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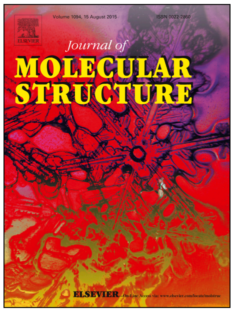

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Manorama Panda, Nazish Fatma, Kabir-ud-Din

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Enhanced aqueous solubility of polycyclic aromatic hydrocarbons by green diester-linked cationic gemini surfactants and their binary solutions

Manorama Panda*, Nazish Fatma and Kabir-ud-Din
Department of Chemistry, Aligarh Muslim University, Aligarh-202002, India

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Abstract

Three homologues of a novel biodegradable diester-linked cationic gemini surfactant series, C_mH_{2m+1} $(CH_3)_2N^+(CH_2COOCH_2)_2N^+(CH_3)_2C_mH_{2m+1}.2Cl^-$ (m-E2-m; m = 12, 14, 16), were used for investigation of the solubilization of polycyclic aromatic hydrocarbons (PAHs) such as naphthalene, anthracene and pyrene in single as well as binary surfactant solutions. Physicochemical parameters of the pure/mixed systems were derived by using conductivity and surface tension measurements. Dissolution capacity of the equimolar binary surfactant solutions towards the PAHs was studied from the molar solubilization ratio (*MSR*), micelle – water partition coefficient (K_m) and free energy of solubilization (ΔG_s^0) of the solubilizates. Influence of hydrophobic chain length of the dimeric surfactants on solubilization was characterized. Aqueous solubility of the PAHs was enhanced linearly with concentration of the surfactant in all the pure and mixed gemini-gemini surfactant systems.

Keywords:
Diester-linked gemini surfactant; Polycyclic aromatic hydrocarbon; Mixed micelle; Synergistic interaction; Micellar solubilization

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*Corresponding author.
E-mail address: manoramapanda01@gmail.com (M. Panda)

1. Introduction

The presence of polycyclic aromatic hydrocarbons (PAHs) in nature is of great concern as these are highly toxic, carcinogenic and mutagenic to microorganism as well as to all living beings including humans [1]. PAHs are highly lipid-soluble, also get readily adsorbed and distributed uniformly in the tissues of the body cell producing carcinogenic effect. The main reason for the prolonged persistence of PAHs in the environment is their low aqueous solubility owing to their hydrophobicity that enhances their sorption to soils and sediments, accumulation in aquatic living organisms and transfer to humans through seafood consumption [2,3]. The biological, physical and chemical methods used to remove these pollutants have some limitations and side effects [4] and, therefore, the apparent water solubility of the hydrophobic hydrocarbons could be improved by the addition of synthetic surfactants [5]. An important property of the surfactants is that they associate in water and form colloidal aggregates called micelles above a threshold concentration known as the critical micelle concentration (*cmc*). Micellar solutions have the ability to increase the aqueous solubility of hydrophobic compounds by incorporating them into the hydrophilic/hydrophobic regions depending upon polarity of the solutes [6]. Solubilization power of the mixed surfactant systems depends not only on the micellar and interface properties of the component surfactant, but also on the hydrophilic/hydrophobic properties of solutes. The amounts of organic compounds that can be solubilized in the micelles depend on the surfactant structure, aggregation number, micelle geometry, ionic strength, temperature, solubilizate chemistry and their size [7]. A good number of studies has been taken up in single surfactant systems [8-24] mostly with relatively high surfactant concentrations that would increase the remediation cost. To reduce the treatment cost, and also the consumption of surfactants, a new class of amphiphiles, i.e., the gemini surfactants, possessing two hydrophobic chains and two hydrophilic head groups joined together through a spacer – that may be rigid or flexible, hydrophilic or hydrophobic – could preferably be used (instead of the conventional surfactants). This is because of their lower *cmc*, higher dissolution capability, good wetting property, and higher efficiency in reducing the surface and interfacial tension of water [25-29]. As mixed micelles possess improved physicochemical properties [30], last few years have witnessed a number of studies in the gemini-conventional mixed surfactant systems toward the solubilization of sparingly soluble compounds [31-36].

Despite the potential use of gemini surfactants for the solubilization of water-insoluble compounds in micelles, solubilization of PAHs in gemini-gemini surfactant mixtures are poorly studied. Structure of surfactant and composition of mixture influence the solubilization capability of the mixed system. The goal of the present investigation is to determine the extent of solubilization of PAHs in pure surfactant solutions as well as their equimolar binary mixtures whereby influence of the hydrophobic chain lengths of the dimeric surfactants on solubilization behavior is also seen. We have used, herein, the ester-linked cationic gemini surfactants, because of their lower *cmc* and low toxicity than the other cationic gemini surfactants [37,38]. Such fundamental and extensive investigations will help to predict the properties of mixed micelles containing gemini surfactants of the same charge, and also the mixing effect on solubilization capabilities that will extend the scope of surfactant–enhanced applications.

2. Experimental Section

2.1. Materials

Molecular formula and properties of the solubilizates used in this study, i.e., the PAHs – naphthalene (≥ 99.0%, Fluka, Switzerland), anthracene (99.5%, Koch-Light Laboratories Ltd., England) and pyrene (99%, Fluka, Switzerland) – are listed in Table 1. The cationic gemini surfactants (m-E2-m, m = 12, 14, 16) were synthesized in the laboratory (Scheme 1), using a known procedure and the details are reported elsewhere [38].

2.2. Methods

Solutions of the gemini surfactants and their equimolar binary mixtures were prepared in double distilled water by mixing pre-calculated volumes of the stock solutions.

