Solubilization capabilities of mixtures of cationic Gemini surfactant with conventional cationic, nonionic and anionic surfactants towards polycyclic aromatic hydrocarbons

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ABSTRACT

Solubilization capabilities of equimolar mixed micellar solutions of Gemini surfactant, $C_{16}H_{33}N^+(CH_3)_2$—$(CH_2)_5$—$N^+(CH_3)_2$ $C_{16}H_{33}$ $2Br^-$ (G) with cetylpyridinium chloride (CPC), sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and Brij56 towards polycyclic aromatic hydrocarbons (PAHs), viz pyrene and anthracene are studied spectophotometerically at 25 °C and then compared. The results showed that irrespective of the surfactant type, the solubility of PAHs increases linearly with increasing surfactant concentration, as a consequence of association between the PAH and micelles. Solubilization capacity has been quantified in terms of molar solubilization ratio (MSR), micelle-water partition coefficient (K_m), ratio of binding constant (K_1) between the micelle and PAH to the aggregation number (N) of surfactant solution and free energy of solubilization (ΔG_s^0) of PAHs. Equimolar binary surfactant mixtures showed higher solubilization capacity than their respective individual surfactants except G-CPC wherein the values were intermediate between the two. The mixed micellization parameters viz interaction parameter, β, micellar mole fraction within the mixed micelle, X_i, and activity coefficients, $f_{i,}$ were evaluated using Rubingh approach. The values of X_i were then employed to evaluate solubilization efficiency of mixed micelles using Regular solution approach (RSA). In addition experimental micelle-water partition coefficients of hydrocarbons have been compared with those predicted theoretically by geometric mean equation for mixed Gemini-conventional surfactant systems. Such mixed systems promise to improve the performance of surfactant enhanced remediation of soils and sediments by decreasing the applied surfactant level and thus remediation cost.

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1. Introduction

Current interest in surfactants, particularly their application in *in situ* flushing of contaminated aquifiers or *ex situ* washing of contaminated soils, stems from the ability of these chemicals to partition hydrophobic organic compounds into their micelle core [1]. Polycyclic aromatic hydrocarbons (PAHs) are of special interest because they are strongly sorbed to soils or sediments [2,3]. As a consequence, remediation of hydrophobic organic contamination in soil–water systems is dependent on desorption of the contaminant from the soil surface and subsequent incorporation of the pollutant into the bulk aqueous phase. Once in the bulk aqueous phase, engineered treatment systems may be used to effect remedi-

ation. Surfactants may be used to incorporate such water insoluble pollutants into the bulk aqueous phase by assisting solubilization of sorbed hydrophobic compounds [4]. In addition, surfactants have also proved to be potential candidates for improving microbial remediation of PAHs in soils by affecting the accessibility of PAHs to microorganisms [5]. Surfactant enhanced remediation (SER) has been suggested as a promising technology for the removal of sorbed PAHs. Gemini surfactants is the family of surfactant molecules possessing more than one hydrophobic tail and hydrophilic head group. These surfactants usually have better surface active properties than corresponding conventional surfactants of equal chain length. Cationic Geminis are used as promising surfactants in detergency, as efficient transfection vehicles in regulation of gene expression and signal transduction [6], the best ion exchangers on silica surfaces compared to nonionic and anionics [7] and have shown efficiency in skin care, antibacterial property and vesicle formation [8]. It has been demonstrated that the solubility of PAH increases linearly with the surfactant concentration above critical micellar concentration, CMC [9] and the addition of surfactants to pure cul-

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tures of microorganisms can increase the extent of PAH metabolism [10]. The amount and type of surfactants applied to remediate a site could also influence the fate of other pollutants in surface water and ground water [11]. The sorbed surfactants may significantly affect the properties of soils/sediments and suspended particles, and thus the fate of organic pollutants. Although reports on PAH solubilization by conventional single/mixed surfactant systems are abundant [12–16], scanty reports of the same in Gemini surfactants are available [17–21]. Moreover, to our knowledge, there is no report of solubilization of PAHs in Gemini-conventional surfactant mixed systems. The objective of the present work is to investigate the solubilization aspects of pyrene and anthracene by single Gemini and mixed Gemini-conventional surfactant systems. More specifically the focus has been made on the effects of head groups of surfactants on solubilization of PAHs and the evaluation of solubilization capabilities of equimolar Gemini-cationic, Gemini-anionic, and Gemini-nonionic of the above surfactants and their intercomparison. Because the Gemini surfactants are considered as better solubilizers than conventional surfactants due to their low CMC, the study is aimed to increase the solubilization capacity of the latter by mixing them with the former.

