



Aggregation behaviour and solubilization capability of mixed micellar systems formed by a gemini lipoamino acid and a non-ionic surfactant

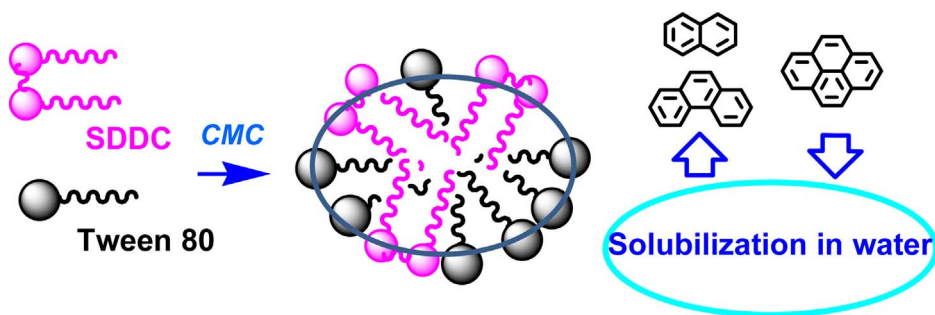


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GRAPHICAL ABSTRACT



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ABSTRACT

In this work we carried out the physicochemical characterization of mixtures of a non-ionic surfactant and a gemini lipoamino acid one. The mixed systems were studied by surface tension measurements, fluorescence quenching and SAXS determinations. Both surfactants formed mixed micelles in different relationships and the properties of the mixtures were more similar to those of their major component. SAXS analysis showed that the micelles were triaxial ellipsoids, type core shell. The mixtures exhibited non-ideal behaviour, as indicated by critical micelle concentrations (CMC) lower than those of the individual surfactants, and negative interaction parameters, β .

The mixed surfactant systems produced enhanced water solubilization of polycyclic aromatic hydrocarbons, viz, naphthalene, phenanthrene and pyrene, quantified in terms of the molar solubilization ratio and the micelle-water partition coefficient. Synergism due to the presence of both surfactants in the mixture was observed for the solubilization of naphthalene and phenanthrene, but not for pyrene. This difference in behaviour might be related to the CMC and structure of the surfactants, the polarity of the solutes, and their association constants with the micellar phase.

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1. Introduction

Over the last years many efforts were made to design and develop new amphiphilic molecules or new systems of amphiphiles with adequate properties for application in different areas or technologies [1–3].

In this respect, gemini surfactants are an interesting type of surfactants consisting of two hydrophobic chains and two hydrophilic heads covalently attached through a spacer [4,5]. These surfactants have attractive properties such as low critical micelle concentrations (CMC), higher surface activity, better solubilizing power and viscoelastic properties than those of monomeric ones [6–8]. However, the synthesis of these surfactants usually requires several steps and, in some cases, it is more expensive than certain commercial monomeric surfactants for application to large volumes. Some mixtures of surfactants show synergism, with better properties than those of the individual components [9,10]. In the presence of synergic effect, the study of mixtures of surfactants could lead to the use of lower amounts of the more expensive or difficult to obtain surfactant, in combination with one more accessible, for different possible applications.

In our laboratory we synthesised, according to the literature [11], a gemini lipoamino acid surfactant named 3,3'-disulfanediyil bis 2-decamido propanoic acid (SDDC), Fig. 1, derived from the amino acid cystine and a fatty acid, decanoic acid. The use of surfactants from renewable sources is also particularly interesting due to the improved properties of these compounds, including enhanced biodegradability and biocompatibility, and a variety of chemical functionalities, with minimal environmental impact [12,13].

Surfactants are important tools for solving many hazardous environmental problems caused by toxic water-insoluble organic compounds [14]. There are many examples in the literature of applications of surfactants to increase the solubilization of insoluble pollutants in water, by partition of the hydrophobic organic compounds in the micellar core [15–17]. Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants formed by incomplete combustion of organic matter due to natural and anthropogenic activities [18]. They display low water solubility and high adsorption capacity, thus their removal from soils depends largely on the desorption of the pollutant from the soil surface and its incorporation into the micelles. A variety of mixed surfactant systems was studied with the aim of obtaining better media to enhance the remediation of PAH contaminated soils, finding synergism in some mixtures [19–21]. A new and not so explored field is the application of gemini surfactants [22,23] or binary systems formed by gemini-gemini [24] or gemini-conventional surfactants on the solubilization of PAHs [25,26]. Synergism is also sometimes shown in these systems.

