSR values. Moreover, in a recent review article, Wang et al [7*e*] has commented that hydrophilic spacer based gemini surfactants may form more packed micellar structure resulting into lower size (and hydrophobic volume). Hence, size and shape may influence the solubilization of PAHs as well as MSR data. However, greener nature of these surfactants makes them potential candidates for the various solubilization based applications (drugs, dyes, pesticides among others).



Scheme 2. Schematic Representation of Anthracene (as PAH) location in the micellar structure of gemini surfactant with different spacers.

Within hydrophilic spacer based geminis (Table 2), solubilization of PAHs has been found nearly same for 12 and 14 series. However, in case of 16 series, isosorbide spacer based geminis have higher solubilization capacity than the others for all the three PAHs. 16-Isb-16 has 1-2 order of magnitude lower cmc (Figure 2*d*), which may be responsible for the higher MSR.

5.3.3. Effect of Alkyl Chain Length (*m*)

MSR values (Table 2), for all surfactant, follow the order: 16 series > 14 series > 12 series. This could be related to the more non-polar (hydrophobic) environment

produced by higher chain length surfactant. Rosen [16] has suggested that solubilization power increases with increasing ***m***. The present data is in consonance with earlier results [16]. Solubilization power difference can also be understood in terms of cmc. Surfactant with lower cmc is expected with higher MSR. However, the opposite trend has been observed when nature of the spacer was related with MSR and cmc. Though, such surfactants have lower cmcs but also have lower MSR too. This means other than cmc, interaction with additive, location and environment may also affect the overall solubilization phenomenon.

5.3.4. PAHs Effect

The MSR and ln K_m values (Table 2) of PAHs is also fall in order: fluo > pyr > anth. In earlier report [8*a*], the solubility of PAH increases with increasing the log K_{ow} value (Table 1) which may result the order: fluo; anth; pyr. However, present results suggest that the fluorene (low log $K_{o/w}$) has highest solubility in the micelles. Such differences in the solubilization patterns may be correlated to their different properties: (a) polarity; (b) relative hydrophobicity; (c) flexibility; (d) solute concentration [17]. These properties of solutes are directly or indirectly can also be correlated to the micellar core size, shape and the space inside as well as between two head groups. Presence of solute in the micelle may change shape (or size) of the micelle. Formation of swollen or grown micelle can also play an important role in the overall solubilization phenomenon [18]. Pyre is more hydrophobic compared to the anth or fluo, and hence, prefer micellar interior (resulting into higher ln K_m).

5.3.5. Standard Free Energy of Solubilization (ΔG^{o}_{s})

To understand the thermodynamics of the solubilization, ΔG^{o}_{s}, can also be obtained using following equation,

$$\Delta G_s^{\circ} = -RT \ln K_m \quad (5)$$

where, R, T and K_m are the universal gas constant, absolute temperature and the molar extinction co-efficient, respectively. The values of ΔG^{o}_{s} are also compiled in Table 2. Negative values of ΔG^{o}_{s} show the spontaneity of the solubilization process. The more negative value of ΔG^{o}_{s} with pyrene-16-***s***-16 combination suggests that solute is solubilized in the micellar interior.

5.4. Conclusion

Comprehensive data on solubilization of PAHs in various cationic gemini surfactants have been computed and critically examined / compared. Solubilization of PAH has been found to be dependent on the nature of the spacer and ***m***. Above cmc, all surfactants systems are showing a linear enhancement of solubility of PAH with their concentration. The MSR data follow the order: fluorene > pyrene > anthracene. Due to interactions of cationic head-π cloud and spacer-PAH, the solubilization ability of gemini surfactants are higher than the conventional surfactant. With changing the spacer from hydrophobic to hydrophilic, the micelle becomes less adaptable to the solubilized PAH. Therefore, biocompatible spacer based geminis have less solubilization power than polymethylene spacer based geminis. However, the present synthesized geminis may prove greener substitute for polymethylene based (lesser biodegradable) gemini systems. Solubilization of solutes not only depends on the cmc values of surfactants but also on micelle-solute (hydrophobic-hydrophobic) interactions. Micellar microstructures (size / shape) may play a role which is still not popular in solubilization studies.

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