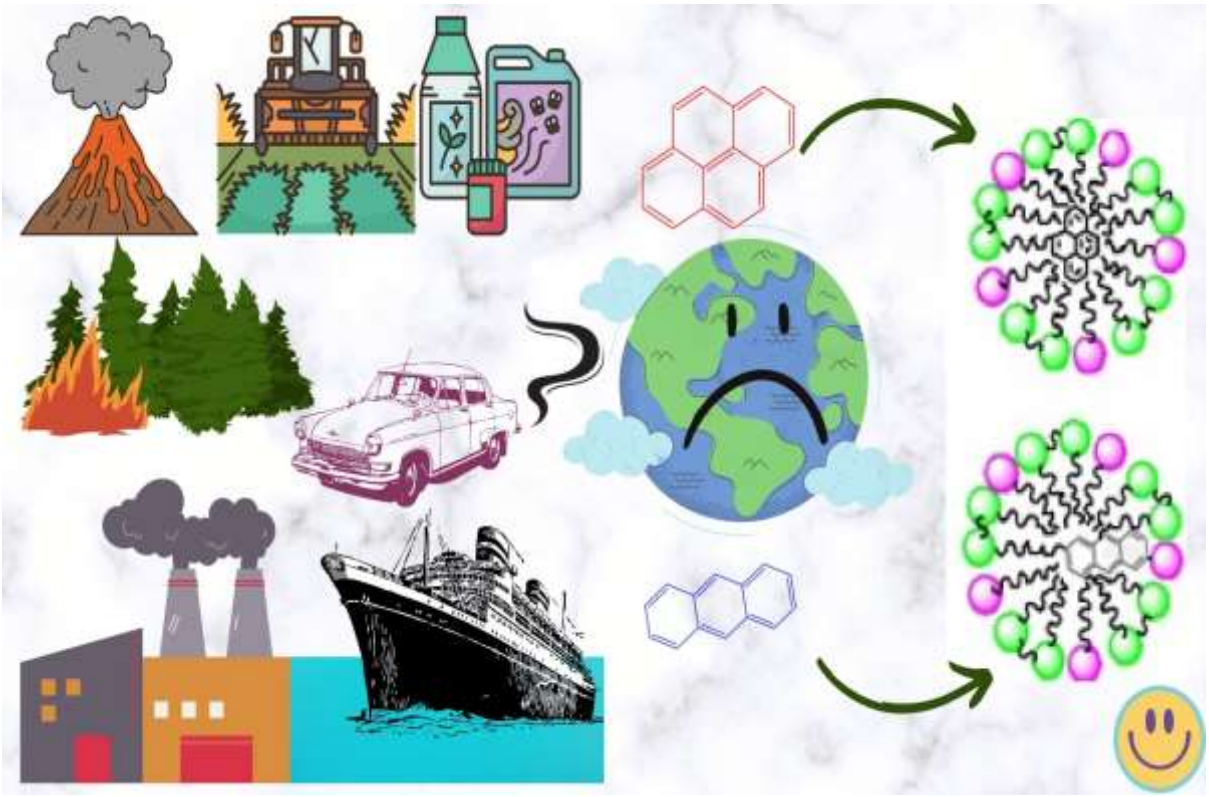
Chapter 7

Solubilization of Polycyclic Aromatic Hydrocarbons (PAHs) in Individual and Mixed Geminis: Implications of Blending



7.1. Introduction

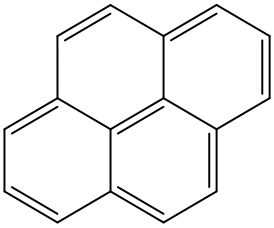
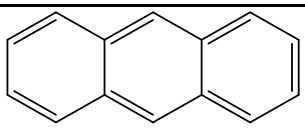
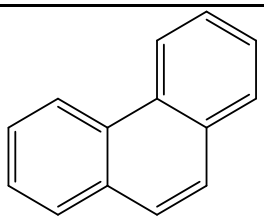
The work conducted in last two chapters (Chapter 5 and 6) shows that performance of blended systems towards solubilization of water insoluble drugs (RLX or CUR). To test the generality of the blended geminis, it is important to consider other hydrophobic material and enlarge the spectrum of gemini blending applications. In this direction, a well-known class of pollutants, polycyclic aromatic hydrocarbons (PAHs), has been selected to establish above proposition. PAHs are well-known water and soil pollutants and forms a global general concern together with insecticides and general organic effluents [1–3].