We had previously studied a mixture of a non-ionic surfactant (Tween 80) with an anionic one (sodium laurate), finding synergism for the solubilization of naphthalene in water [27] and for the desorption of naphthalene and phenanthrene from solid matrices [28]. The behaviour observed in that system was attributed to the formation of mixed micelles between both surfactants. In this work, we studied a new mixture of surfactants formed by the same non-ionic surfactant previously used (Tween 80) and the anionic gemini surfactant, SDDC, synthesised in our laboratory (Fig. 1). The aim of this work was twofold: first, to characterize the new mixed micellar system, where the previous anionic surfactant was changed for a compound with two

hydrophobic chains and two anionic charges in the working conditions. The studies included surface tension, fluorometric determinations, and small-angle X-ray scattering measurements (SAXS). The changes in the structure of the anionic surfactant influenced considerably the characteristics of the mixed micellar system, providing it with different properties. Second, we proposed to analyse the application of these systems in the solubilization of naphthalene, phenanthrene, and pyrene (as representative PAHs) in water, seeking synergism in the mixture of surfactants.

2. Experimental section

2.1. Materials

Aqueous solutions were prepared from Milli Q water (Millipore purification equipment). Methanol (HPLC grade, J. T. Baker) was used as received.

PAHs were obtained from Sigma-Aldrich with purity higher than 98%.

The non-ionic surfactant, Tween 80, was obtained from Sigma-Aldrich and used without purification. SDDC was synthesised in the laboratory according to the literature by the reaction of cystine with decanoic chloride [11].

The solutions were prepared in buffer of pH 9.16 (0.01 M $\text{Na}_2\text{B}_4\text{O}_7$, 0.02 M NaCl) so that they could be compared with a previous study [27]. Stock solutions of PAHs were prepared in methanol.

2.2. Surface tension measurements

Surface tension of the solutions of Tween 80/SDDC was measured by a Du Nöuy ring tensiometer (Cole Parmer Surface Tensiomat 21) at 30.0 °C as previously described [27]. The surface tension value obtained was an average of at least three consecutive measurements, yielding almost the same value.

2.3. Fluorescence measurements

We determined the fluorescence spectrum of monomeric pyrene in water and the fluorescence intensity ratio (I_3/I_1) of the first (I_1 , 373 nm) and third (I_3 , 384 nm) vibronic peaks. The excitation wavelength was 335 nm. The concentration of pyrene in the solutions was 2.0×10^{-6} M. A Perkin Elmer LS 55 fluorescence spectrometer was used for the measurements.

The determination of aggregation number was performed measuring fluorescence quenching with the same equipment, with a 1 cm optical path length quartz cell. The concentrations of the probe (pyrene) and surfactant were maintained constant ($[\text{Pyrene}] = 2.0 \times 10^{-6}$ M, $[\text{Surfactant}]_{\text{total}} = 2.0 \times 10^{-2}$ M) and the quencher concentration was varied (quencher = cetylpyridinium bromide, CPB). CPB solutions were prepared in water. The final solutions (probe, quencher, and surfactant) were shaken for five hours at 30 °C in a bath. The percentage of methanol in those solutions was 0.4 vol%. The excitation wavelength was 335 nm and the spectra were registered in 350–500 nm range. The bandwidths of the excitation and fluorescence slits were both set as 3.0 nm. Pyrene forms excimers due to self-association, thus the concentration of pyrene was maintained low enough to avoid their formation [29]. All the fluorescence experiments were performed at 30 °C.

2.4. Dynamic light scattering (DLS) determinations

DLS experiments were performed using a Beckman Coulter Delsa NanoC equipment. The apparent hydrodynamic diameters of the aggregates could only be determined for pure Tween 80 and for the mixture where the molar fraction of Tween 80 was 0.8 ($\alpha_{\text{TW80}} = 0.8$). In mixtures where the amount of SDDC was larger, aggregates were too

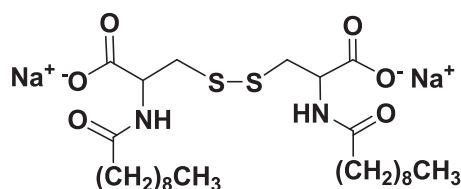


Fig. 1. Structure of the gemini lipoamino acid surfactant SDDC at pH 9.16.

small to be detected by this technique. The solutions were filtered with 0.45 μm PTFE membranes prior to measurements. The scattering intensity was measured at an angle of 165°. The apparent hydrodynamic diameters were obtained using CONTIN algorithm. The polydispersity index of the measurements was always below 0.2.

2.5. SAXS experiments

SAXS measurements were performed in the SAXS-1 line at the Brazilian Synchrotron Light Laboratory, Campinas, Brazil. The incident photon wavelength was $\lambda = 1.5 \text{ \AA}$ and the nominal sample-detector distance was 1 m. Intensity is expressed as a function of the modulus of the scattering vector $q = (4\pi \sin 2\theta/2)/\lambda$, the scattering angle being 2θ . We carried out two types of experiments: a) measuring the systems at a constant surfactant concentration of 8 mM, varying the molar fraction of Tween 80 in the mixtures (α_{TW80}); b) measuring the systems at constant equimolar surfactant mixture ($\alpha_{\text{TW80}} = 0.5$), varying the total surfactant concentration. Samples were placed in cells for liquids with mica windows (1 mm optical path) and temperature was maintained at 30 °C. A Pilatus 300 K X-ray detector from Dectris was used to record the two-dimensional SAXS patterns. The contribution of the buffer was subtracted as background from the SAXS profile and the resulting signal was radially integrated using Fit 2D. The scattering profile was fitted with several core-shell models for micelles employing the free software SASfit.

