Different behaviours in the solubilization of polycyclic aromatic hydrocarbons in water induced by mixed surfactant solutions

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ABSTRACT

Water solubility of polycyclic aromatic hydrocarbons (PAHs), viz, naphthalene and phenanthrene, in micellar solutions at 25 °C was investigated, using two series of different binary mixtures of anionic and nonionic surfactants. Tween 80 and Brij-35 were used as nonionic surfactants whereas fatty acids or amphiphilic cyclodextrins (Mod-β-CD) synthesized in our laboratory were used as anionic ones. Solubilization capacity has been quantified in terms of the molar solubilization ratio and the micelle–water partition coefficient, using UV–visible spectrophotometry. Anionic surfactants exhibited less solubilization capacity than nonionics. The mixtures between Tween 80 and Mod-β-CD did not show synergism to increase the solubilization of PAHs. On the other hand, the mixtures formed by Tween 80 and fatty acids at all mole fractions studied produced higher enhancements of the solubility of naphthalene than the individual surfactants. The critical micellar concentration of the mixtures of Tween 80/sodium laurate was determined by surface tension measurements and spectrofluorimetry using pyrene as probe. The system is characterized by a negative interaction parameter (β) indicating attractive interactions between both surfactants in the range of the compositions studied.

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1. Introduction

The mixture of surfactants has received particular attention in the last years due to their efficient solubilization, suspension, dispersion, and transportation capabilities (Yoshimura et al., 2004). In view of this, bi- and ternary combinations of ionic and nonionic surfactants have been studied in relation to their mixed micelle formation and adsorption at the air–water interface (Alargova et al., 2001; Zhang et al., 2002). Several theories have been used to analyse the experimental results and explain synergism in mixed surfactant systems.

Polycyclic aromatic hydrocarbons (PAHs) are formed by natural and anthropogenic pyrolysis of organic matter during forest fires, chemical manufacture, and use of fossil fuel (Gallego et al., 2008). The contamination of soils and water by these carcinogenic pollutants is a widespread environmental concern (Wang et al., 2008). Several attempts, involving physical, chemical, biological and their combined technologies, have been made to remedy PAH contaminated soils and groundwater. Surfactant enhanced remediation (SER) has been suggested as a promising technology for the removal of hydrophobic pollutants from soil and groundwater (Bernardez and Ghoshal, 2004). Surfactant molecules above their critical

micelle concentration (*CMC*) form aggregates in water, called micelles. These aggregates have a hydrophobic core and a hydrophilic outer surface. Micelles are capable of dissolving hydrophobic PAHs in their hydrophobic core, resulting in an increased aqueous solubility of the compounds (Garon et al., 2002).

To quantify the efficiency of the SER, considerable research has been conducted, including mainly the solubilization of PAHs by single surfactant systems (Wang and Mulligan, 2004). Anionic and nonionic surfactants are mostly used for soil washing or flushing (Mulligan et al., 2001). However, too hard subsurface water may be detrimental to the effectiveness of anionic surfactants since this kind of surfactants may precipitate. On the other hand, nonionic surfactants are more likely to adsorb onto clay fractions compared with anionic ones (Tsomides et al., 1995), requiring higher concentration of surfactants. As a consequence, attempts have been made to improve the performance of SER in contaminated soils by employing mixed surfactant systems (Zhou and Zhu, 2005a).

β-Cyclodextrin (β-CD), an environmentally friendly compound, enhances the solubility and removal of contaminants from solid surfaces by formation of host–guest complexes (Lubomska et al., 2005). β-CD was successfully used to reduce the toxicity of sludges by forming inclusion complexes with pesticides (Oláh et al., 1988). Some β-CD derivatives, such as hydroxypropyl-β-cyclodextrin and methyl-β-cyclodextrin, significantly influence PAH removal from

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contaminated soils (Reid et al., 2000), in some cases with an extraction enhancement factor of about 200 compared with water (Viglianti et al., 2006).