PAHs are the result of insufficient burning of charcoal, gasoline or firewood [4–7]. PAHs have higher adhering capacity on soil particles owing to their hydrophobic nature. Once the PAH entered in the aqueous environment, various strategies are adopted for remediation [8,9]. Surfactant based systems can be one of the potential approaches to treat contaminated soil/aqueous bodies [10–12]. The solubility enhancement of hydrophobic material in a blended geminis can be a fruitful choice as was observed in previous studies (Chapter 5 and 6).

Recent investigations have revealed insights from work involving the incorporation of PAHs using surfactant blends [13–15]. In these directions various combinations of cationic-cationic/nonionic-nonionic/nonionic-cationic/nonionic-anionic surfactants are tried towards entrapment of PAHs [16–20]. Above studies suggests that nature and composition of the blend together with micellar structures involved, can control PAH solubility in a particular blend. It has been reported that PAHs solubilization in aqueous surfactant blends has also been found upon micelle architectures present in the solution. In this chapter, various blends of geminis are used to study PAH solubilization. The role of alkyl tail length, nature of gemini spacer and blend composition have been investigated. Various PAHs namely, pyrene, anthracene and

phenanthrene are taken as model compounds. Structures and various properties of above PAHs are summarised in Table 1. Solubilization of PAHs has been studied spectrophotometrically. Various solubilization parameters were computed and correlated with the micellar structure nature and nature of the blend. MSR data have also been compared with other surfactant-based systems (individual and blended) and performances are critically examine and discussed. The study has potential to optimize surfactant blend for other hydrophobic material e.g., dye or dye-based effluents.

Table 1. Molecular structure and properties of polycyclic aromatic hydrocarbons (PAHs)

PAHs	**Chemical Structure**	**Molecular weight (g/mol)**	**Molar extinction coefficient (ε) ($M^{-1}\cdot cm^{-1}$)**	**Solubility (mol/L) in water at 298 K**	**log K_{ow}**
Pyrene		202.25	4.71×10^4 at 264 nm	6.57×10^{-7}	5.18
Anthracene		178.23	1.82×10^5 at 254 nm	2.53×10^{-7}	4.45
Phenanthrene		178.23	4.138×10^4 at 360 nm	6.6×10^{-6}	4.46

7.2. Results and Discussion

7.2.1. Solubilization of PAHs

Various gemini mixtures of different compositions (x = 0-1) are taken for the solubilization studies of PAHs. Typical absorption spectra for the solubilization of each PAH in different blends of m-4-m (m = 10-14) + 12-4-12A (total surfactant concentration = 10 mM) are given in Figures 1-3.