2. Experimental section

2.1. Materials

The nonionic amphiphile (Brij56), cationic amphiphiles (cetylpyridinium chloride, CPC), and anionic amphiphile (sodiumbis(2-ethylhexyl) sulfosuccinate, AOT) were all Aldrich products and used as received. Gemini surfactant (G) was synthesized by refluxing the α,ω-dibromopentane (Br(CH$_2$)$_5$Br with n,n-hexadecyl-N,N-dimethylamine in dry ethanol for 48 h. The purification and characterization of synthesized Gemini surfactant was done as discussed previously [8]. The solvent was removed under vacuum and the solid thus obtained was recrystallized thrice from hexane/ethylacetate mixture to obtain pure surfactant. Pyrene (PYR) and anthracene (ANT) were Himedia (India) products (98%). The important properties of PYR and ANT are presented in Table 1.

2.2. Methods

2.2.1. Solubilization experiments

The solubility of PYR and ANT in different surfactant solutions was measured between 0 mM and 3 mM. Such concentration range was taken to study the effect of micellar concentration on solubilization; however one can use any concentration above CMC. Excess amounts of PYR and ANT were added to vials containing 1 ml of the surfactant solutions to ensure maximum solubility. The sample vials having 5 ml capacity were sealed with a screw cap fitted with a Teflon lined septum to prevent any loss. These samples were then agitated for a period of 24 h on a magnetic stirrer at a temperature of 25 ± 0.5 °C. The magnetic Teflon pieces were previously dropped in vials for stirring. The solutions were subjected to centrifugation at 15,000 rpm to remove the undissolved PAH. The concentration of solubilized PAH was determined spectrophotometrically with a Shimadzu spectrophotometer (Model UV–1650) following appropriate

Table 1
Important properties of PAHs used (Ref.: [9]).

Property	Anthracene	Pyrene
Molecular weight	178.2	202.3
Solubility	2.53×10^{-7} mol/L	6.57×10^{-7} mol/L
log K_{OW}	4.54	5.18
Molar volume	157.6 Å^3	161.9 Å^3
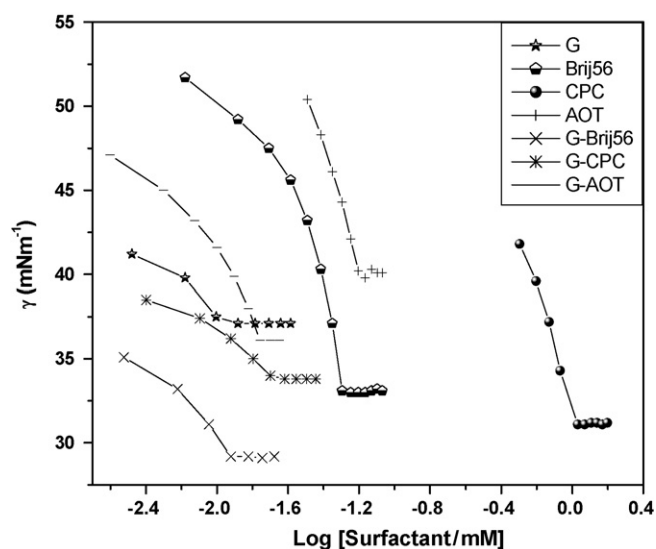
Fig. 1. Plots of the surface tension (γ) vs the total surfactant concentration (C_t) of single and equimolar binary surfactant combinations.

dilution of an aliquot of the supernatant with the corresponding surfactant concentration. The surfactant concentration was kept the same in both the reference and the measurement cells to eliminate the effect of surfactant on UV–absorbance. The solubility of PYR and ANT were determined at the wavelengths 337 nm and 358 nm, respectively. The extinction coefficient of PYR and ANT calculated were 47680.3 M^{-1} cm^{-1} and 7695.5 M^{-1} cm^{-1} from the standard curve of PAH established in methanol. Using these extinction coefficients, their aqueous solubilities were determined which tallied well with the literature values [9]. Therefore, these extinction coefficients were used in surfactant solutions to calculate concentration of PYR and ANT. All of the solubility measurements were carried out in triplicates and the typical error in the measurement was less than 5%.

2.2.2. CMC determination

The CMC values were determined from the surface tension (γ) vs logarithm of surfactant concentration (log C_t) plots shown in Fig. 1. Surface tension measurements were made with a Krüss 9 tensiometer by the platinum ring detachment method. Temperature was maintained at desired value (within ±0.1 °C) by circulating water from a HAAKE GH thermostat through thermostable vessel holder. Each surface tension measurement was carried out in triplicate and the accuracy of measurements was within ±0.1 dyne cm^{-1}.