2.2.1. Surface tension measurement

The surface tension (γ) measurement, used to determine the cmc values, was based on the Platinum ring detachment method with a Kruss11 Tensiometer (K11MK3, Germany). The values were measured until consistency in γ was noticed (Fig. 1a) indicating that the equilibrium was attained. Intersection of linear portions of the plots of γ against log C (logarithm of the total surfactant concentration for the pure solution or the equimolar binary mixture) was the *cmc*.

2.2.2. Conductance measurement

Conductometry was also used for the *cmc* determination. The specific conductivity data were collected with a ELICO conductivity bridge model CM82T using a platinum electrode with cell constant of 1.026 cm^{-1}. The data obtained for all the measurements for all the solutions at 30 ± 0.1 °C were perfectly reproducible. In each case, *cmc* was determined as the concentration at intersection of the linear portions of the plots of specific conductance *versus* concentration of surfactants (Fig. 1b).

2.2.3. Solubility determination

Solubility of the PAHs was measured in pure gemini and mixed gemini-gemini micellar solutions. Above *cmc*, surfactant solutions of different concentrations were prepared in double distilled water. To ensure maximum solubilization, excess of the solute was added to 3 mL of solvent in screw-capped sealed vial, and then the mixture was shaken on a magnetic stirrer for 24 h at room temperature. The mixture was centrifuged at 12000 rpm to remove the undissolved solutes and then aliquot of the sample was collected. Concentrations of the dissolved solutes were determined by taking absorbance of the solutions at wavelengths 276 nm, 253 nm and 272 nm, respectively, for naphthalene, anthracene and pyrene, using the Shimadzu UV-Vis (UV-mini-1240) spectrophotometer. The surfactant concentration was kept the same in both the reference and measurement cells to minimize the error on UV absorbance. Absorbance of the clear solution (i.e., the supernatant liquid taken after centrifugation) was determined at λ_{max} of the PAH after suitable dilution with the appropriate solvent. Solubility was calculated by multiplying the PAH concentration, so obtained, by the appropriate dilution factor. From the absorbance data, concentration of the PAH was calculated by using the Lambert-Beer law (molar extinction coefficients of naphthalene, anthracene and pyrene are 5.2×10^3 $M^{-1}cm^{-1}$, 1.82×10^5 $M^{-1}cm^{-1}$ and 4.71×10^4 $M^{-1}cm^{-1}$, respectively, as reported by Moroi et al. [13]).

3. Results and Discussions

The present study mainly focuses on the micellar solubilization of PAHs by ester-bonded pure and mixed gemini-gemini surfactant systems. Solubilization is directly related to solution properties of the surfactant systems and it is important to understand the behavior of micelles and mixed micelles in aqueous medium. Before the solubilization study, it is necessary to discuss the micellar and surface properties of the pure and mixed surfactant systems.

3.1. Mutual interaction between the gemini surfactants in mixed surfactant systems

Pseudophase separation model, based on Clint's equation [39], was used to calculate the ideal cmc (cmc_{ideal}) which can then be compared with the experimental cmc (cmc_{12})

$$\frac{1}{cmc_{ideal}} = \frac{\alpha_1}{cmc_1} + \frac{\alpha_2}{cmc_2} \tag{1}$$

where cmc_1, cmc_2 are the *cmc*s and α_1, α_2 are the stoichoimetric mole fractions of surfactant 1 and surfactant 2, respectively, in the mixed micelle solution.

cmc_{12} values of the binary mixtures are lower than the *cmc*s of the individual components (Table 2). Negative deviation of cmc_{12} from the cmc_{ideal} values in all the mixtures implies that the mixed micelles show synergism indicating nonideality of the systems. The order of cmc_{12} values is 16-E2-16 + 14-E2-14 < 16-E2-16 + 12-E2-12 ≅ 14-E2-14 + 12-E2-12.

A quantitative estimation of the nonideality and nature of interactions among both the components can be made by the regular solution theory, based on Rubingh's approach, which explains nonideal mixing of the components in mixed systems [40]. Rubingh's model was used to find out the contribution of each surfactant in the form of mole fraction in micellar state (X_1^{m}) and interaction parameter (β^{m}) by means of the equations (2) and (3).

$$\frac{(X_1^{\mathrm{m}})^2 \ln(cmc_{12}\alpha_1 / cmc_1 X_1^{\mathrm{m}})}{(1-X_1^{\mathrm{m}})^2 \ln\{cmc_{12}(1-\alpha_1)/cmc_2(1-X_1^{\mathrm{m}})\}} = 1 \tag{2}$$

$$\beta^{\mathrm{m}} = \frac{\ln(cmc_{12}\alpha_1 / cmc_1 X_1^{\mathrm{m}})}{(1-X_1^{\mathrm{m}})^2} \tag{3}$$

The β^{m} values, listed in Table 2, give an idea about the type of interactions among the two components in the mixed micelles, which lead to their deviation from ideality. Positive β^{m} values are related to the net repulsive interaction between the two components, while negative β^{m} are caused by an attractive interaction. In all the systems, we have obtained negative β^{m} values indicating synergistic interaction between both the geminis in the mixed surfactant systems which again favors the mixed micellization process. Highest β^{m} value was obtained for the system containing both the components of higher hydrophobicity, i.e., the 16-E2-16 + 14-E2-14 system. The system 14-E2-14 + 12-E2-12, in which both the components are of lower hydrophibicity, shows least synergism.

The ideality/non-ideality of mixed micelles and the presence of synergistic interaction among the surfactants can be suggested by evaluating the activity coefficients of *i*th component, i.e., $f_{\mathrm{i}}^{\mathrm{m}}$.

$$f_1^{\mathrm{m}} = \exp\{\beta^{\mathrm{m}}(1 - X_1^{\mathrm{m}})^2\} \tag{4}$$

$$f_2^{\mathrm{m}} = \exp\{\beta^{\mathrm{m}}(X_1^{\mathrm{m}})^2\} \tag{5}$$

The results, $f_1^{\mathrm{m}} > f_2^{\mathrm{m}}$, for 14-E2-14 + 12-E2-12 and 16-E2-16 + 12-E2-12 implies that the activity coefficient of 12-E2-12 is lower than the more hydrophobic gemini surfactant present in the system, whereas for 16-E2-16 + 14-E2-14 system, $f_1^{\mathrm{m}} < f_2^{\mathrm{m}}$, and activity coefficient of 16-E2-16 is lower than that of 14-E2-14 (Table 2).