The esterification of β-CD with 3-(dodec-2-enyl)-dihydrofuran-2,5-dione gave modified cyclodextrins (Mod-β-CD) with varying substitution degrees depending on the conditions of the synthesis (González and de Rossi, 2001). These modified cyclodextrins exhibit amphiphilic properties and are highly efficient at diminishing the surface tension of water and water/dimethylsulfoxide solutions, forming aggregates at very low concentration. We have shown that in the aggregates of Mod-β-CD with a ten-carbon-atom hydrophobic chain, the cavity is available to interact with external molecules such as phenolphthalein, 1-amino adamantane and Prodan (Silva et al., 2008). The results indicate that the aggregates have two binding sites to interact with a hydrophobic compound: the cavity of the cyclodextrin and the apolar heart of the micelle. This fact could increase the solubilization of pollutants due to the presence of two possible sites where the substrate could be located. Therefore the use of modified cyclodextrins, alone or mixed with other surfactants, might introduce efficient systems for the solubilization and extraction of pollutants from soils.

The objective of the present work was to investigate some solubilization aspects of naphthalene and phenanthrene (as representative PAHs) by binary surfactant systems. We studied binary mixtures of a nonionic (Tween 80 or Brij-35) and an anionic surfactant. More specifically, the focus has been set on (i) the effects of mixtures of nonionic surfactants with Mod-β-CD for analysing the change in the chain length and substitution degree of the cyclodextrin; (ii) the effect of mixtures of nonionic surfactants with fatty acids with the same number of carbons in the hydrocarbon chain as that in the Mod-β-CD used. Scheme 1 depicts the structures of these surfactants.

The surfactant systems used were chosen with the aim to find synergism in the mixtures to solubilize PAHs, finding good systems to be applied in SER technologies. The surfactants chosen are environmentally safe compounds.

2. Experimental section

2.1. Materials

Aqueous solutions were prepared from water purified in a Millipore apparatus. Methanol HPLC grade (Sintorgan) was used without purification.

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

The nonionic surfactants, Tween 80 and Brij-35, and the sodium salts of fatty acids, laurate and miristate, were obtained from Sigma–Aldrich and used as received. Mod-β-CD_{12} with twelve carbon atoms in the aliphatic chain (average degree of substitution = 1 or 2.4 per cyclodextrin molecule) were synthesised in the laboratory as was described previously (González and de Rossi, 2001) by the reaction of 3-(dodec-2-enyl)-dihydrofuran-2,5-dione with β-CD. A fourteen-carbon-atom derivative (Mod-β-CD_{14}) was similarly synthesised. When we will refer to modified cyclodextrin with substitution degrees different from 1, we will add the number to the name. Mod-β-$CD_{12}(2.4)$, for instance, indicates a β-cyclodextrin substituted by alkenyl succinic acid with 12 carbon atoms in the alkenyl chain, and a 2.4 degree of substitution.

The experiments of solubilization of pollutants in the presence of Mod-β-CD were done in a buffer of pH 7.20 (0.05 M KH_2PO_4, 0.033 M NaCl) whereas those in the presence of fatty acids were performed at pH 9.16 (0.01 M $Na_2B_4O_7$, 0.02 M NaCl) to achieve the complete dissolution of surfactants. Mixed surfactant solutions

were prepared by dissolving different amounts of the two surfactants of the mixture in the same buffer. PAHs were dissolved in methanol for stock solutions.