2.6. Solubilization tests

The solubilization of the PAHs in single and mixed surfactant solutions at different surfactant concentrations was performed as previously reported [27]. The only difference found in relation to previous determinations can be attributed to the fact that, in these experiments, temperature was maintained at 30 °C due to the value of Kraft temperature of SDDC [11].

3. Results and discussion

3.1. Micellar properties of mixed surfactant systems

The CMC of the pure surfactants and the Tween 80/SDDC mixtures were determined by surface tension measurements (Table 1). The break points in the plots of surface tension against the logarithm of the concentration of surfactants were taken as CMC values. Fig. 2 shows a representative plot. From Table 1 it can be seen that the experimental CMCs at different compositions of the mixture range between the CMC values of gemini surfactant and Tween 80, except the value for $\alpha_{\text{TW80}} = 0.8$ that is even lower than the CMC of Tween 80.

The micropolarity of the micellar interface in pure and in the

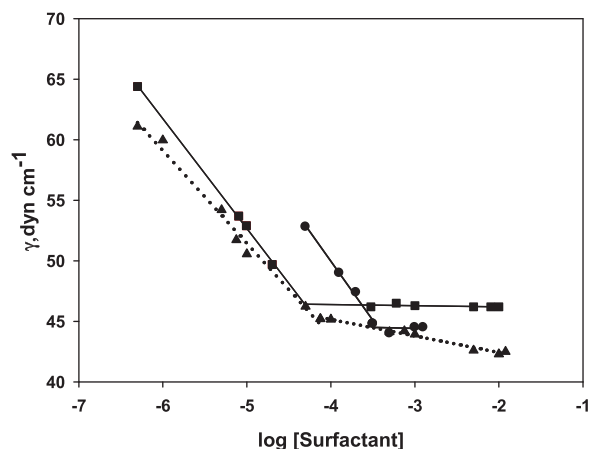


Fig. 2. Surface tension measurements in aqueous Tween 80 (■), SDDC (●), and Tween 80/SDDC mixture, $\alpha_{\text{TW80}} = 0.5$ (▲); $T = (30.0 \pm 0.1) \text{ }^\circ\text{C}$.

mixtures of surfactants was determined using pyrene as polarity probe [30] (Table 1). The ratio of the fluorescence intensity for the vibronic bands of pyrene (I_3/I_1) was higher for the gemini surfactant than for Tween 80, implying a less polar interface in the gemini (the value for this ratio was 0.63 in water [30]). This is the behaviour expected since, in general, the aggregates of anionic surfactants present less polar interfaces than those of non-ionic ones [30]. For instance, the value of I_3/I_1 ratio was 1.20 for the anionic surfactant sodium dodecyl sulfate and 0.93 for the non-ionic Brij-35 [31]. The polar head of Tween 80 has several hydroxyl groups that provide higher polarity to the interface. Indeed, the value observed for this ratio in the mixtures agrees with those obtained for some alcohols, for instance 1-pentanol and 2-propanol (1.07 and 1.10 [30]). Thus, we could consider that the dielectric constant or permittivity (ϵ) of the mixed surfactant solutions here studied is closer to those of simple polar solvents like the alcohols mentioned (ϵ between 15 or 20), but not so high as the value corresponding to water ($\epsilon = 78.54$), nor so low as the value for hydrocarbon solvents ($\epsilon \sim 2$) [30].

From the fluorescence intensity ratio of a probe like pyrene, in the presence (I) and absence (I_0) of a quencher (Q), it is possible to calculate the aggregation number (N), according to Eq. (1) [32]

$$\ln\left(\frac{I_0}{I}\right) = \frac{[Q]N}{[S]_{\text{tot}} - [\text{CMC}]}$$
 (1)

where Q is the concentration of quencher and $[S]_{\text{tot}}$ is the total concentration of a given surfactant or a mixture of surfactants. Aggregation numbers were determined from the slope of a plot of the left-hand side of Eq. (1) (corresponding to the fluorescence of pyrene) against the quencher concentration [Q] (Q = cetylpyridinium bromide), at constant surfactant concentration. Table 1 shows the aggregation numbers obtained in this way. At $\alpha_{\text{TW80}} = 0.2$, the aggregation number was lower than that obtained for pure SDDC. At $\alpha_{\text{TW80}} = 0.5$, the values were not reproducible. This fact could be related to selective solubilization of pyrene in the different surfactants, as previously described [33]. With the further increment in α_{TW80} , N increased again, becoming closer to the value of pure Tween 80 (Fig. S1).