3.2. Interfacial properties of the pure and mixed surfactant systems

Maximum surface excess ($\Gamma_{\max}$) generally represents the amount of surfactant adsorbed at the air-water interface. It can be evaluated, for the dilute solution, by Gibbs equation

$$\Gamma_{\max} = -\frac{1}{2.303\mathrm{nRT}}\left(\frac{\partial\gamma}{\partial\log\mathrm{C}}\right) \tag{6}$$

where γ, *n*, *C*, *R* and *T* are the interfacial tension, number of counter ions, concentration of surfactant, universal gas constant and temperature of the surfactant solutions, respectively. Here, the values of *n* are taken as 3 and 4, respectively, for pure and mixed gemini-gemini surfactant systems. $\Gamma_{\max}$ values for the mixed micelles of 16-E2-16 + 12-E2-12 are greater than the other systems (Table 2) which indicates that greater is the difference in hydrophobicity higher is the adsorbing tendency at the air-water interface.

The minimum surface area of surfactant molecule ($A_{\min}$) can be determined by Eq. (7)

$$A_{\min} = \frac{1}{N_{\mathrm{A}}\,\Gamma_{\max}} \tag{7}$$

The values of $\Gamma_{\max}$ and $A_{\min}$ for the single and binary solutions are listed in Table 2. $A_{\min}$ values of the surfactant mixtures are higher than the pure surfactants because of the electrostatic repulsion which requires larger area per molecule. Among all the surfactant mixtures, A_{min} is highest for the 14-E2-14 + 12-E2-12 system which may be due to relatively shorter alkyl chains.

There is genuine interest in determining the thermodynamic parameters of mixed micelles like the standard free energy of micellization ($\Delta G^{\mathrm{o}}_{\mathrm{m}}$) and excess free energy of micellization ($\Delta G^{\mathrm{m}}_{\mathrm{ex}}$) as these quantify the relative importance of the hydrophobic interactions and head group repulsions (for ionic amphiphiles).

$\Delta G^{\mathrm{o}}_{\mathrm{m}}$ and $\Delta G^{\mathrm{m}}_{\mathrm{ex}}$ were calculated using the following equations

$$\Delta G^{\mathrm{o}}_{\mathrm{m}} = RT \ln X_{\mathrm{cmc}} \tag{8}$$

$$\Delta G^{\mathrm{m}}_{\mathrm{ex}} = RT\,[X_1{}^{\mathrm{m}} \ln f_1^{\mathrm{m}} + (1 - X_1{}^{\mathrm{m}}) \ln f_2^{\mathrm{m}}] \tag{9}$$

The values of free energies ($\Delta G^{\mathrm{o}}_{\mathrm{m}}$, $\Delta G^{\mathrm{m}}_{\mathrm{ex}}$) were found to be negative suggesting the stability and spontaneity of the formation of mixed micelles.

3.3. Solubilization capacity of the single/binary surfactant systems towards PAHs

In this investigation, we have mainly focused on the solubilization of PAHs in the micellar solution of cationic dimeric surfactants with variable hydrophobic chain lengths (m-E2-m) and their equimolar binary mixtures. Micellar solubilization is associated with the properties of surfactant solutions.

3.3.1. Molar solubilization ratio and micelle phase/aqueous phase partitioning of PAHs

Plots of the variation of solubility of naphthalene, anthracene and pyrene, as a function of total surfactant concentration of the single/binary surfactant systems, are shown in Figs. 2 and 3. Solubility of the PAHs was significantly enhanced by the single/binary surfactant solutions – the linear increase over the range of surfactant concentrations above *cmc* suggests micellar solubilization of the solutes. These results demonstrate the potential capacity of the pure and mixed micelles to enhance the solubility of PAHs efficiently due to adsorption at micelle–water interface, in addition to solubilization inside the micelles.

In order to quantify these observations, the solubilization capacities were analyzed in terms of molar solubilization ratio (*MSR*) [10]. *MSR* depends on the ratio of the number of solubilizate molecules inside an aggregate and the number of surfactant molecules constituting the micelle. Evidently, mole fraction of the solutes in the micellar pseudophase (X_m) and the *MSR* are related as $X_m = MSR / (1 + MSR)$.

$$MSR = (S_t - S_{cmc}) / (C_t - C_{cmc}) \tag{10}$$

where S_t is total apparent solubility of the solute in a given surfactant solution at a specific total surfactant concentration, C_t is concentration above *cmc*, S_{cmc} is the apparent solubility of PAH at *cmc*. *MSR* values of the single/mixed surfactant systems were obtained from the slope of the straight line obtained from the plot of the concentration of solubilizate against the total surfactant concentration above *cmc* (Figs. 2 and 3). The most interesting variable, which influences the solubilization of the PAHs [8], is the *cmc*.

To further measure the effectiveness of solubilization, the micelle-water partition coefficients (K_m), which depend on the molecular structure of the solubilizate [12-14,41], were determined. K_m is a thermodynamic parameter that represents the affinity of a given solubilizate to micellar phase as compared to the aqueous phase, and is used to determine the amount of PAH molecules solubilized by the micelles. For evaluation of K_m, Eq. (11) was used

$$K_m = MSR / \{[S_{cmc}]\, V_m\, (1 + MSR)\} \tag{11}$$

Here V_m is the molar volume of water (= 0.01807 $\mathrm{L\,mol^{-1}}$ at 30 °C). The increase in K_m parallels the increase in hydrophobicity of the solubilizate indicating that the solubilization is controlled mainly by the hydrophobic interactions.