2.2. Solubilization tests

Batch tests for the solubilization of various PAHs in single and binary surfactant solutions of mixed surfactants with different total concentration were performed in borosilicate glass tubes. In these mixtures, the molar ratio of nonionic surfactant was varied in relation to the ionic one (or the cyclodextrin). Each surfactant–PAH system involved 5–7 batch tests with surfactant solution having a range of concentrations above and below the CMC. Triplicate tests were performed for each sample. An aliquot of the stock solution of PAH was added to each tube in an amount considerably higher than the required to saturate the solution. The solvent was evaporated by bubbling dry N_2; the surfactant solution was then added. The samples were shaken during 48 h in a thermostated shaker bath maintained at 25 °C. We chose that solubilization time because the measurements done at 24, 48 and 72 h give the same results, so we were sure that at 48 h the equilibrium was reached. Afterwards, the samples were centrifuged to separate the undissolved contaminant. An appropriate aliquot of the supernatant was diluted to reach the necessary concentration with buffer adding 20% of methanol to carry out the quantification of the sample by UV–visible absorption in a Shimadzu Multispec 1501 spectrophotometer. The naphthalene and phenanthrene solubility in each surfactant system was determined at 267 and 251 nm, respectively, and then taken as the mean of the triplicate readings. The data were reproducible and the error in the determinations was always lower than 5%.

2.3. Fluorescence measurements

CMC of Tween 80/sodium laurate mixtures were determined by fluorescence at 25 °C. The CMC values were measured by monitoring changes in pyrene fluorescence intensity and fine structure as a function of surfactant concentration. The typical monomer fluorescence spectra were observed by exciting at 334 nm. The spectra were used to determine the fluorescence intensity ratio (I_1/I_3) of the first (I_1, 374 nm) and third (I_3, 385 nm) vibronic peaks of monomeric pyrene. These measurements were made with a Jasco FP 777 spectrofluorimeter.
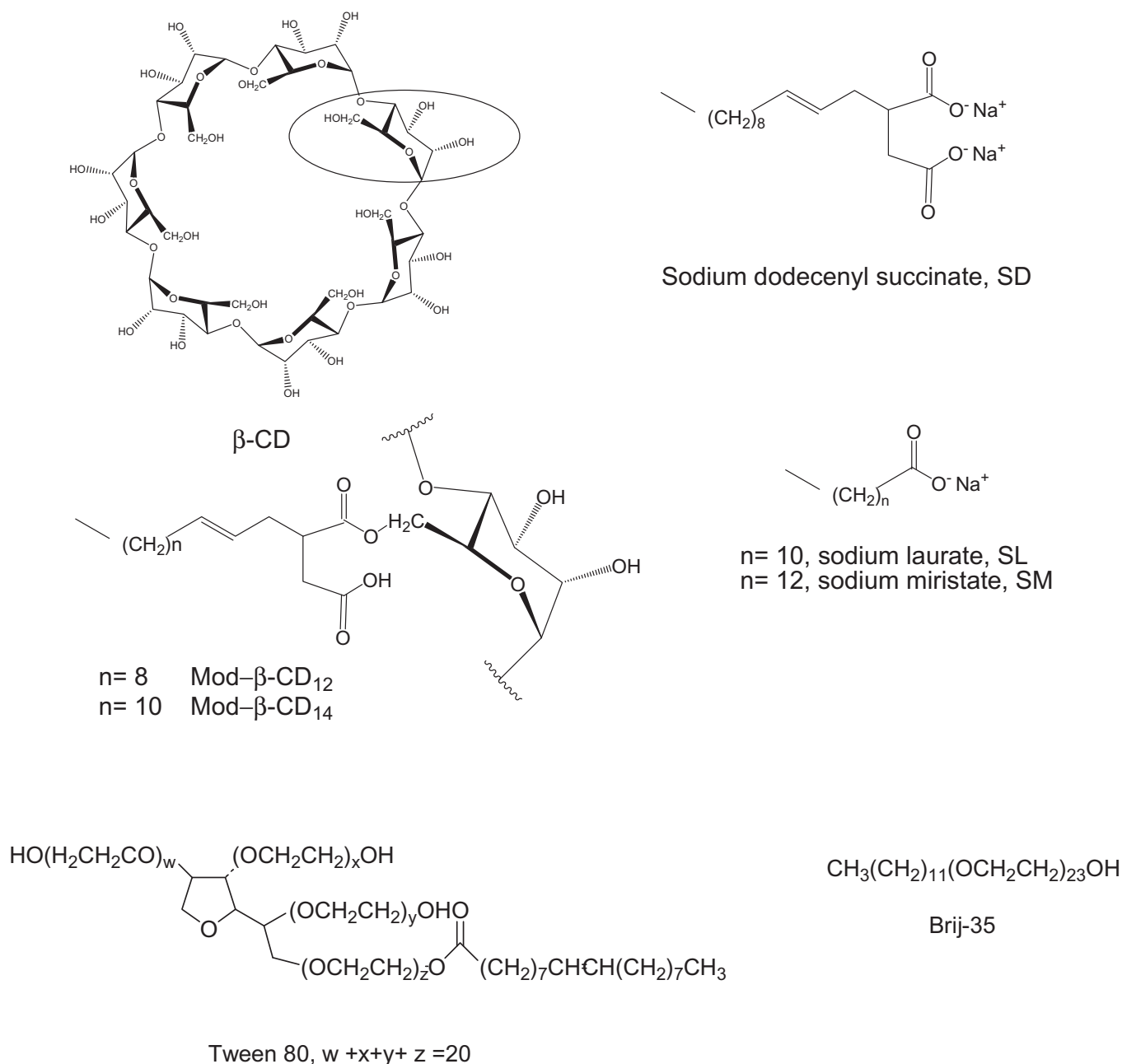
2.4. Measurements of surface tension