The single and mixed surfactant systems were analysed by SAXS. Fig. 3 shows the experimental X-ray scattering intensities $I(q)$ of each individual and mixed surfactant system. All the scattering profiles tend to be horizontal at low q , suggesting the formation of micelles. The bump of micelles is displaced to higher q values for SDDC, indicating smaller micelles. The bump of pure Tween 80 is located at lower q . This indicates the largest micelles. The mixtures show proportional displacement of q (without broadening). All this suggests monodisperse mixed micelles. From these experiments it was possible to establish the shape and size of the aggregates by fitting the data to different micelle

Table 1
Characterization of the aggregates in the mixed system Tween 80/SDDC^a.

α_{TW80}	CMC, 10^{-4} M^b	I_3/I_1^c	N^d	Diameter, nm
0.0	3.5 ± 0.3	1.18	22.9 ± 0.5	3.8^f
0.2	1.0 ± 0.1	1.18	15 ± 1	4.4^f
0.5	0.57 ± 0.01	1.25	n.d. ^e	6.0^f
0.8	0.26 ± 0.01	1.13	29.0 ± 0.2	$7.6^f (10.6)^g$
1.0	0.49 ± 0.02	1.09	44.0 ± 0.3	$8.8^f (11.2)^g$

^a Buffer pH = 9.16.

^b Determined by surface tension.

^c Polarity of the aggregate interface (pyrene fluorescence).

^d Aggregation number determined by quenching of the fluorescence of pyrene in the presence of the quencher cetylpyridinium bromide.

^e Not determined.

^f SAXS (diameters were calculated considering equivalent radii, R_{equiv} , informed in Table 2).

^g DLS.

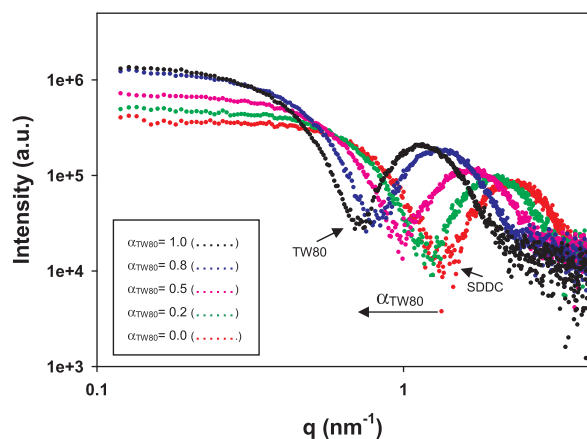


Fig. 3. SAXS experimental curves of water solutions of Tween 80 (black), SDDC (red) and Tween 80/SDDC mixtures, $\alpha_{\text{TW80}} = 0.2$ (green), 0.5 (pink), and 0.8 (blue); [Surfactant]_{total} = 8×10^{-3} M; T = (30.0 ± 0.1) °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 2
Summary of the main structural data from SAXS.

α_{TW80}	a ^a (nm)	b ^a (nm)	c ^a (nm)	Shell ^b (nm)	R _{equiv} ^c (nm)
0.0	2.46	1.86	1.43	0.21	1.9
0.2	2.83	2.22	1.67	0.36	2.2
0.5	3.47 (oblate)	3.47	2.21	1.43	3.0
0.8	4.64	3.98	2.86	1.61	3.8
1.0	5.71	4.72	3.35	2.18	4.4

^a a–c are the axes of the ellipsoid.

^b Shell is the thickness of the polar headgroup of the amphiphile (it is included in a–c as a constant value).

^c R_{equiv} is the radius of a sphere with identical volume to the ellipsoid (reported in Table 1 for comparison against DLS values). In the particular case of $\alpha_{\text{TW80}} = 0.5$, the two major semi-axes converge in a single value (oblate micelle).

models. The micelles were core-shell type triaxial ellipsoids. Table 2 shows the calculated axes (see the fits for the pure surfactants in Fig. S2). The values of the equivalent radius (R_{equiv}) obtained from these results are in good agreement with those determined by DLS (Table 1) and they can be extended to values not accessible by this technique. DLS values are slightly higher since this technique measures hydrodynamic radii. Finally, the increase in the concentration of both surfactants at a fixed molar ratio ($\alpha_{\text{TW80}} = 0.5$) does not alter the SAXS curve (data not shown). As a comparison, from atom level molecular dynamics simulations, considering a self-assembly of Tween 80 micellar system comprising 30 molecules in water, a prolate-like shape micelle was obtained, in agreement with the results obtained here [34].