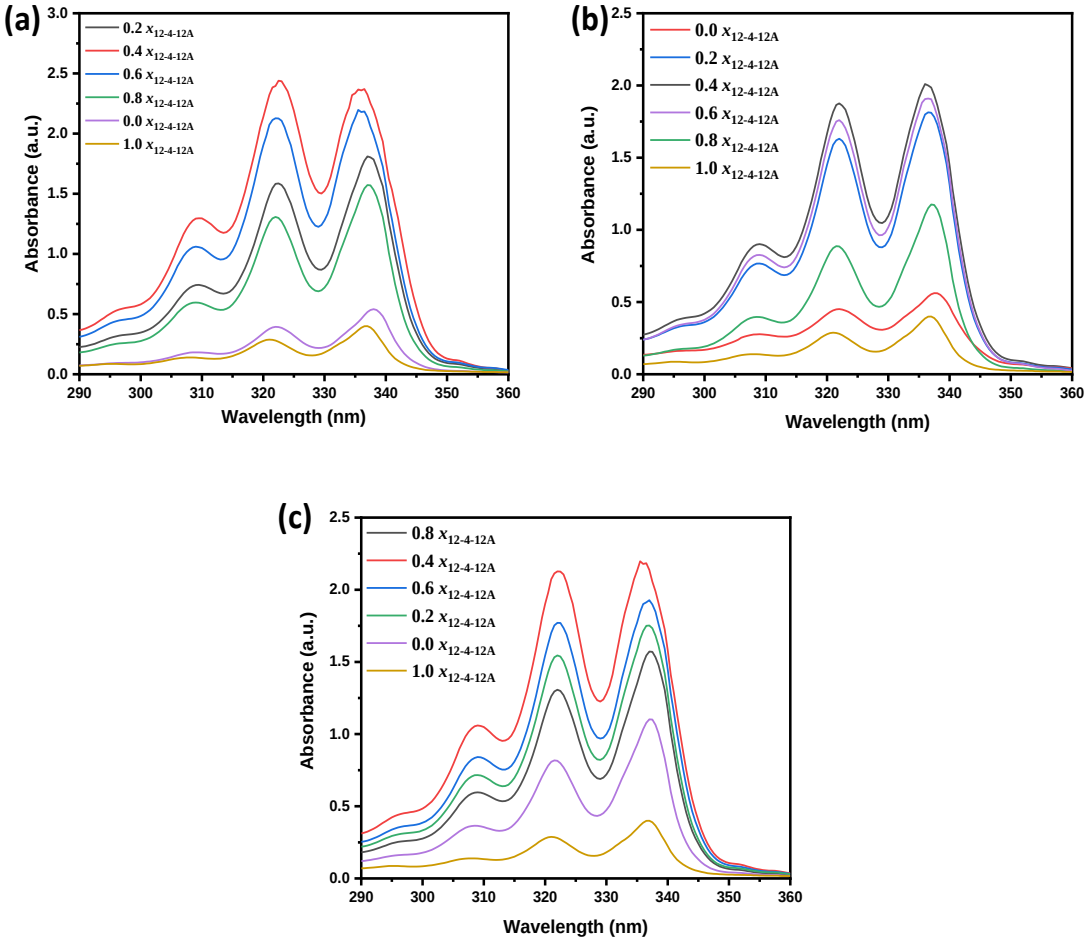


Figure 1. Representative UV-visible spectra of **pyrene** solubilized in 10 mM mixed gemini surfactant system at different $x_{12\text{-}4\text{-}12A}$: (a) 14-4-14, (b) 12-4-12, and (c) 10-4-10.

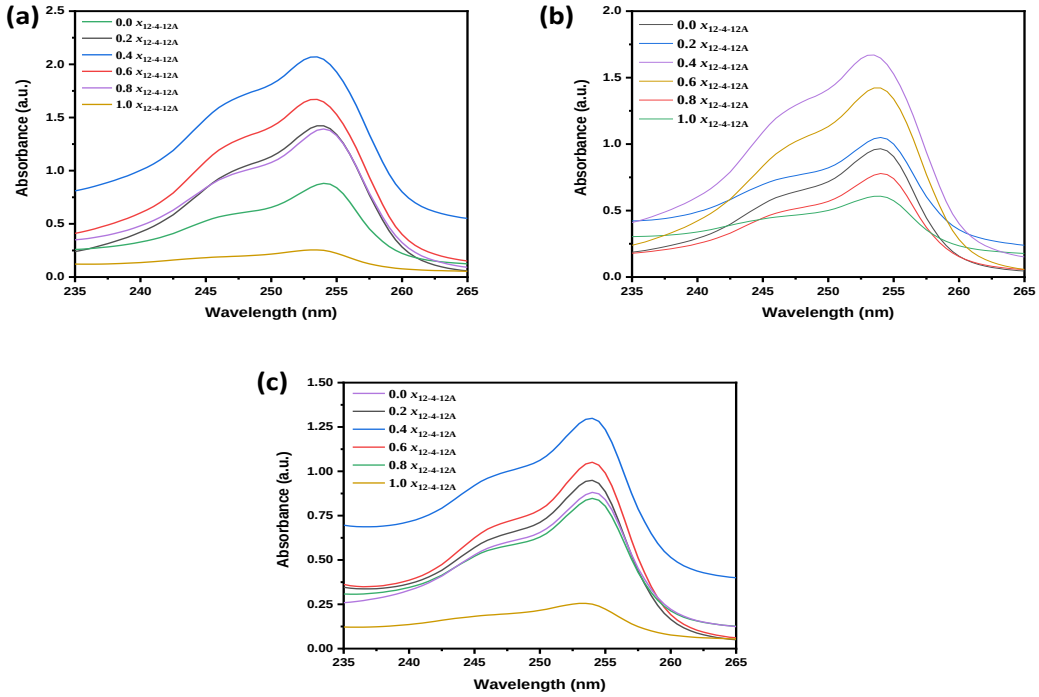


Figure 2. Representative UV-visible spectra of **anthracene** solubilized in 10 mM mixed gemini surfactant system at different $x_{12\text{-}4\text{-}12A}$: (a) 14-4-14, (b) 12-4-12, and (c) 10-4-10.