3. Results and discussions

3.1. Interaction of Gemini surfactant with conventional surfactants in mixed micelles

CMC values of single as well as equimolar binary mixed surfactant systems of Gemini with conventional surfactants are presented in Table 2. The values for pure surfactants are in good agreement with literature values (Table 2). For ideal mixing in binary surfactant systems, the ideal CMC values, CMC$_{ideal}$ were calculated using the Clint equation [22] (Table 2).

$$\frac{1}{CMC_{ideal}} = \sum_{i=1}^{2} \frac{\alpha_i}{CMC_i} \qquad (1)$$

Due to the interaction between the components of mixed micelle, the experimental CMC, CMC$_{exp}$, values of mixed surfactants

Table 2
(CMC_{exp}), (X_1^M), (β) and (f_i) of equimolar binary surfactant mixtures using Rubingh's method at 25 °C.

Surfactant system	CMC_{exp} (literature) (mM)	Mixed surfactant system	CMC_{exp} (CMC_{ideal}) (mM)	β	X_1^M/X_2^M	f_1/f_2
G	0.011(0.009)[b]	G-Brij56	0.0110 (0.0181)	−2.55	0.66/0.34	0.75/0.32
Brij56	0.051(0.040)[c]	G-CPC	0.0215 (0.0218)	−0.80	0.98/0.02	0.99/0.46
CPC	1.032 (1.064)[d]	G-AOT	0.0175 (0.0216)	−3.33	0.85/0.15	0.93/0.08
AOT	0.680 (0.640)[a]					

Error limits of CMC_{exp}, X_i^M β and f_i are ±4%.
 [a] Ref.: [40].
 [b] Ref.: [41].
 [c] Ref.: [42].
 [d] Ref.: [39]

are usually different from theoretical CMC's. In this case experimental CMC's are lower than those predicted by Clint equation, indicating that mixed micelle formation shows a negative deviation with respect to ideal mixture. However, CMC of G–CPC surfactant system does not differ significantly from ideal CMC, indicating its almost ideal behavior. The regular solution theory has proven to be remarkably successful in modeling the nonideal behavior of mixed surfactant systems. According to this theory, the deviation of the CMC_{exp} of mixed surfactant systems from CMC_{ideal} can be represented with the interaction parameter β [9,23] given by

$$\beta = \frac{\ln(CMC_{12}\alpha_1/CMC_1 X_1^M)}{(1 - X_1^M)^2} = \frac{\ln(CMC_{12}\alpha_2/CMC_2 X_2^M)}{(1 - X_2^M)^2} \tag{2}$$

where X_1^M and X_2^M are the micellar mole fraction of surfactants 1 and 2, respectively and α_1 and α_2 are their corresponding bulk mole fractions. A negative value of β indicates a reduction in free energy of micellization over that predicted by the ideal solution theory. The larger negative value of β denotes the greater negative deviation of CMC's from CMC_{ideal}. The activity coefficients, f_i, of individual surfactants within the mixed micelles are related to the interaction parameter through the equations

$$f_1 = \exp\left\{\beta\left(1 - X_1^M\right)^2\right\} \tag{3a}$$

$$f_2 = \exp\left\{\beta X_1^{M2}\right\} \tag{3b}$$

the values of X_i^M, f_i and β are presented in Table 2 for the selected equimolar binary systems. The negative values of β for G-Brij56 binary system are a consequence of the fact [24] that for cationic–nonionic mixed surfactant systems significant electrostatic self-repulsion of cationics and weak steric self-repulsion of nonionics before mixing are weakened by dilution effects after mixing and the electrostatic self-repulsion of the cationic surfactants is replaced by the attractive ion-dipole interaction between hydrophilic groups of cationic and nonionic surfactants. In case of G-AOT system the β value is largely negative due to strong electrostatic attraction between the oppositely charged head groups of two different surfactants. In case of G-CPC β is slightly negative due to the combined effect of hydrophobic interaction among tails and electrostatic repulsion among head groups. It is reported that the existence of synergism in mixtures containing two surfactants depends not only on the strength of the interaction between them (measured by the value of β), but also on the relevant properties of individual surfactant components of the mixture [25].

The mole fractions of individual amphiphiles in the mixed micelles are different from stiochiometric composition: $X_{cpc/Brij/AOT}$ are much lower than $\alpha_{cpc/Brij/AOT}$ but X_G fairly higher than α_G. This may be due to the more propensity of Gemini surfactant to form micelles as evident from its lower CMC value. The activity coefficients of CPC, Brij56 and AOT are very low, but are close to unity for Gemini indicating its predominance in mixed micelles.