In single surfactant systems, the order of *MSR* is 16-E2-16 > 14-E2-14 > 12-E2-12 for naphthalene, 14-E2-14 > 12-E2-12 > 16-E2-16 for anthracene and 14-E2-14 > 16-E2-16 > 12-E2-12 for pyrene (Table 3). With the increase of surfactant concentration above *cmc*, the number of micelles increases thereby enhancing the PAH solubility. There are different possible localization sites in the micelles for availability of the solubilizate. Their structural arrangement and polarity decide the location sites in the micellar systems. Slight polarity of the aromatic hydrocarbons allows these compounds to be located both in outer shell and also in the hydrophobic core of surfactant micelles [9,11,15,17]. Naphthalene is slightly polar and participates in hydrogen bonding with water because of the presence of π-electrons in the aromatic rings [17,42]. Surface of the micelles, space between the hydrophilic head groups, i.e., palisade layer, and inner core of micelles are the possible localization sites of the solutes affecting the extent of solubilization.

In mixed micelles the order of solubilization for naphthalene is 16-E2-16 + 12-E2-12 > 16-E2-16 + 14-E2-14 > 14-E2-14 + 12-E2-12, but for anthracene and pyrene the order is 16-E2-16 + 12-E2-12 > 14-E2-14 + 12-E2-12 > 16-E2-16 + 14-E2-14. Higher *MSR* values were obtained for the 16-E2-16 + 12-E2-12 system for all the three solubilizates which might be due to the difference in chain length of both the component surfactants in the mixed systems. In general, electrostatic interaction between the π-electrons of PAH and positive charge on the quaternary ammonium head groups facilitate micellar solubilization. The outer hydrophilic corona of the micelles has efficiency for solubilizing the slightly polar naphthalene of smaller molecular volume. The presence of diester bonded spacer may also play an important role in solubilization as compared to the polymethylene spacer. Longer spacer provides hydrophobic environment by looping upon itself whereas ester-linked spacer facilitates the solubilization of slightly polar naphthalene as there is a possibility of interaction between the π-electrons of naphthalene and the carbonyl group, i.e., [−CO(O)−]. Naphthalene gets solubilized at the micelle/water interface and between the hydrophilic head groups, i.e., the palisade layer.

Higher *MSR* and K_m values for pyrene than anthracene in all the surfactant systems indicates that anthracene is less soluble in micelles because of its larger lateral dimension resulting in lesser intercalation in the micelles as compared to pyrene. The extent of solubilization depends upon molecular architecture of the solute and space between the head groups of the surfactants in micelles. In general, there is a positive correlation between the micellar core size and the solubility enhancement, although the potential of expansion of micelles due to addition of the solute (i.e., formation of swollen micelles) also plays an important and additional role in solubilization [22,42]. The fused aromatic rings makes pyrene more hydrophobic than naphthalene and is responsible for its deeper occupancy resulting in the increase of more hydrophobic region, i.e., micellar core volume. This is indicated by the appreciably larger K_m values for the binary mixtures. Such difference in solubilization probably suggests the location of the PAHs in micelles. The dicationic gemini-gemini surfactant mixtures represent better systems for solubilization of PAHs than the other studied surfactant systems [31-34]. For anthracene and pyrene, higher *MSR* and K_m values were observed in the mixed systems than the single surfactant systems. The synergism is attributable to the reduced polarity of the mixed micelles which results the increase of *MSR* (or K_m).

3.3.2. Micelle-water partitioning of the PAHs

Each surfactant mixture is different from the other because it contains the gemini surfactants with unequal length of hydrophobic tails. From thermodynamic point of view [43, 44], the partition coefficient in mixed micelle, K_{m12}, can be expressed as a function of the micellar composition. The partition coefficient of PAH between the aqueous and micellar phases in the binary surfactant solutions can be evaluated by using Eq. (12)

$$\ln K_{\mathrm{m12}} = X_1^{\mathrm{m}} \ln K_{\mathrm{m1}} + (1 - X_1^{\mathrm{m}}) \ln K_{\mathrm{m2}} + B\, X_1^{\mathrm{m}} (1 - X_1^{\mathrm{m}}) \qquad (12)$$

K_{m1}, K_{m2}, K_{m12} are the micelle-water partition coefficients of the PAHs in micelles having component 1 (gemini surfactant with higher chain length), component 2 (gemini surfactant with lower chain length) and in mixed micelles, respectively (Table 4). B is an empirical parameter that considers both the surfactant-surfactant (as in β^{m}) and surfactant-solute interactions. When $B = 0$, mixing has no effect on the partitioning of a solute between the aqueous and micellar phases [45]. B values are positive for all the binary surfactant mixtures except for naphthalene in 14-E2-14 + 12-E2-12 and 16-E2-16 + 14-E2-14 (Table 4). Negative value of B implies that the solubilization decreases upon mixing of surfactants.

Deviation ratio (R) can be defined as the ratio of MSR (experimental) and MSR_{ideal} (ideal MSR), given as $R = MSR/MSR_{\mathrm{ideal}}$, where $MSR_{\mathrm{ideal}} = \Sigma_i MSR_{\mathrm{i}} \alpha_{\mathrm{i}}$. MSR_{i} is the experimental MSR value of solubilizate in the pure *i*th surfactant solution whose bulk mole fraction in the mixture is α_{i}. Values of the parameter R, from Table 4, show positive deviation from ideality for all the binary surfactant mixtures except for the solubilization of naphthalene in 14-E2-14 + 12-E2-12 and 16-E2-16 + 14-E2-14. Positive R value implies the positive mixing effect of the amphiphiles on the PAHs, negative R for the dissolution of naphthalene in 14-E2-14 + 12-E2-12 and 16-E2-16 + 14-E2-14 may possibly be due to the reduction in surface adsorption of naphthalene molecules in the mixed micelles. Such a variation of deviation ratio depends upon the surfactant molecular microstructures (packing of surfactant molecules at micelle–water interface as well as in the mixed micelle core), and also on the surfactant-solute interaction in the mixed micelles. As compared to the other cationic gemini-gemini mixed surfactant systems, diester-linked cationic gemini surfactant mixtures show notably higher R values, implying greater positive effect of mixing on solubilization [33,34].