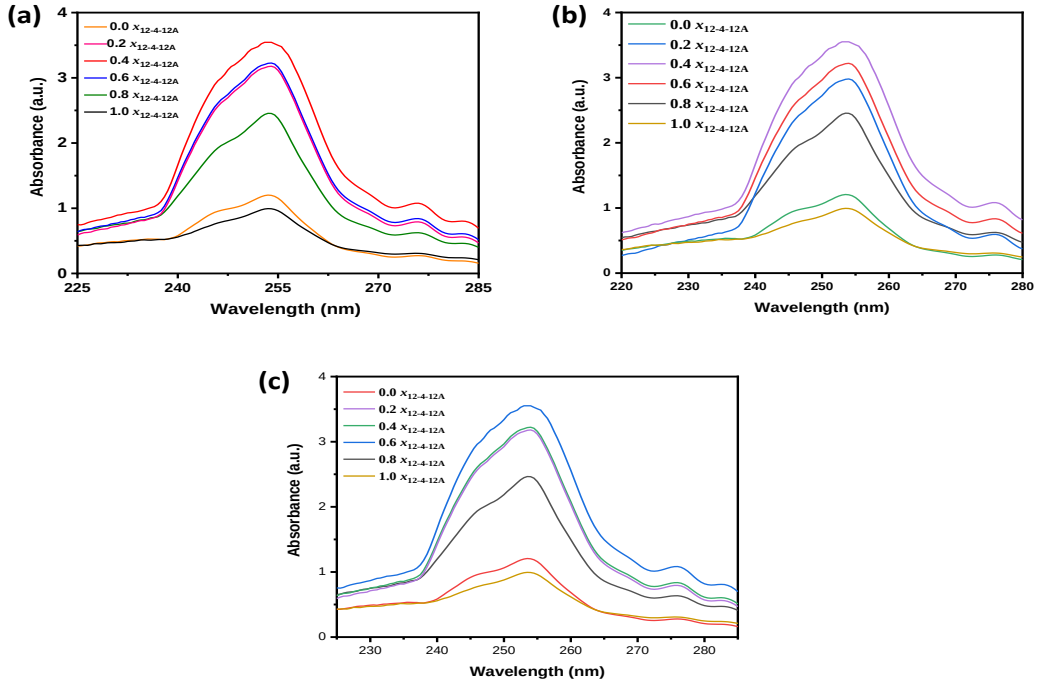


Figure 3. Representative UV-visible spectra of **phenanthrene** solubilized in 10 mM mixed gemini surfactant system at different $x_{12\text{-}4\text{-}12A}$: (a) 14-4-14, (b) 12-4-12, and (c) 10-4-10.

Similar spectra were observed with other geminis, having various spacers, are acquired but not shown. Absorbance changes by changing the composition of the blended gemini mixture. However, maximum absorbance was observed with composition having nearly same concentration (x = 0.4 or 0.6) of the mixing components. Similar observations were noted in the case of RLX and CUR (Chapters 5 and 6). Therefore, composition based microstructural transition playing a role in PAHs solubilization.

MSR data for each PAHs have been obtained by the similar computational method as given for RLX. Above MSR values were used to obtain ln K_m and ΔG_s^0. MSR values for each PAHs in terms of composition/morphology/spacer nature are compiled in Table 2-7. A perusal of MSR data clearly dictates that maximum MSRs with each PAHs are observed at either x = 0.4 or x = 0.6. These two compositions are related to minimum charge (ζ) and non-spherical morphology (cylindrical micelle or vesicle) (Chapter 4). Therefore, solubilization potential can be maximised by judicious selection of the composition of counter charged geminis together with an appropriate spacer as observed with other hydrophobic material (RLX or CUR).

Table 2. Solubilization parameters (molar solubilization ratio, MSR; micelle-aqueous phase partition coefficient, ln *K*m; Gibbs free energy,ΔG_s^0) of 10 mM single and mixed gemini surfactants in aqueous solution at 303 K.