3.2. Solubilization capabilities of surfactant solutions towards PAHs

Water solubility enhancements of PAHs such as PYR and ANT by both single as well as equimolar binary mixed systems of Gemini with CPC, Brij56 and AOT were evaluated and compared. The solubility of PAHs were greatly enhanced by all the surfactant systems where solubility increased with increasing surfactant concentrations above CMC. A measure of the effectiveness of a surfactant in solubilizing a given solubilizate is the molar solubilization ratio (MSR) equivalent to increase in solubilizate concentration per unit increase in micellar surfactant concentration. In the presence of excess of hydrophobic organic compound MSR, given by the equation [9]:

$$MSR = \frac{([S_t] - [S_{CMC}])}{(C_t - CMC)} \tag{4}$$

is obtained from the slope of the curve that results when solubilizate concentration is plotted against surfactant concentration. $[S_t]$ is the total apparent solubility of PAH in single/mixed surfactant solutions at a particular total surfactant concentration, C_t, above CMC. $[S_{CMC}]$ is the apparent solubility of PAH at CMC taken equal to their water solubility (S_w) since it changes very slightly upto the CMC of the surfactant. All the concentrations are expressed in mol/L. The variations of solubilities of PYR and ANT in single and equimolar binary surfactant systems are plotted in Fig. 2. The aqueous solubilities of PYR and ANT increase linearly over the range of single or mixed surfactant concentrations above CMC indicating their solubility enhancement in water. This phenomenon is due to solubilization of PAHs within single/mixed surfactant micelles. The values of MSR calculated from the above plots using Eq. (4) for all systems studied herein are given in Table 3.

The effectiveness of solubilization can also be expressed in terms of partition coefficient, K_m, of PAH between the micelle and aqueous phases and defined as, $K_m = X_m/X_a$, the ratio of mole fraction of PAH in micellar phase, X_m, to that in aqueous phase, X_a. The value of K_m is a function of temperature and the nature of surfactant and solubilizate. The value of X_m in terms of MSR can be written as $X_m = MSR/(1 + MSR)$ while as 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 °C. With these expressions, K_m becomes [9]:

$$K_m = \frac{MSR}{\{[S_{CMC}]V_m(1 + MSR)\}} \tag{5}$$

the K_m values of PYR and ANT for single/mixed systems, calculated using Eq. (5) are presented in Table 3.

Among single surfactant systems, MSR and K_m are found to be in the order of CPC > Brij56 > G > AOT for both PYR and ANT. The order of solubilizing power for organic solutes by inner nonpolar core of micelles has been reported to be nonionic > cationic > anionic surfactants having same nonpolar chain length [18]. Our data also supports this finding except for CPC. It has been reported that cationic Gemini surfactants show higher solubilization power than
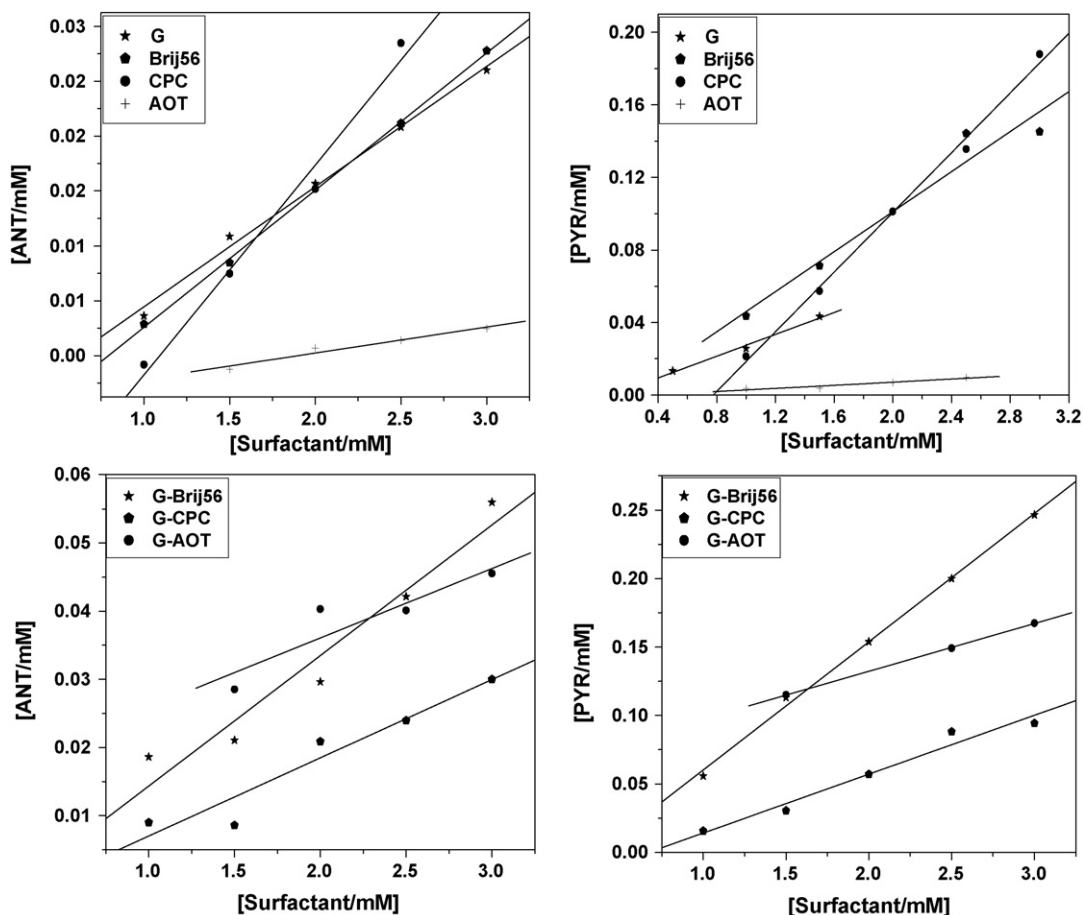
Fig. 2. Variation of solubility of anthracene and pyrene with total surfactant concentration (C_t) of single and equimolar binary surfactant combinations.