The standard free energy of solubilization, ΔG_S^0, was obtained by using Eq. (13) [46]

$$\Delta G_S^0 = -RT \ln K_m \tag{13}$$

The ΔG_S^0 values come out to be negative for all the mixed systems (Table 4) indicating spontaneous solubilization. Solubilization of the studied bi-component micelles can be considered as a normal partitioning of the solubilizates between the micellar and aqueous phases. ΔG_S^0 values of the mixed micelles for different solubilizates follow the order: pyrene > anthracene > naphthalene. Among all the surfactant mixtures the magnitude of ΔG_S^0 is maximum in case of 16-E2-16 + 12-E2-12 for all the three PAHs.

4. Conclusion

Physicochemical properties of pure and mixed (1:1) surfactant solutions of the biodegradable ester-linked dicationic geminis of different chain length (m-E2-m: m = 12, 14, 16) were investigated by the conductivity and surface tension methods. Various surface and micellar properties were evaluated in the light of several theoretical models suggested by Clint and Rubingh. All the mixed surfactant solutions showed nonideality as indicated by the *cmc* and β^m values. Effect of the solution compositions of the selected single/binary gemini-gemini surfactant systems on solubilization of three PAHs – naphthalene, anthracene and pyrene – were studied. The single/binary surfactant solutions increase the aqueous solubility of PAHs which illustrates potential capacity of the used systems to facilitate the solubilization in water. Anthracene and pyrene were solublized synergistically in all the mixed systems. In the gemini-gemini mixed surfactant micelles the solution properties are influenced not only by the constituents but also by electrostatic interaction of the head groups of surfactants with the π-electron ring of PAHs. The binary surfactant solutions have relatively selective solubilization capacities towards the PAHs.

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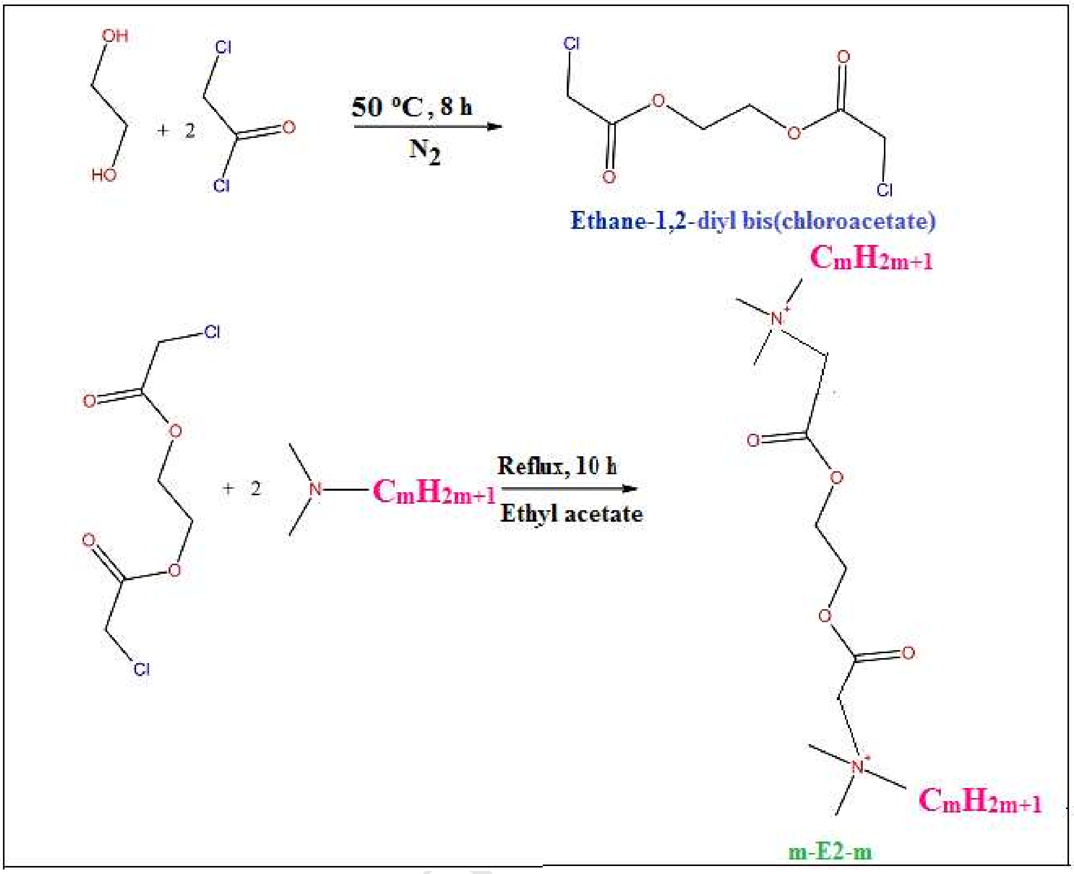


Scheme 1. Synthesis route of the biodegradable cationic gemini surfactants (m-E2-m; m = 12, 14, 16).