Surface tension of the solutions was measured by the ring method using a Du Nöuy ring tensiometer (Cole Parmer Surface Tensiomat 21) at 25.0 °C. The temperature was maintained constant by circulating thermostated water through a jacketed vessel containing the solution. The CMC was determined by measuring the surface tension of surfactant solutions over a wide concentration range and noting the inflection point in the plot of surface tension versus logarithm of surfactant concentration. The surface tension value was measured when an stable reading was obtained for a given surfactant concentration, as indicated by at least three consecutive measurements sharing almost the same value.

3. Results and discussion

3.1. Solubilization of PAHs by single surfactant systems

We studied the effect of Mod-β-CD on the solubilization of phenanthrene and in some cases we conducted some experiments with naphthalene for comparison purposes. The apparent solubility of phenanthrene in the presence of Mod-β-CD with different

β-CD

Sodium dodecenyl succinate, SD

n= 8   Mod–β-CD$_{12}$
n= 10   Mod–β-CD$_{14}$

n= 10, sodium laurate, SL
n= 12, sodium miristate, SM

HO(H$_2$CH$_2$CO)$_w$ (OCH$_2$CH$_2$)$_x$OH

(OCH$_2$CH$_2$)$_y$OHO

(OCH$_2$CH$_2$)$_z$O (CH$_2$)$_7$CHCH(CH$_2$)$_7$CH$_3$

Tween 80, w +x+y+ z =20

CH$_3$(CH$_2$)$_{11}$(OCH$_2$CH$_2$)$_{23}$OH

Brij-35

Scheme 1. Structure of the different surfactants used in this work. The circle in the β-cyclodextrin indicates the unit of glucose that is shown in the Mod-β-CDs.

substitution degrees and chain lengths was measured (Fig. 1 is representative). The solubility of phenanthrene in water is 4.6×10^{-6} M. The aqueous solubility of this compound increased linearly with the surfactant concentration above the CMC. This behaviour is generally attributed to the incorporation or partitioning of organic solutes within surfactant micelles. The effect of surfactant monomers is assumed to be negligible.

The measurement of the effectiveness of a particular surfactant to solubilize a given solute is known as molar solubilization ratio (MSR) (Edwards et al., 1991). MSR represents the number of moles of organic compound solubilized per mole of surfactant forming micelles, and it is expressed by Eq. (1), and can be obtained from the slope of Fig. 1.

$$MSR = (S_{PAH,mic} - S_{PAH,CMC})/(C_{surf} - CMC) \qquad (1)$$

In Eq. (1) $S_{PAH,CMC}$ is the solubility of a PAH compound at the CMC, which is the same as their water solubility; $S_{PAH,mic}$ is the total solubility of the PAH in micellar solution at a particular surfactant concentration higher than CMC; and C_{surf} is the surfactant concentration at which $S_{PAH,mic}$ was evaluated. All the concentrations are expressed in moles per litre.