conventional alkyltrimethylammonium cationic surfactants of the same chain length [26]. This difference has been attributed to more hydrophobic content of Gemini as well as its lower CMC than corresponding conventional alkyltrimethylammonium surfactants. However higher solubilization power of CPC, in present case may be due to aromatic ring present in its head group having delocalized positive charge. This may help the aromatic hydrophobic solutes in solubilization due to wide spread interaction of

Table 3
MSR, $\log K_m$, (ΔG_s^0), (K_1/N), (R) and (B) for single and binary surfactant systems at 25 °C.

Surfactant	MSR	$\log K_m$	ΔG_s^0 (kJ/mol)	K_1/N (10^5) (mol^{-1} dm^3)	R	B
Anthracene						
G	0.009	6.03	−34.4	1.77		
Brij56	0.010	6.08	−34.7	1.82		
CPC	0.015	6.26	−35.7	3.77		
AOT	0.002	5.36	−30.6	0.56		
G-Brij56	0.019	6.36	−36.3	4.22	2.02	3.33
G-CPC	0.012	6.14	−35.0	2.53	0.96	12.25
G-AOT	0.010	6.09	−34.8	2.24	1.85	6.25
Pyrene						
G	0.030	6.39	−36.5	0.42		
Brij56	0.055	6.64	−37.9	0.79		
CPC	0.082	6.81	−38.8	1.43		
AOT	0.004	5.56	−31.7	0.07		
G-Brij56	0.096	6.86	−39.1	1.20	2.26	4.06
G-CPC	0.043	6.54	−37.3	0.66	0.77	16.28
G-AOT	0.035	6.45	−36.8	0.53	2.23	7.69

Error limits in the measurement of MSR, $\log K_m$ and K_1/N are ±7%, ±4% and ±4%, respectively.

π-electrons of arenes with positive charge. Higher solubilization power of Brij56 than G and AOT may be due to its larger micellar size helping in more micellar core solubilization [27]. AOT, being negatively charged surfactant, presents least MSR and K_m values due to repulsive interaction between π-electrons of solutes and negative charge in addition to possessing less micellar size because of difficulty in packing within the micelles. The MSR and K_m values, in general, increase with increase in hydrophobicity of PAHs (PYR > ANT) in tune with the early findings [9], positively proportional to their octanol-water coefficients ($\log K_{ow}$). It is found that $\log K_m > \log K_{ow}$, indicating that PAH partition efficiency with the micellar phase is superior to that with octanol phase.

Moroi [28] has demonstrated the evaluation of Ist stepwise association constant, K_1, of a solubilizate incorporated into micelles in case of solubilization to which Poisson distribution can be applied. As per this formulation K_1, which serves as an 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

$$\frac{([S_t] - [S_{CMC}])}{[S_{CMC}]} = \frac{K_1}{N.(C_t - CMC)} \tag{6}$$

the value of K_1/N can be evaluated from the slope of ($[S_t] - [S_{CMC}]$)/$[S_{CMC}]$ against C_t−CMC (Fig. 3). The ratio K_1/N which can also be taken as a measure of solubilizing power of a micelle shows the same trend as that of MSR and K_m values (Table 3).