3.2. Interaction parameters for surfactants in mixed micelles of Tween 80/SDDC

Eq. (2) (Clint equation) [35] was used to calculate the ideal CMC values for the different compositions of the mixtures, CMC_{ideal} , considering ideal mixing of both surfactants.

$$\frac{1}{CMC_{\text{ideal}}} = \frac{\alpha_1}{CMC_1} + \frac{\alpha_2}{CMC_2} \quad (2)$$

In this equation, CMC_{ideal} is the critical micelle concentration of the mixture of surfactants and CMC_1 and CMC_2 are the CMC of the individual pure components 1 and 2, respectively; α_1 and α_2 represent the mole fraction of surfactants 1 and 2 in mixed surfactant solutions, respectively.

Despite Eq. (2), experimental CMCs of surfactant mixtures usually differ from the theoretical or ideal CMCs due to the interaction between

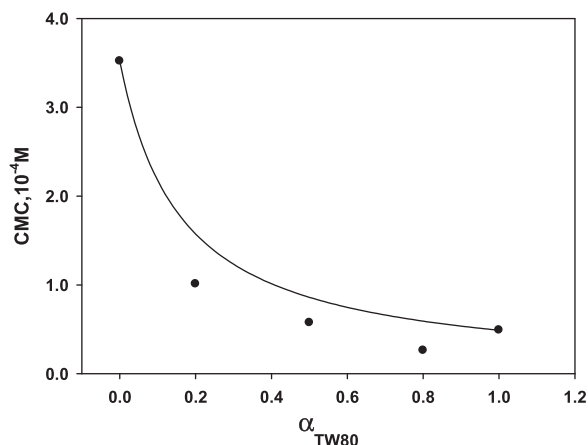


Fig. 4. Experimental CMC of mixtures of Tween 80/SDDC (●). The line represents the theoretical ideal CMC (CMC_{ideal}) calculated according to Eq. (2).

the components in the mixed micelle. Indeed, there are differences between the experimental and the calculated values for the Tween 80/SDDC mixed system. The CMC values observed were lower than the ideal ones, indicating negative deviation from ideal behaviour in the mixed micelles (Fig. 4).

The non-ideal behaviour of mixed surfactants has been frequently modelled by the regular solution theory. According to that, the interaction parameter, β , represents the observed deviation of the experimental CMCs values from the theoretical ideal CMCs. β can be calculated from Eqs. (3) and (4) [36],

$$1 - \frac{(x_1)^2 \ln(\alpha_1 CMC_{12}/x_1 CMC_1)}{(1-x_1)^2 \ln[(1-\alpha_1)CMC_{12}/(1-x_1)CMC_2]} = 0 \quad (3)$$

$$\beta = \frac{\ln(\alpha_1 CMC_{12}/x_1 CMC_1)}{(1-x_1)^2} \quad (4)$$

where CMC_1 and CMC_2 are the experimental CMC of the individual surfactants, α_1 and x_1 are the stoichiometric fraction of the non-ionic surfactant in the mixture (α_{TW80}) and in the mixed micelle, respectively. CMC_{12} is the experimental CMC determined at each composition of the mixtures (i.e., at each α_1). β is proportional to the free energy of the mixture of surfactants and represents the degree of compatibility between the surfactants in the mixtures. Negative β values imply that the interactions between the surfactants in the mixtures are attractive; however, if β is positive, the mixing of surfactants results in repulsive interactions. The β values obtained for the mixtures studied here are -2.5 and -5.9 , for $\alpha_{\text{TW80}} = 0.5$ and 0.8, respectively. The obtention of negative β values in the mixture of anionic and non-ionic surfactants was previously observed in several mixtures [37], which can be explained considering that the electrostatic self-repulsion present in anionic surfactants, and the steric self-repulsion in the micelles of non-ionic ones, may be weakened by dilution of the surfactants in the mixed micelles. However, it is important to mention that in the non-ideal solution theory there are some assumptions and approximations that preclude considering strictly the β values calculated in that way, hence, they are only useful for estimation purposes [38].

3.3. Solubilization of PAHs by single surfactant systems

We compared the effect of Tween 80 and SDDC on the solubilization of naphthalene, phenanthrene, and pyrene in buffer pH = 9.16. Fig. 5 shows the apparent solubility of naphthalene in both surfactants. A plot of the aqueous solubility of this compound vs surfactant concentration showed a linear increment above the CMC of each detergent, and the same behaviour was observed with the other PAHs, phenanthrene and pyrene (Fig. S3). Although the solubility of naphthalene in buffer is 1.78×10^{-6} M, from Fig. 5 it can be seen that, in the presence of 4 mM