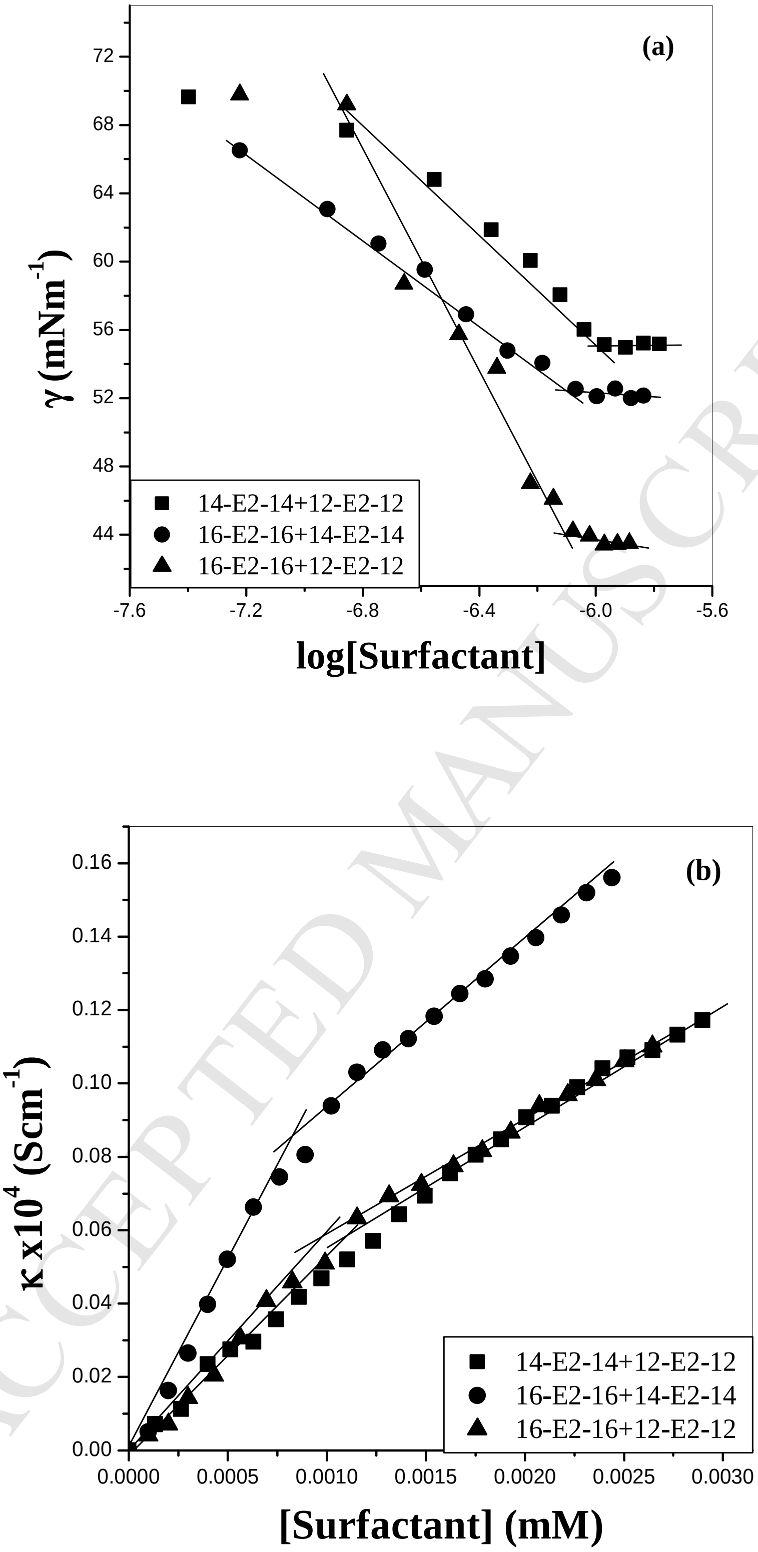


Fig. 1. Plots of (a) surface tension *vs.* logarithm of surfactant concentration and (b) specific conductivity *vs.* surfactant concentration.