Solubilities of PYR and ANT in mixed G-conventional surfactant systems were determined and compared with those in single surfactant systems. The plots of solubilities of PYR and ANT against total surfactant concentration in G-Brij56, G-CPC, and G-AOT mixed
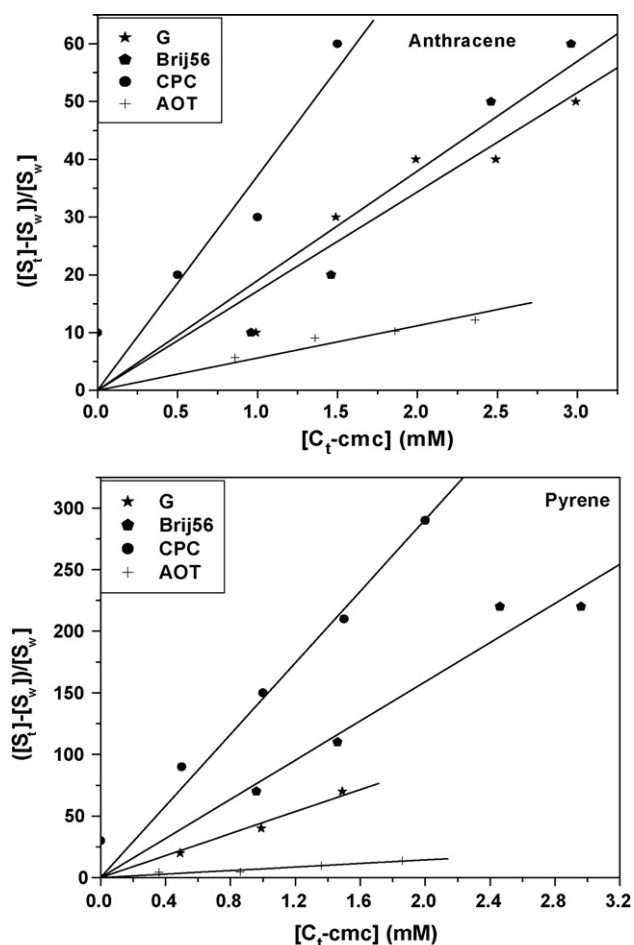
Fig. 3. Plots of $([S_t] − [S_w])/[S_w]$ of pyrene and anthracene against surfactant concentration in micellar form (C_t–CMC) of single surfactant systems.

surfactant systems are also presented in Fig. 2. It is observed that the MSR and K_m values (Table 3) of PYR and ANT in mixed surfactant solutions are higher than those in single surfactant solutions except in G-CPC system which showed intermediate values among those of their individual surfactants indicating slight mixing effect. However, the order of solubilization observed was G-Brij56 > G-CPC > G-AOT. This illustrates the potential capacity of mixed surfactants to enhance the recovery of pollutants in SER. The solubilizing power of G-mixed surfactants towards PYR and ANT increased with increasing log K_{ow} of PAHs.

The higher solubilization power of mixed surfactant systems over that of single surfactant systems may be due to the larger effective solubilization area in the mixed micelles than that of single surfactant systems as a result of an increase in the radius of the mixed micelle including the electric dipole [23]. Substantial increase in MSR when Brij56 is mixed with the G indicates increased stability of solubilizates in the mixed G-Brij56 surfactant systems relative to pure G and G-CPC surfactant systems. It has been observed [29] that in addition to micellar core solubilization, PYR and ANT are adsorbed at the cationic micelle-water interface due to electrostatic interactions between π-electrons of arenes and the positive charges. In G and G-CPC systems lower values of MSR and K_m can, therefore, be attributed to limited solubilization at micelle-water interface and micellar core. In case of nonionics, due to weak interaction of oxygen of POEs with π-electrons of arenes, more of micellar core solubilization would be prevalent. However in G-Brij56 mixed micelles, slight positive charge [30] on mixed micelles facilitates micelle-water interface adsorption in addition

to micellar core solubilization characteristic of nonionics. Consequently, we expect larger values of MSR and K_m than those of individual surfactants. Thus the incorporation of G surfactant into Brij56 micelles facilitates the solubilization of arenes due to their additional micelle-water interface adsorption.