The values of MSR determined for phenanthrene in the presence of different Mod-β-CD are the following: 9×10^{-3} for Mod-β-CD$_{12}$, 35×10^{-3} for Mod-β-CD$_{12}$(2.4) and 5×10^{-3} for Mod-β-CD$_{14}$. The comparison between Mod-β-CD with the same substitution degree and different aliphatic chain length indicates that the cyclodextrin with the shorter chain is slightly more efficient to solubilize the pollutant. The increment in the substitution degree also increases the MSR value.
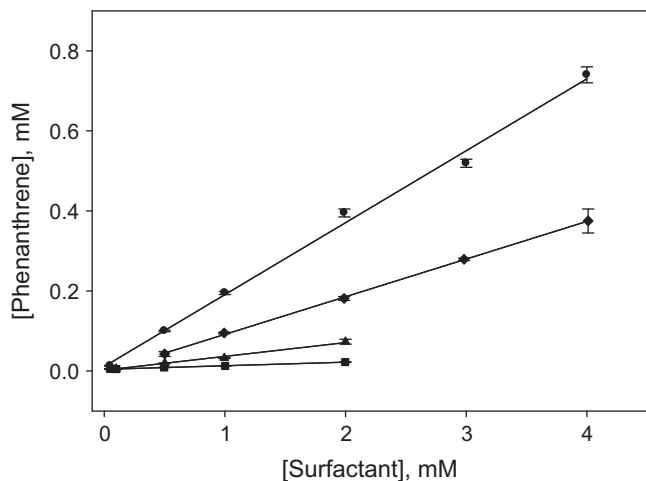
Fig. 1. Water solubility enhancements of phenanthrene by single surfactant systems at 25 °C, pH = 7.20: (●) Tween 80; (♦) Brij-35; (▲) Mod-β-CD$_{12}$(2.4); (■) Mod-β-CD$_{12}$.

It is known that in conventional surfactants the longer chain produces higher concentrations of solubilized contaminants. For instance, the solubilization of a dye in water solutions of potassium alkanoates increases with the rise in the number of carbon in the aliphatic chain of the surfactant: tetradecanoate > dodecanoate > decanoate > octanoate (Holmberg et al., 2006). With Mod-β-CD, however, the effect was the opposite. This behaviour is probably due to the interaction of the hydrocarbon chain with the cavity. The alkenyl chain is included in the cavity of another Mod-β-CD$_{10}$ molecule (Silva et al., 2008) and it is known that the compounds with longer chains have more affinity for the cavity than the shorter ones. The association constant of fatty acids with β-CD are 6.4×10^2, 3.7×10^3 and $1.4 \times 10^4\,M^{-1}$ for octanoic, decanoic and dodecanoic acids respectively (Parker and Stalcup, 2008). Therefore, it is likely that Mod-β-CD$_{14}$ has a lower number of free hydrocarbon chains, and a lower number of free cavities to include phenanthrene, compared with Mod-β-CD$_{12}$.