$x_{12\text{-}4\text{-}12A}$	Morphology	Pyrene			Anthracene			Phenanthrene		
		MSR	ln K_m	$-\Delta G_s^0$ (kJ mol^{-1})	MSR	ln K_m	$-\Delta G_s^0$ (kJ mol^{-1})	MSR	ln K_m	$-\Delta G_s^0$ (kJ mol^{-1})
					14-4-14					
0.0	Ellipsoidal	0.008	13.477	33.952	0.007	14.307	36.041	0.004	10.517	26.495
0.2	Rod	0.031	14.754	37.168	0.007	14.331	36.103	0.087	13.413	33.790
0.4	Vesicle	**0.050**	15.212	38.322	**0.011**	14.499	36.527	**0.107**	13.412	33.789
0.6	Rod	0.043	15.066	37.953	0.009	14.723	37.089	0.087	13.606	34.277
0.8	Rod	0.026	14.573	36.713	0.004	13.853	34.897	0.083	13.372	33.688
1.0	Ellipsoidal	0.007	13.282	33.461	0.001	12.486	31.455	0.0002	7.792	19.629
					14-Eg-14					
0.0	Ellipsoidal	0.033	14.809	37.306	0.006	14.079	35.468.	0.024	12.191	30.711
0.2	Rod	0.017	14.150	35.647	0.004	13.698	34.509	0.022	12.097	30.474
0.4	Rod	0.032	14.781	37.236	0.005	13.927	35.084	0.026	12.269	30.907
0.6	Rod	**0.037**	14.925	37.599	**0.006**	14.020	35.318	**0.028**	12.340	31.087
0.8	Rod	0.008	13.511	34.036	0.003	13.451	33.887	0.010	11.375	28.655
1.0	Ellipsoidal	0.007	13.282	33.461	0.001	12.486	31.455	0.0002	7.792	19.629

Table 3. Solubilization parameters (molar solubilization ratio, MSR; micelle-aqueous phase partition coefficient, ln *K*m; Gibbs free energy,ΔG_s^0) of 10 mM single and mixed gemini surfactants in aqueous solution at 303 K.

$x_{12\text{-}4\text{-}12A}$	Morphology	Pyrene			Anthracene			Phenanthrene		
		MSR	ln K_m	$-\Delta G_s^0$ (kJ mol^{-1})	MSR	ln K_m	$-\Delta G_s^0$ (kJ mol^{-1})	MSR	ln K_m	$-\Delta G_s^0$ (kJ mol^{-1})
					14-Isb-14					
0.0	Ellipsoidal	0.025	14.546	36.645	0.007	14.292	36.003	0.030	12.411	31.266
0.2	Rod	0.030	14.721	37.084	0.006	14.103	35.529	0.029	12.403	31.246
0.4	Rod	**0.043**	15.053	37.920	**0.006**	14.138	35.615	**0.041**	12.711	32.022
0.6	Rod	0.035	14.867	37.453	0.006	14.137	35.614	0.032	12.465	31.402
0.8	Rod	0.016	14.091	35.499	0.003	13.289	33.479	0.011	11.424	28.780
1.0	Ellipsoidal	0.007	13.282	33.461	0.001	12.486	31.455	0.0002	7.792	19.629
					14-Eda-14					
0.0	Ellipsoidal	0.037	14.925	37.598	0.0058	14.049	35.394	0.027	12.291	30.962
0.2	Ellipsoidal	0.029	14.666	36.947	0.0051	13.919	35.066	0.025	12.224	30.795
0.4	Vesicle	0.035	14.856	37.426	**0.0113**	14.709	37.054	0.028	12.338	31.083
0.6	Vesicle	**0.043**	15.069	37.962	0.0091	14.495	36.514	**0.042**	12.727	32.061
0.8	Ellipsoidal	0.021	14.388	36.246	0.0046	13.817	34.807	0.022	12.126	30.548
1.0	Ellipsoidal	0.007	13.282	33.461	0.0012	12.486	31.455	0.0002	7.792	19.629

Table 4. Solubilization parameters (molar solubilization ratio, MSR; micelle-aqueous phase partition coefficient, ln *K*m; Gibbs free energy,ΔG_s^0) of 10 mM single and mixed gemini surfactants in aqueous solution at 303 K.