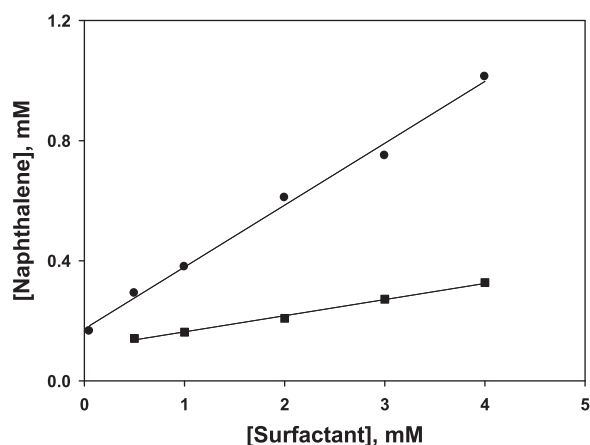


Fig. 5. Water solubility enhancements of naphthalene by single surfactant systems at 30 °C, pH = 9.16, (●) Tween 80, (■) SDDC.

of Tween 80, it is possible to solubilize approximately 1 mM of the pollutant. This increment in the solubilized amount can be attributed to the incorporation or partition of the organic compounds within surfactant micelles. Surfactant monomers produce no effect on the solubilization of the hydrocarbons.

Molar solubilization ratio (MSR) is a measurement of the effectiveness of a determined surfactant to solubilize a given solute [39] and can be expressed by Eq. (5). MSR means the amount of moles of organic compound solubilized per mole of surfactant-forming micelles. Experimentally, MSR can be obtained for each surfactant and for each pollutant, from the slopes of the plots in Figs. 5 and S3.

$$\text{MSR} = (S_{\text{PAH,mic}} - S_{\text{PAH,CMC}}) / (C_{\text{surf}} - \text{CMC}) \quad (5)$$

In Eq. (5), $S_{\text{PAH,CMC}}$ corresponds to the solubility of a PAH at the CMC of the surfactant, also corresponding to their buffer solubility; $S_{\text{PAH,mic}}$ is the total solubilized amount of the compound in micellar solution at a given surfactant concentration (higher than CMC); and C_{surf} is the concentration of surfactant at which $S_{\text{PAH,mic}}$ is analyzed.

Table 3 shows the values of MSR determined for naphthalene, phenanthrene, and pyrene in the presence of both pure surfactants. The non-ionic surfactant is the most efficient, despite the fact that gemini surfactant has two hydrophobic chains, but shorter than that of Tween 80. In addition, gemini surfactant is negatively charged and presents a higher CMC than Tween 80. The non-ionic surfactant then, with a lower CMC, is more efficient than the gemini. That behaviour was previously reported by other authors. For instance, Brij 58 and Triton X-100 were more efficient at solubilizing pyrene than the cationic gemini surfactant ethane-1,2-diyl bis(*N,N*-dimethyl-*N*-hexadecyl-ammoniumacetoxyl) dichloride (16-E2-16). The MSR for those systems were 0.0902, 0.0134 and 0.0408 respectively [40]. The values of MSR for the non-ionic surfactants were similar to the value obtained in this work for the solubilization of pyrene in Tween 80. However, the cationic gemini surfactant seems to be more efficient than SDDC.

Another way to evaluate the effectiveness of solubilization of PAHs by surfactants is analyzing the micelle-water partition coefficient, K_m . This parameter is defined as the ratio of the mole fraction of the organic compound in the micellar pseudophase (X_m) to the mole fraction of the

compound in the aqueous pseudophase (X_a), Eq. (6) [42]. In this equation, $X_m = \text{MSR} / (1 + \text{MSR})$ and $X_a = [S_{\text{PAH,CMC}}]V_w$, where V_w is the molar volume of water (0.01807 L/mol at 30 °C [43]).

$$K_m = X_m / X_a \quad (6)$$

K_m can be then expressed as in Eq. (7):

$$K_m = \text{MSR} / \{ [S_{\text{PAH,CMC}}]V_w (1 + \text{MSR}) \} \quad (7)$$

The value of K_m is dependent on several factors: the chemistry of the surfactant and the solubilize, and the temperature of the system. Table 3 shows the K_m values for naphthalene, phenanthrene, and pyrene in pure surfactant solutions. The octanol-water partition coefficients ($K_{o/w}$) for each hydrocarbon are also included [41]. It is common to observe that the partition of a given solubilize into the micellar phase increases as the $K_{o/w}$ value increases, as seen here with pure surfactants. Additionally, $\log K_m$ is higher than $\log K_{o/w}$, indicating that the PAH partition efficiency is higher in the micellar phase than in the octanol phase. In this work, the values of K_m for the association of the different hydrocarbons with the gemini surfactant (Table 3) follow a linear behaviour with $K_{o/w}$ (Fig. S4), as with Tween 80 [27] and with other systems [39]. On the other hand, the values of K_m for Tween 80 are higher than the corresponding values for SDDC, thus the association between the hydrocarbons and the non-ionic surfactant is favoured. This is also evidenced by the higher MSR values obtained for Tween 80. In general, the order of solubilizing power for organic solutes by micelles has been reported to be non-ionic > cationic > anionic surfactants, having the same non-polar chain length [25]. The results obtained here are agreement with that fact.