In order to evaluate both binding sites of Mod-β-CD separately, solubilization experiments of phenanthrene with native β-CD and sodium dodecenyl succinate (SD) were done. The solubility obtained in the presence of 1×10^{-3} M of β-CD was 1.08×10^{-5} M whereas that measured with the same concentration of Mod-β-CD$_{12}$(2.4) was 3.65×10^{-5} M. It is known that native cyclodextrins increase the solubility of some organic compounds (Omar et al., 2007), however, the increment achieved with Mod-β-CD is larger. On the other hand, the solubility of the same contaminant in the presence of 2.4×10^{-3} M of SD, (the same content of aliphatic chain supplied for the modified cyclodextrin used) is 1.88×10^{-5} M. Experiments with native β-CD and SD in the same solution were also carried out. The solubility of phenanthrene in a solution containing 1×10^{-3} M of β-CD and 2.4×10^{-3} M of SD is 1.84×10^{-5} M, a value lower than that obtained with 1×10^{-3} M of Mod-β-CD$_{12}$(2.4). In addition, the MSR obtained at different blend concentrations, always maintaining the relation of 2.4 between SD and β-CD, is 0.016. This value is considerably lower than that observed with Mod-β-CD$_{12}$(2.4), namely 0.035. As seen from the results, the increase in the solubilized amounts of phenanthrene produced by Mod-β-CD, is related to the structure of this interesting surfactant, which has two binding sites available: the cyclodextrin cavity and the core of the micelle.

MSR obtained for naphthalene in the presence of Mod-β-CD$_{12}$ was 0.089, 10 times higher than that for phenanthrene with the same surfactant.

Data in Fig. 1 also show the solubilization of phenanthrene by single Tween 80 and Brij-35. The solubility was enhanced by each of the surfactant solution, increasing linearly with growing surfactant concentrations. The MRS for phenathrene in Tween 80 and in Brij-35 are 0.184 and 0.094 respectively, whereas the corresponding values for naphthalene are 0.234 and 0.214. The nonionic surfactants are considerably better to the different Mod-β-CD used to solubilize the PAHs studied.

Although the values of MSR for the solubilization of naphthalene in the several media studied are always higher than those obtained for phenanthrene, the real increment in solubilization must be evaluated taking account of the initial solubility of each PAH in water. Fig. 2 displays improvements in the solubility for both contaminants in water by Tween 80. S_w^* is the solute solubility at each surfactant concentration; S_w is the solute solubility in pure water. As the S_w value for phenanthrene (4.6×10^{-6} M) is considerably lower than that for naphthalene (1.7×10^{-4} M), the solubility enhancement factor, S_w^*/S_w, is higher for the less soluble compound, as can be seen from Fig. 2. This fact is in agreement with previous data from solubilization of the same contaminants in the presence of nonionic surfactants (Zhu and Feng, 2003).

The apparent solubilities of naphthalene and phenanthrene in aqueous solutions of sodium laurate (SL) were also determined (Supplementary material, Fig. S1). The solubilities of the pollutants in the presence of the surfactant above its CMC are higher than those in water. The MSR values obtained from the plots are 0.040 and 0.011 for naphthalene and phenanthrene respectively.

Sodium miristate was not soluble in water, however, its solubilization was possible in mixtures with a nonionic surfactant, with a molar fraction of nonionic detergent higher than 0.5. This could evidence the formation of mixed micelles between the fatty acid and the nonionic surfactants. Although it was not possible to analyse the effect of sodium miristate alone, its study could be performed in mixtures with nonionic surfactants. Accordingly, these results are discussed below.

The micelle–water partition coefficient (K_m) is a parameter that also allows characterizing the partitioning of organic solutes between the surfactant micelles and the water phase. K_m is defined as the ratio of the mole fraction of the compound in the micellar pseudophase (X_m) to the mole fraction of the compound in the aqueous pseudophase (X_a) (Hayase and Hayano, 1977). The value of K_m is dependent on surfactant chemistry, solubilizate chemistry and temperature. Experimentally, K_m may be calculated using Eq. (2) as follows:
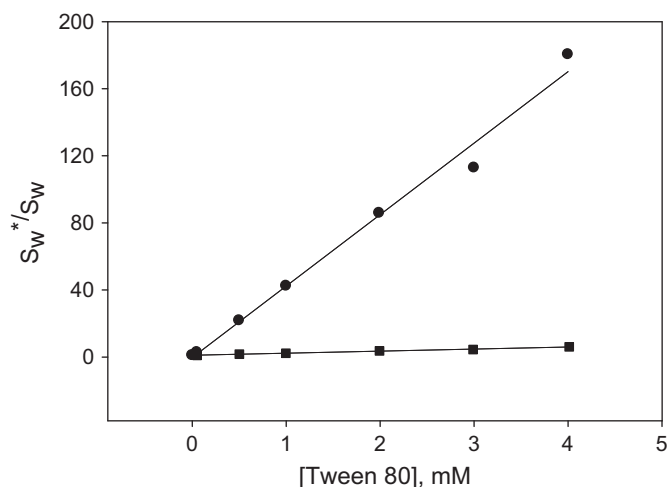