$X_{12\text{-}4\text{-}12A}$	Morphology	Pyrene			Anthracene			Phenanthrene		
		MSR	ln K_m	$-\Delta G_s^0$ (kJ mol^{-1})	MSR	ln K_m	$-\Delta G_s^0$ (kJ mol^{-1})	MSR	ln K_m	$-\Delta G_s^0$ (kJ mol^{-1})
					12-4-12					
0.0	Ellipsoidal	0.033	14.819	37.333	0.009	14.506	36.542	0.043	12.755	32.132
0.2	Ellipsoidal	0.061	15.388	38.765	0.009	14.568	36.699	0.089	13.441	33.861
0.4	Multilamellar vesicle	**0.186**	16.398	41.309	**0.074**	16.534	41.653	**0.235**	14.283	35.981
0.6	Vesicle	0.081	15.660	39.450	0.033	15.754	39.686	0.167	13.998	35.263
0.8	Ellipsoidal	0.039	14.969	37.709	0.003	13.322	33.561	0.085	13.399	33.755
1.0	Ellipsoidal	0.007	13.282	33.461	0.001	12.486	31.455	0.0002	7.792	19.629
					12-Eg-12					
0.0	Ellipsoidal	0.033	14.799	37.282	0.007	14.191	35.749	0.033	12.505	31.502
0.2	Ellipsoidal	0.042	15.031	37.865	0.008	14.392	36.257	0.046	12.815	32.283
0.4	Vesicle	**0.094**	15.796	39.794	0.031	15.705	39.562	**0.188**	14.097	35.513
0.6	Vesicle	0.080	15.648	39.421	**0.032**	15.743	39.658	0.185	14.087	35.487
0.8	Ellipsoidal	0.024	14.502	36.534	0.004	13.614	34.294	0.079	13.327	33.574
1.0	Ellipsoidal	0.007	13.282	33.461	0.001	12.486	31.455	0.0002	7.792	19.629

Table 5. Solubilization parameters (molar solubilization ratio, MSR; micelle-aqueous phase partition coefficient, ln *K*m; Gibbs free energy,ΔG_s^0) of 10 mM single and mixed gemini surfactants in aqueous solution at 303 K.

$x_{12\text{-}4\text{-}12A}$	Morphology	Pyrene			Anthracene			Phenanthrene		
		MSR	ln K_m	$-\Delta G_s^0$ (kJ mol^{-1})	MSR	ln K_m	$-\Delta G_s^0$ (kJ mol^{-1})	MSR	ln K_m	$-\Delta G_s^0$ (kJ mol^{-1})
					12-Isb-12					
0.0	Ellipsoidal	0.032	14.769	37.206	0.007	14.296	36.014	0.036	12.587	31.708
0.2	Ellipsoidal	0.039	14.978	37.732	0.008	14.421	36.329	0.043	12.744	32.105
0.4	Vesicle	**0.075**	15.582	39.252	0.033	15.757	39.694	**0.202**	14.157	35.664
0.6	Vesicle	0.071	15.537	39.142	**0.035**	15.806	39.817	0.201	14.155	35.658
0.8	Ellipsoidal	0.025	14.522	36.584	0.003	13.414	33.792	0.036	12.591	31.717
1.0	Ellipsoidal	0.007	13.282	33.461	0.001	12.486	31.455	0.0002	7.792	19.629
					12-Eda-12					
0.0	Ellipsoidal	0.041	15.010	37.813	0.008	14.381	36.227	0.042	12.743	32.102
0.2	Ellipsoidal	0.045	15.112	38.070	0.009	14.458	36.422	0.076	13.297	33.497
0.4	Rod-shaped	0.087	15.731	39.627	**0.063**	16.374	41.247	0.116	13.682	34.467
0.6	Vesicle	**0.099**	15.844	39.912	0.062	16.359	41.210	**0.221**	14.235	35.858
0.8	Ellipsoidal	0.031	14.736	37.123	0.004	13.610	34.286	0.090	13.449	33.882
1.0	Ellipsoidal	0.007	13.282	33.461	0.001	12.486	31.455	0.0002	7.792	19.629

Table 6. Solubilization parameters (molar solubilization ratio, MSR; micelle-aqueous phase partition coefficient, ln *K*m; Gibbs free energy,ΔG_s^0) of 10 mM single and mixed gemini surfactants in aqueous solution at 303 K.