K_m values afford important information on the partitioning of the organic compounds in simple micelle-water systems, that can be useful for further understanding of the partition of organic compounds in mixed micelles.

3.4. Solubilization of PAHs by Tween 80/SDDC mixed systems

In this section we performed the same kind of analysis that in the previous one but with mixtures of different composition of Tween 80 and SDDC.

In order to evaluate the potential of the mixture of surfactants studied, we made some comparisons with other systems. Wei et al. analyzed the solubilization of naphthalene in the presence of the cationic gemini surfactant $C_{12-2-12}$, the nonionic $C_{12}E_{23}$, and their mixtures [44]. The solubilization of naphthalene in those individual surfactants was more important than in the surfactants used here. MSR values for cationic gemini and non-ionic surfactants were 0.1677 and 0.3953 respectively (see Table 3 for comparison with SDDC and Tween 80). However, the equimolar mixture of Tween 80/SDDC (MSR = 0.450) was more efficient than the mixture $C_{12}E_{23}/C_{12-2-12}$ (MSR = 0.3065).

The equimolar mixture of the gemini surfactant *N,N*-bis(dimethyldodecyl)-1,2-pentanediammonium dibromide (12-5-12) and the non-ionic hexaethylene glycol monododecyl ether ($C_{12}E_6$) showed a MSR value of 0.075 for naphthalene and of 0.073 for pyrene [45]. That implies that this mixture is considerably less efficient at solubilizing naphthalene than the system of this work (MSR = 0.450); however, it is better at solubilizing pyrene (our MSR = 0.01).

Table 3

Molar solubilization ratios and micellar affinity constants of the hydrocarbons in micellar systems^a.

PHA	MSR _{TW80}	MSR _{SDDC}	$\log K_m^{\text{TW80}}$ [27]	$\log K_m \propto_{\text{TW80}} = 0.5$	$\log K_m^{\text{SDDC}}$	$\log K_{o/w}$ [41]
Naphthalene	0.240	0.054	4.77	4.99	4.22	3.36
Phenanthrene	0.184	0.009	6.27	6.21	5.01	4.57
Pyrene	0.080	0.004	6.47	5.61	5.15	5.18

^a pH = 9.16, T = 30 °C.

Yadav et al. studied a mixture formed by a phosphate head group based anionic gemini surfactant (AG) and cationic conventional ones (dodecyltrimethylammonium bromide, DTAB, and tetradecyltrimethylammonium bromide, TTAB) [46]. The MSR values for pyrene solubilization by mixtures of AG/DTAB and AG/TTAB at molar relation 0.6/0.4 are 0.0124 and 0.0154 respectively. These values are comparable to the value obtained at equimolar relation of Tween 80/SDDC (0.010).

From all these results, it is clear that it is very difficult to make generalizations, hence, it is important to evaluate each new system before application.

To quantify the mixing effect of the surfactant systems on the solubilization of PAHs, the deviation ratio (R) between the experimental molar solubilization ratio, MSR_{exp} , and the ideal value, MSR_{ideal} , can be defined as $R = MSR_{exp}/MSR_{ideal}$ where $MSR_{ideal} = \sum_i MSR_{i,oxi}$. MSR_i is the experimental MSR value of solubilize in the pure i -th surfactant solution, whose bulk mole fraction in the mixture is α_i . A R value higher than 1 implies a positive mixing effect of the surfactants on solubilization, i.e., synergism.

The solubilities of the PAHs were measured as a function of the total surfactant concentration in Tween 80/SDDC mixtures at different α_{TW80} . The mixtures increased the solubility of each hydrocarbon with respect to buffer. The calculated values of R were higher than 1 (between 1.5 and 2.3) for naphthalene and phenanthrene but lower than 1 for pyrene (Table S1). In the last case, it seems that the mixtures were worst when the amount of Tween increased. Fig. 6 shows these results, comparing the solubilized PAH amount by the single surfactants and an equimolar mixture of both. It is clear that in those conditions, the mixture is more efficient than the individual surfactants at solubilizing naphthalene and phenanthrene, but not pyrene. Although the interaction between the surfactants is favourable from the parameter β obtained, the solubilization of pyrene is not improved in the mixture, being better in Tween 80 alone. Hydrophilic-hydrophilic interactions between surfactant molecules occurring at the mixed micelle-water interface could affect the solubilization of the less hydrophobic compound, in this case, naphthalene. In the micellar core, instead, hydrophobic-hydrophobic interactions take place, affecting mainly the solubilization of the pyrene, the most hydrophobic compound. As mentioned, the strong interaction between both surfactants, with the concomitant formation of a more closely packed micelle, could prevent pyrene entering the micellar phase from aqueous phase by diffusion, finally reducing the solubilization capability of the micelle. Similar results have been observed in other systems, for instance for the solubilization of phenanthrene in Tween 80/sodium laurate mixtures, where no synergism was observed [27]. Wei et al. also found no synergic effect in the study of solubilization of PAHs in equimolar mixed gemini surfactant solutions, although in those systems the CMCs were also lower than the ideal CMC, and β values were negative [15].