Fig. 2. Solubility enhancements relative to water solubility of phenanthrene and naphthalene by Tween 80 solutions, (■) naphthalene; (●) phenanthrene.

$$K_m = X_m/X_a \qquad (2)$$

where $X_m = MSR/(1 + MSR)$ and $X_a = [S_{PAH,CMC}]V_w$. V_w are the molar volume of water, i. e., 0.01805 L/mol at 25 °C (Lide, 1991), then K_m can be expressed as:

$$K_m = MSR/\{[S_{PAH,CMC}]V_w(1 + MSR)\} \qquad (3)$$

The K_m values for naphthalene and phenanthrene in the different surfactant solutions used are shown in Table 1 and compared with their octanol–water partition coefficients (K_{ow}). In general, the partitioning of a given solubilizate into the micellar phase increases as the K_{ow} value increases. As seen, the values of K_m for both organic compounds follow the same tendency as that of K_{ow}. It can be observed that $\log K_m > \log K_{ow}$ which indicates that the PAH partition efficiency in the micellar phase is higher than that in the octanol phase. This is the behaviour usually found in the interaction of hydrophobic compounds with surfactants. The values of K_m for a particular surfactant and K_{ow} are found to have a good linear relationship when several PHAs are correlated (Edwards et al., 1991; Zhou and Zhu, 2005b). In this work, the values of K_m obtained with the nonionic surfactants (Table 1) are in close agreement with those found in the literature (Zhu and Feng, 2003), for instance the value reported for $\log K_m$ of phenanthrene with Tween 80 is 6.25 (Zhao et al., 2005).

Characterization of the partitioning in simple micelle–water systems as provided through K_m values is an essential prerequisite to the proper modelling of hydrophobic organic compounds partitioning in mixed surfactant systems.

3.2. Solubilization of PAHs by non-ionic surfactants/Mod-β-CD mixed systems

The solubility of PAHs was determined in nonionic surfactant systems (Tween 80 or Brij-35) with Mod-β-CD$_{12}$ (0.9 or 2.4). The experiments were done by varying the nonionic surfactant concentration at a constant concentration of Mod-β-CD.

The experimental solubility of phenanthrene in the mixed surfactant solutions (S_{exp}) can be compared with those calculated on the basis of the ideal additivity rule (S_{cal}). The values S_{cal} were calculated from:

$$S_{cal} = (S_{non} + S_{anionic}) - S_w \qquad (4)$$

where S_{non} and $S_{anionic}$ represent the solubility of the compound in nonionic and anionic surfactant solutions of the same concentration used in the mixed system and can be obtained from the plots of the solubility of the aromatic compound versus the concentration of each single surfactant. S_w is the intrinsic solubility of the corresponding compound in water.