$x_{12\text{-}4\text{-}12A}$	Pyrene			Anthracene			Phenanthrene		
	MSR	**ln K_m**	**$-\Delta G_s^0$ (kJ mol^{-1})**	**MSR**	**ln K_m**	**$-\Delta G_s^0$ (kJ mol^{-1})**	**MSR**	**ln K_m**	**$-\Delta G_s^0$ (kJ mol^{-1})**
				10-4-10					
0.0	0.022	14.399	36.273	0.005	13.996	35.259	0.034	12.530	31.565
0.2	0.025	14.541	36.629	0.008	14.321	36.078	0.034	12.543	31.596
0.4	**0.095**	15.806	39.817	**0.033**	15.768	39.721	0.166	13.991	35.244
0.6	0.085	15.704	39.561	0.028	15.615	39.336	**0.177**	14.049	35.393
0.8	0.013	13.902	35.022	0.004	13.728	34.585	0.049	12.871	32.425
1.0	0.007	13.282	33.461	0.001	12.486	31.455	0.0002	7.792	19.629
				10-Eg-10					
0.0	0.017	14.182	35.725	0.005	13.868	34.935	0.023	12.138	30.579
0.2	0.018	14.200	35.772	0.006	14.108	35.539	0.030	12.413	31.269
0.4	**0.058**	15.338	38.641	**0.027**	15.571	39.226	0.113	13.658	34.406
0.6	0.054	15.285	38.505	0.024	15.456	38.936	**0.156**	13.938	35.111
0.8	0.012	13.792	34.744	0.003	13.478	33.954	0.035	12.569	31.664
1.0	0.007	13.282	33.461	0.001	12.486	31.455	0.0002	7.792	19.629

Table 7. Solubilization parameters (molar solubilization ratio, MSR; micelle-aqueous phase partition coefficient, ln *K*m; Gibbs free energy,ΔG_s^0) of 10 mM single and mixed gemini surfactants in aqueous solution at 303 K.

$x_{12\text{-}4\text{-}12A}$	Pyrene			Anthracene			Phenanthrene		
	MSR	ln K_m	$-\Delta G_s^0$ (kJ mol^{-1})	MSR	ln K_m	$-\Delta G_s^0$ (kJ mol^{-1})	MSR	ln K_m	$-\Delta G_s^0$ (kJ mol^{-1})
				10-Isb-10					
0.0	0.013	13.928	35.087	0.005	13.892	34.996	0.027	12.291	30.962
0.2	0.016	14.106	35.536	0.005	13.936	35.106	0.039	12.669	31.916
0.4	0.061	15.396	38.784	**0.032**	15.718	39.596	**0.162**	13.969	35.191
0.6	**0.062**	15.412	38.825	0.027	15.571	39.224	0.132	13.792	34.744
0.8	0.012	13.820	34.815	0.003	13.351	33.633	0.037	12.613	31.774
1.0	0.007	13.283	33.461	0.001	12.486	31.455	0.0002	7.792	19.629
				10-Eda-10					
0.0	0.021	14.373	36.208	0.005	13.951	35.143	0.024	12.200	30.734
0.2	0.017	14.189	35.745	0.006	14.149	35.645	0.075	13.282	33.460
0.4	**0.087**	15.728	39.622	**0.032**	15.745	39.665	**0.165**	13.990	35.243
0.6	0.082	15.670	39.475	0.030	15.684	39.509	0.147	13.889	34.989
0.8	0.012	13.832	34.845	0.003	13.521	34.062	0.052	12.928	32.567
1.0	0.007	13.282	33.461	0.001	12.486	31.455	0.0002	7.792	19.629

The order of MSR values with respect to PAHs solubilization has been found: Phenanthrene > Pyrene > Anthracene. This order is similar as found in aqueous solution (Table 1) though the solubilities enhanced drastically in blended gemini mixtures. Another point worth noting was dependence of MSR on alkyl tail length of cationic gemini component of the blend. When the blended mixture contains geminis of equal alkyl chain lengths, solubility potential has been found maximum. This can be interpreted in terms of chain length compatibility (equal alkyl chain length, m = 12) and its effect on microstructural transition which plays a role in entrapping PAH. This ability was further dependent upon the geometrical structure of the PAH and the sites at which it is solubilised in the blended aggregate. The solubilization data with PAHs in blended geminis are in line as observed with RLX or CUR.

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