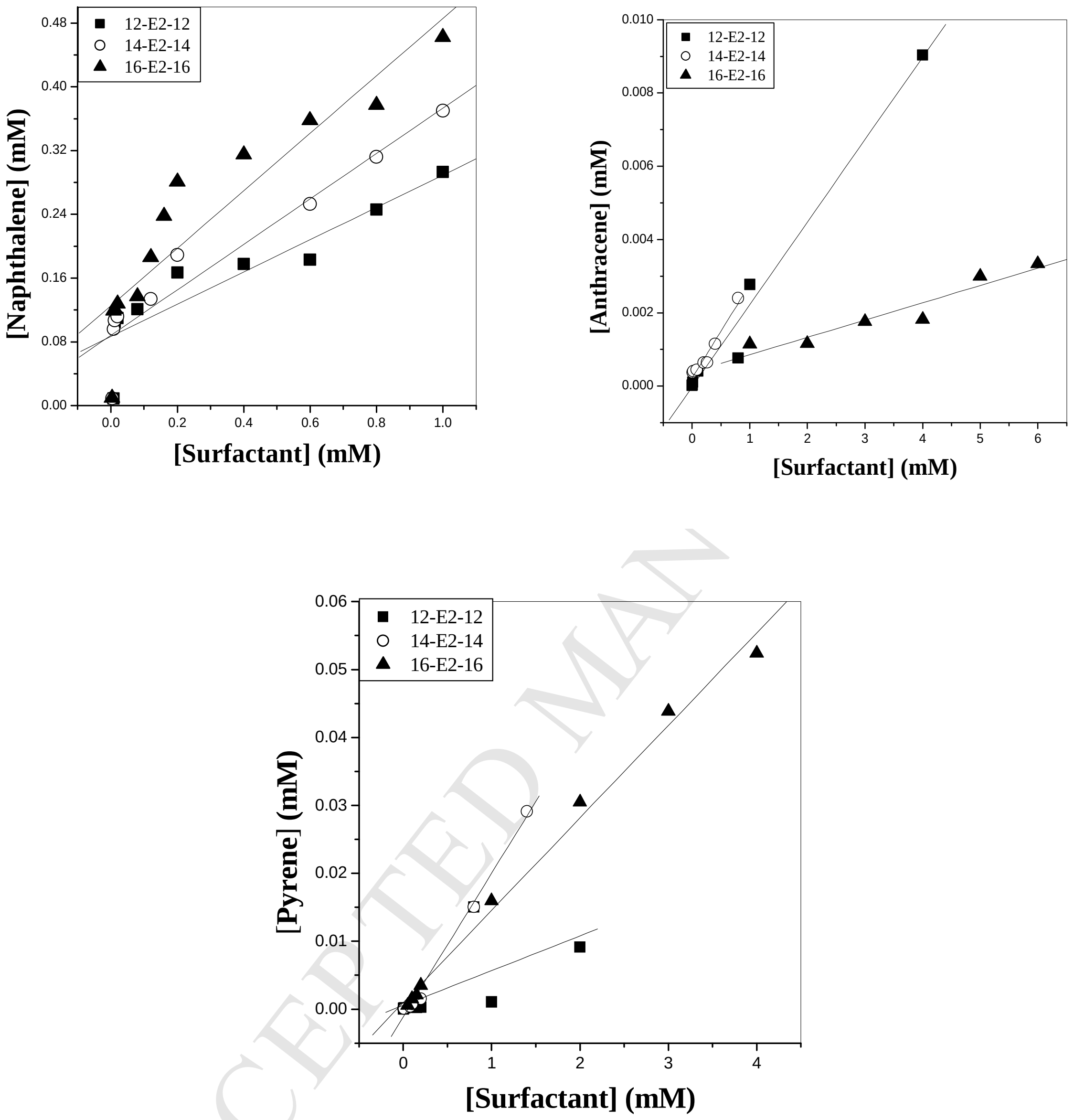


Fig. 2. Variations of solubility of naphthalene, anthracene and pyrene in pure cationic gemini surfactants (m-E2-m: m = 12, 14, 16).

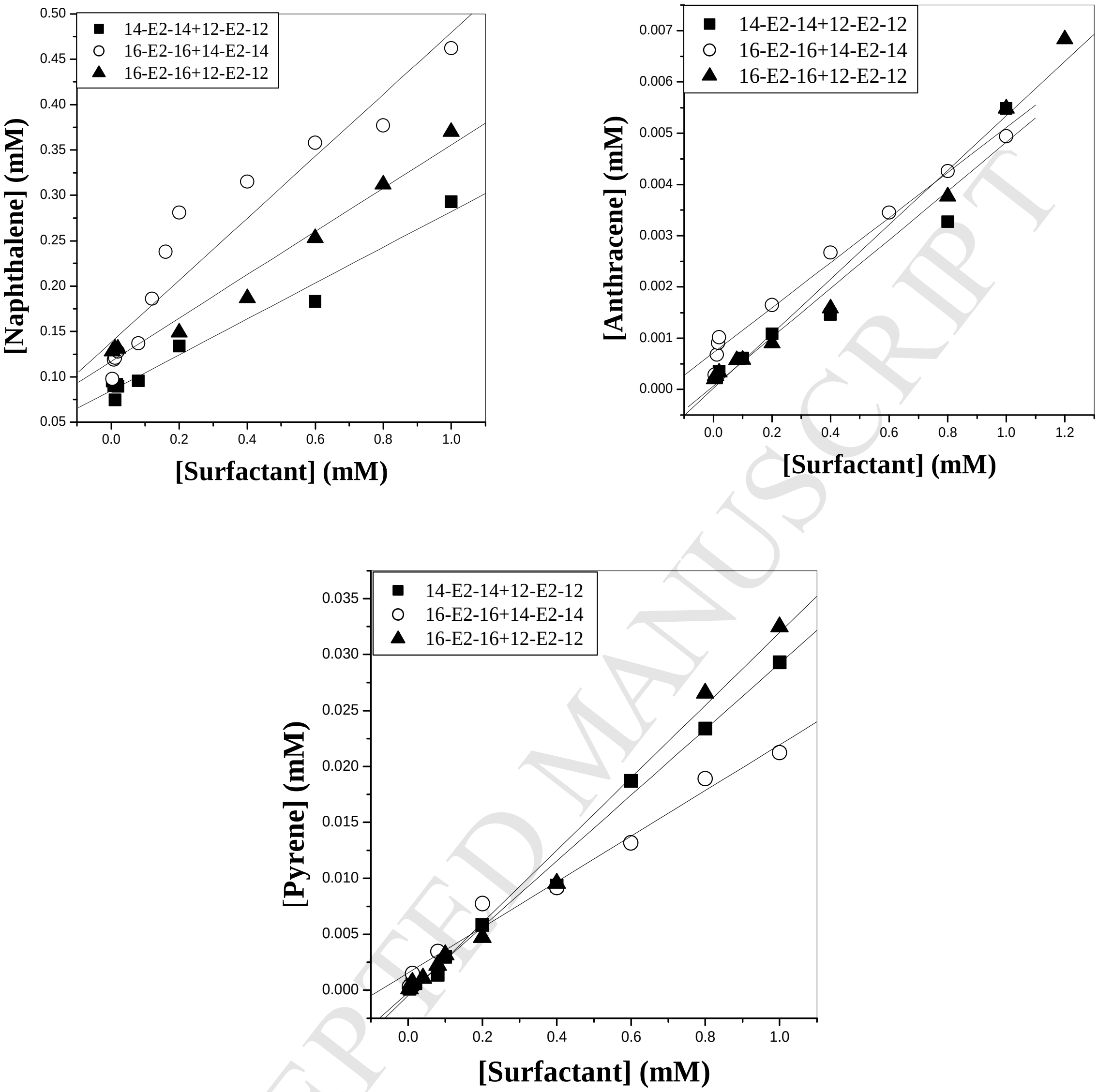
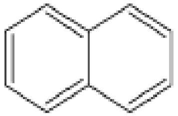
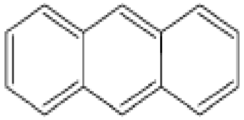
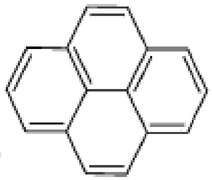


Fig. 3. Variation of solubility for naphthalene, anthracene and pyrene in different concentrations of gemini surfactants in their equimolar binary mixtures.