The CMC of Brij56, CPC and AOT decreases sharply in the presence of G in mixed surfactant systems because of the formation of mixed micelles. For example, CMC (in mM) is reduced from 0.051 to 0.011 for Brij56, from 1.064 to 0.0215 for CPC and from 0.68 to 0.0175 for AOT in solutions containing 0.5 mol fraction of G surfactant. As such, the micelle concentration in mixed surfactant mixtures increases considerably over that in single surfactant systems. Meanwhile, the K_m (or MSR) values in mixed surfactant systems may also increase. Although, for G-Brij56 and G-AOT mixed surfactant solutions an increase in K_m is coupled with a decrease in CMC, for G-CPC only a decrease in CMC value is noted. This indicates that decrease in CMC is not the only criteria for increase in mixed micellar solubilization towards PAHs. Hence K_m and CMC are the two important factors influencing the solubilization of mixed surfactant solutions for organic compounds. In discussing the mixing effect of surfactants on solubilization for PYR and ANT, the mixing effect on the CMC and K_m must be considered simultaneously. The positive mixing effect on the CMC is the embodiment of the negative deviation of CMC$_{exp}$ from CMC$_{ideal}$. For the solubilization of PYR and ANT in G-Brij56 and G-AOT, both the mixing effect on the CMC (Table 2) and K_m (Table 3) are positive, the conjunct effect of which results in the greater positive deviation of MSR from ideal mixture determined by the deviation ratio (R) between the experimental MSR, MSR$_{exp}$, and ideal MSR, MSR$_{ideal}$, evaluated according to the equation $R = $ MSR$_{exp}$/MSR$_{ideal}$. Here MSR$_{ideal} = \Sigma_i$MSR$_i\alpha_i$ where MSR$_i$ is the experimental MSR value of solubilizate in pure ith surfactant whose bulk mole fraction in the mixture is α_i. When $R > 1$, this indicates that there is positive mixing effect of mixed surfactants on solubilization. Values of R are also presented in Table 3 and show that for each PAH, R is greater than 1 for G-Brij56 and G-AOT surfactant mixtures indicating that such G-mixed surfactant systems have positive mixing effect on solubilization for PAHs. However in case of G-CPC binary system the values of R for both the PAHs are slightly less than unity indicating their almost ideal behavior. Since G-CPC binary system form ideal mixed micelles as reflected in their slight negative β value, no significant gain in solubilizing efficiency is achieved by mixing G with CPC. This is in conformity with the lower values of K_1/N, MSR and K_m. However, G-Brij56 surfactant carries slight positive charge due to incorporation of cationic G surfactant into the Brij56 micelles. This facilitates micelle-water interface adsorption in addition to micellar core solubilization, characteristic of nonionics, resulting in the value of R greater than unity. It is pertinent to mention that PAHs may change their locus of solubilization with increased surfactant concentration [31], however such change in locus of solubilization of PAHs within the micelle is reflected [32] from the shifts of wavelengths of maximum absorption of PAHs with increased surfactant concentration. Such shifts indicate the change of locus from the corona to the core of micelle or vs depending on the micro polarity of the environment. The solubilizate changes its locus of solubilization only when its previous locus gets saturated. In the present system, since no shifts of λ_{max} of PAHs with increased surfactant concentration were observed, it indicates that solubilization occurs only at one site i.e. either in core or at interface.

To gain better understanding of the mixing effect of G-mixed surfactants on solubilization of PAHs, it is preferable to discuss the mixing effect on solubilization based on thermodynamic ground. On the basis of regular Solution approximation (RSA), Treiner et al. [33–35] have suggested that the partition coefficient of a neutral organic solute between micellar and aqueous phases in mixed

binary surfactant solution can be represented by the relationship:

$$\ln K_{m12} = X_1^M \ln K_{m1} + (1 - X_1^M) \ln K_{m2} + B X_1^M (1 - X_1^M) \tag{7}$$

where K_{m12}, K_{m1} and K_{m2} are the micelle-water partition coefficients of the solute in mixed and single surfactants systems, respectively and X_1^M (X_2^M) represents the micelle mole fraction of surfactant 1 (2). B has the same origin as β in Eqs. (3) and has no provision for either solute–solute or solute–solvent interactions except through individual K_m values [35].Thus, for $B = 0$, there would be no mixing effect of surfactants on the partitioning of a solute. Also $B > 0$ ($B < 0$) implies that K_m in mixed surfactant is larger (smaller) than predicted by the ideal mixing rule. This treatment, at least, can be viewed as a useful empirical method and convenient and pertinent tool for the interpretation of experimental observations.

Table 3 lists the values of B evaluated for studied equimolar binary surfactant mixtures. X_1^M values were taken from the Rubingh's formulation given in Table 2 for respective surfactant systems. The values of B are found to be positive for all surfactant mixtures. Here, there is no distinct relationship between the values of B and β, because the value of B must depend both on surfactant–surfactant and on surfactant–solute interactions in the mixed micelles. According to values of B, the mixing effect of G with Brij56 or AOT on the partitioning of PYR/ANT is positive ($B > 1$) in G-Brij56 and G-AOT mixed systems and consistent with the positive deviation of MSRs from ideal mixture ($R > 1$), which seemingly can be used to interpret mixing effect of G with Brij56 or AOT on the solubilization of PYR/ANT. Such mixtures yielded large positive values of B in tune with large negative values of β. This shows that stabilization of mixed micelles through negative β values enhance the solubilization capacity of mixed surfactants indicated by large B values, in agreement with the results obtained in early findings [9]. However, the mixing effect of G and CPC on the partitioning of PYR/ANT in G-CPC mixed systems is largely positive (large B values), which are contradictory to the slight negative deviation of MSRs from ideal mixture (R slightly less than 1). Similar contradictory results have also been found in studies [36,37] involving solubilization of organic compounds in mixed surfactant systems. Large positive B values in such mixed systems are also contradictory to the slight negative β value. A thorough analysis of such similarly charged mixed surfactant systems show [35] that important structural micellar changes occur upon mixed micelle formation with consequences upon solubilization which depend upon degree of solute hydrophobicity. The nature of these changes either leads to large-sized micelles or partial demixing, leading to disagreement of B with R and β values. This indicates that B could not be utilized as the sole factor to account for the solubilization of PAHs in mixed micelles. The B values become more positive with an increase in the K_{ow} of PAHs (PYR > ANT), indicating the greater the hydrophobicity of PAHs, the larger is the positive mixing effect of surfactants on the partitioning of PAHs.