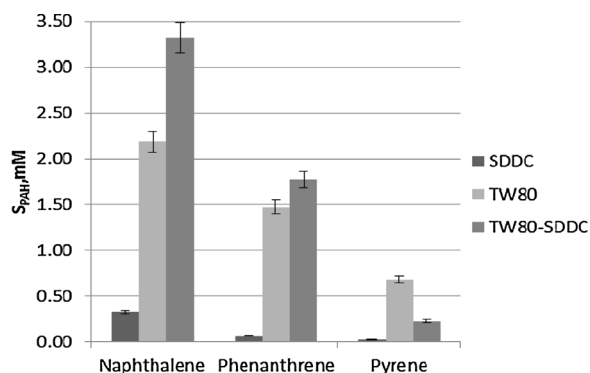


Fig. 6. Effect of single or mixed surfactants on the solubilization of PAHs in buffer solution. Tween 80/SDDC mixture at $\alpha_{TW80} = 0.5$, $[Surfactant]_{total} = 8 \times 10^{-3}$ M, $pH = 9.16$, $T = 30$ °C. S_{PAH} means PAH concentration solubilized in these conditions.

In mixed surfactant systems with a very negative β value, the micelle becomes densely packed [25], which can reduce its solubilization capability. It is also known that as the compound becomes bigger, it sits more deeply in the interior of the micelle, compared with the smaller compound [47]. Fatma et al. reported that in mixtures of a cationic gemini surfactant (ethane-1,2-diyl bis(N,N -dimethyl- N -dodecylammoniumacetoxyl) dichloride) and conventional surfactants, pyrene is incorporated in the non-polar micellar core, whereas in a smaller compound, anthracene, the probable localization site is the palisade layer [48]. In the other hand, in the study of the effect of aqueous micellar solution of dodecylammonium trifluoroacetate on the solubilization of PAHs, a change was found in the solubilization site of the hydrocarbon with the increment in the number of carbon atoms, confirming that the relation of size and hydrophobicity of the hydrocarbon and the polar region of the micelle determines solubilization effects [47]. Taking into account the negative β values in this system and the large size of pyrene, both effects can be combined to produce a reduction in the solubilization of pyrene into the micelles. Table 3 shows the K_m values obtained for the hydrocarbons in an equimolar mixture of Tween 80/SDDC. K_m values are higher in the mixture with $\alpha_{TW80} 0.5$ than those in SDDC alone. However, the value for pyrene is notably low, K_m being lower than the value in Tween 80. The affinity of naphthalene for the mixed micelle is higher than that for the individual surfactants, whereas for phenanthrene, it is practically the same as that for the Tween 80 micelles. The association constant of pyrene and the mixed micelles is considerably lower than with Tween 80, according to the lack of synergism found in this system.

The variation in the behaviour observed in the mixed systems studied (synergism for solubilization of naphthalene and phenanthrene and inhibition for the solubilization of pyrene) depends upon the surfactant molecular microstructure (packing of surfactant molecules in the mixed micelle core) and on the surfactant-solute interaction in the mixed micelles.

The mixing effect seen on the solubilization of the hydrocarbons studied (synergism or inhibition) confirms a non-ideal interaction among the surfactants in the mixtures [49].

4. Conclusions

We investigated the properties of mixed surfactant solutions formed by a commercial surfactant, Tween 80, and the liposamine acid derivative SDDC. The mixed micelles had triaxial ellipsoid shape with properties in between both pure surfactants. The mixtures showed a non-ideal behaviour as indicated by a lower CMC than that of the individual surfactants, and negative interaction parameter, β , values.

The solubility of naphthalene, phenanthrene, and pyrene was measured in solutions of the individual surfactants and in their mixtures to gain additional information on the nature of the interaction of surfactants. All the amphiphilic systems solubilized higher concentrations of pollutants than pure water, Tween 80 being a better system than the gemini surfactant. The mixture of both surfactants proved to be more efficient at solubilizing naphthalene and phenanthrene, as compared with the values calculated for a mixture considering individual behaviour. For pyrene, however, no synergism on the solubilization was observed in the mixture of surfactants. This different behaviour is probably related to different solubilization sites of the hydrocarbons in the aggregates and to a very attractive interaction of both surfactants in the mixture, making a compact micelle precluding the deep enough incorporation of pyrene. When discussing the mixing effect of surfactants on the solubilization of PAHs, the CMC and structure of the surfactants, as well as the polarity of the solutes and their association constants with the micellar phase, must be considered simultaneously. They are all important factors influencing the solubilization of organic compounds by mixed surfactant solutions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2017.08.011>.

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