Table 1

Some important properties of the PAHs used for the study.

Property	Naphthalene	Anthracene	Pyrene
			
Molecular formula	$C_{10}H_8$	$C_{14}H_{10}$	$C_{16}H_{10}$
Molecular weight	128.2	178.2	202.3
Aqueous Solubility (mol/dm^3)	2.44×10^{-4}	2.53×10^{-7}	6.57×10^{-7}
^{a} log K_{OW}	3.36	4.54	5.18
Molecular volume (Å^3)	126.90	157.60	161.90

$^a K_{OW}$ is octanol-water partition coefficient.

Table 2

Experimental cmc (cmc_{12}), ideal cmc (cmc_{ideal}), micellar mole fraction (X_1^{m}), interaction parameter (β^{m}), activity coefficients (f_1^{m}, f_2^{m}), maximum surface excess concentration (Γ_{max}), minimum area per head group (A_{min}), excess free energy of micellization ($\Delta G_{\mathrm{ex}}^{\mathrm{m}}$) and standard free energy of micellization ($\Delta G_{\mathrm{m}}^{\mathrm{o}}$) of the binary surfactant (1:1) solutions at 30 °C.

Mole Fraction, α_1	cmc, ${}^{a}cmc_{12}$ (mM)	cmc_{ideal} (mM)	X_1^{m}	β^{m}	f_1^{m}	f_2^{m}	$\Gamma_{\mathrm{max}} \times 10^7$ (mol m^{-2})	A_{min} (Å^2)	$-\Delta G_{\mathrm{ex}}^{\mathrm{m}}$ (kJmol^{-1})	$-\Delta G_{\mathrm{m}}^{\mathrm{o}}$ (kJmol^{-1})
	14-E2-14+12-E2-12									
0.0	0.0016[b]	-	-	-	-	-	8.41	197.38	-	--
0.5	0.0010[a]	0.0015	0.5234	−1.49	0.7130	0.6650	7.14	232.53	0.93	44.9
1.0	0.0014[c]	-	-	-	-	-	8.83	188.04	-	44.1
	16-E2-16+14-E2-14									
0.0	0.0014[c]	-	-	-	-	-	8.83	188.04	-	44.1
0.5	0.0008[a]	0.0014	0.4891	−2.12	0.5741	0.6013	7.85	211.46	1.34	45.5
1.0	0.0013[d]	-	-	-	-	-	11.80	140.68	-	43.9
	16-E2-16+12-E2-12									
0.0	0.0016[b]	-	-	-	-	-	8.41	197.38	-	--
0.5	0.0010[a]	0.0016	0.5093	−1.79	0.6501	0.6288	7.88	210.54	1.13	45.4
1.0	0.0013[d]	-	-	-	-	-	11.80	140.68	-	43.9

[a] Average of the *cmc* values obtained by conductivity and surface tension measurements.

[b] Ref. [38a], [c] Ref. [38d], [d] Ref. [38c].

Table 3

MSR, MSR_{ideal} for naphthalene, anthracene, pyrene in the pure/mixed surfactant systems at 30 °C.

	Naphthalene		Anthracene		Pyrene	
System	*MSR*	MSR_{ideal}	*MSR*	MSR_{ideal}	*MSR*	MSR_{ideal}
12-E2-12	0.6070		0.0064		0.0183	
14-E2-14	0.8550		0.0076		0.0634	
16-E2-16	1.0820		0.0014		0.0408	
14-E2-14+12-E2-12	0.5910	0.7312	0.0143	0.0070	0.0884	0.0409
16-E2-16+14-E2-14	0.7170	0.9687	0.0132	0.0045	0.0612	0.0521
16-E2-16+12-E2-12	1.0400	0.8445	0.0160	0.0039	0.0941	0.0296

Table 4

Partition coefficient (ln K_m), free energy of solubilization (ΔG_s^0), deviation ratio (R), and experimental interaction parameter (B) for the binary surfactant (1:1) systems at 30 °C.

System	ln K_m	R	B	ΔG_s^0 (kJmol^{-1})
		Naphthalene		
14-E2-14+12-E2-12	11.34	0.81	−0.48	−28.58
16-E2-16+14-E2-14	11.60	0.74	−0.25	−28.88
16-E2-16+12-E2-12	11.66	1.23	0.17	−29.38
		Anthracene		
14-E2-14+12-E2-12	14.94	2.11	3.01	−37.65
16-E2-16+14-E2-14	14.86	1.95	5.73	−37.46
16-E2-16+12-E2-12	15.05	3.90	6.60	−37.93
		Pyrene		
14-E2-14+12-E2-12	15.73	2.16	3.53	−39.66
16-E2-16+14-E2-14	15.39	1.17	0.69	−38.80
16-E2-16+12-E2-12	15.79	3.18	4.68	−39.82

Highlights

- Mixed micellization of diester-linked cationic gemini surfactants was studied.
- PAHs (naphthalene, anthracene and pyrene) were effectively solublized in pure/mixed systems.
- Solubilization was influenced by hydrophohobicity of the PAHs.
- Anthracene and pyrene were solublized synergistically in all the mixed systems.