The standard free energy of solubilization $\triangle G_S^0$ [38] was negative for all systems indicating spontaneous solubilization.

4. Theoretical estimation of partition coefficient, K_M by geometric mean equation

Researchers have developed many methods to evaluate and/or predict surfactant enhanced solubilization of hydrophobic organic compounds (HOCs). Recently a simple method to estimate K_M of hydrocarbons in micellar solutions was developed by Liu et al. [43]. The authors assumed that the two liquid mixtures, arenes with water and arenes with micelles, are in a typical quasi-crystalline state (lattice array) and the intermolecular force effectively acts on the surface area of the nearest neighbour molecules and developed

Table 4
Estimated ($\log K_M$) and predicted ($\log K_m$) Partition coefficients of pyrene and anthracene in different micellar media with their surface tension reductions.

Surfactant	π_{CMC}(exp.)/erg cm^{-2}	Anthracene		Pyrene	
		$\log K_M$	$\log K_m$	$\log K_M$	$\log K_m$
G	35	5.65	6.03	5.96	6.39
Brij56	39	5.96	6.08	6.29	6.64
CPC	41	6.11	6.26	6.45	6.81
AOT	33	5.48	5.36	5.79	5.56
G-Brij56	43	6.26	6.36	6.61	6.86
G-CPC	38	5.88	6.14	6.21	6.54
G-AOT	36	5.73	6.09	6.04	6.45

Eq. (8) to predict the surfactant enhanced solubilization of HOCs.

$$\log K_M = \left(\frac{N}{2.3RT} \right) (\pi_{20} \pi_{CMC})^{1/2} (TSA) \tag{8}$$

In this equation K_M values of HOCs in the dilute solution range are estimated from the product of the geometric mean, $(\pi_{20} \pi_{CMC})^{1/2}$ of the two surface tension reductions (π_{CMC} is surface pressure at CMC and π_{20} is the surface tension reduction equal to 20 m N/m) by the surfactant solution and the total molecular surface area of the arenes, TSA. The rationality is that the interfacial tension reduction, a macroproperty of the solution is a reflection of a microproperty of the surfactant solution and the TSA is a measure of the hydrophobicity of the arenes. The authors tested the validity of the developed equation for different HOCs in various single surfactant systems. Good agreement was found between the $\log K_M$ values predicted by geometric mean equation and experimental $\log K_m$ values for nonpolar hydrocarbons. However a significant diference was obtained between the two for polar compounds. No report was given to estimate the validity of the equation in mixed binary surfactant systems. The endeavor of the present work is to test the validity of the geometric mean equation for nonpolar (pyrene, anthracene) in mixed surfactant systems containing Gemini surfactant. The $\log K_M$ values of these arenes predicted using Eq. (8) are listed in Table 4. Table 4 also lists the π_{CMC} values of different surfactant solutions used. It is clear from Table 4 that the predicted $\log K_M$ values of arenes with Eq. (8) are almost the same as the experimentally determined values. The average absolute difference between the predicted $\log K_M$ values with Eq. (8) and the experimental values of these arenes are less than 0.4 log units, indicating the developed equation is well valid in mixed binary micellar solutions for nonpolar solubilizates. It is concluded that the geometric mean equation can be generalized for its application to predict $\log K_M$ values of the arenes in both single as well as mixed surfactant systems. Considering that the measurement of π_{CMC} is much easier than the analysis of solubility of solubilzates in surfactant solutions, the developed equation may be more applicable in practice. Because this is the first time that Eq. (8) has been used to predict micelle-water partition coefficient of solubilizate in mixed binary surfactant systems, more research is needed to validate its use, especially for predicting the K_M of polar solubilizates.

5. Summary

The present study reveals the solubilization capabilities of Gemini (16-5-16) and mixed Gemini with conventional surfactant solutions towards PYR and ANT. The solubilization capacity has been quantified in terms of MSR and $\log K_m$ values. In general anionic surfactant showed less solubilization capacity while CPC showed the highest solubilization capacity among Gemini, CPC, Brij56 and AOT single surfactant systems. In binary combinations of Gemini with conventional surfactants, solubilization capacity of pure Gemini was more enhanced when mixed with Brij56 than with CPC or AOT. The solubilization capacity increased with the increase

in hydrophobic character of PAHs in all surfactant mixtures. The study when used to test the validity of the geometric mean equation in Gemini-conventional mixed surfactant systems indicated its fair applicability to calculate micelle-water partition coefficient theoretically.

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