To quantify the mixing effect of surfactant systems on the solubilization of naphthalene and phenanthrene, 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 $MSR_{ideal} = \sum_i MSR_i X_i$. MSR$_i$ is the experimental MSR value of solubilizate in the pure i-th surfactant solution, whose bulk mole fraction in the mixture is X_i. A value of R higher than 1 implies a positive mixing effect of the surfactants on solubilization, i.e. synergism. For phenanthrene, S_{calc} is equal to S_{exp} at the different compositions of the mixed system (Fig. S2), implying that R is practically 1; hence, no mixing effect on the solubilization of phenanthrene is revealed. In addition, no synergic effect was observed in all the systems assayed: Tween 80/Mod-β-CD$_{12}$, Tween 80/Mod-β-CD$_{12}$(2.4) and Brij-35/Mod-β-CD$_{12}$ at different concentrations and with both PAHs. In some cases, S_{calc} was even greater than S_{exp}. The absence of mixing effect might indicate that Mod-β-CD do not form mixed micelles with the non ionic surfactants used. Therefore, each surfactant in the mixture continues solubilizing the same quantities of contaminants that do individually. Although the interaction between native β-CD with different non-ionic surfactants is known, (Cabaleiro-Lago et al., 2006), the lack of association here could be attributed to the strong interaction among the Mod-β-CD molecules. As mentioned above, we have demonstrated that Mod-β-CD$_{10}$ forms big aggregates not only through the interaction of the hydrophobic tails as in common amphiphilic compounds, but also through the inclusion of the alkenyl chain into the cavity of another Mod-β-CD$_{10}$ molecule (Silva et al., 2008). Although the cavity is still available to interact with external guests, it is possible that the energetic cost associated with the breakdown of Mod-β-CD aggregates to form mixed micelles with nonionic surfactants would be excessively high, thus the surfactants do not mix.

3.3. Solubilization of PAHs by non-ionic surfactants/fatty acid sodium salts mixed systems

The solubilities of phenanthrene and naphthalene were measured as a function of Tween 80/SL mixed surfactant concentrations at different solution compositions. Fig. 3 depicts data of the solubility of PAHs in the presence of a constant concentration of sodium laurate (2×10^{-2} M) and a variable concentration of Tween 80. The mixtures increased the solubility of the contaminant with respect to water, and similar results were obtained with the other concentrations of SL assayed (data not shown). The lines calculated
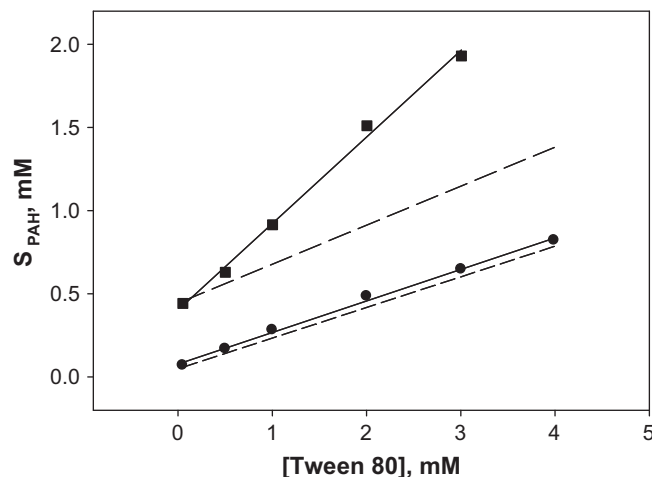
Table 1
Log K_m for the distribution of PAHs in surfactant solutions.

Solubilization system	Naphthalene	Phenanthrene
Tween 80	4.77[b]	6.27[b]
Brij-35	4.74[b]	6.01[a]
Mod-β-CD$_{12}$	4.41[a]	5.03[a]
Mod-β-CD$_{12}$(2.4)		5.61[a]
SL	4.04[b]	5.12[b]
log K_{ow}[c]	3.36	4.57

Mod-β-CD$_{12}$: modified monosubstituted cyclodextrin with an amphiphilic chain of twelve carbons; Mod-β-CD$_{12}$(2.4): modified cyclodextrin with amphiphilic chain of twelve carbons and substitution degree of 2.4; SL: sodium laurate.

[a] pH 7.2.
[b] pH 9.16.
[c] Log K_{ow} values from An et al., 2002.

Fig. 3. Solubilization of PAHs in Tween 80/SL mixed surfactants. [SL] = 2×10^{-2} M, pH = 9.16. (■) $S_{exp}^{naphthalene}$; (– – –) $S_{calc}^{naphthalene}$; (●) $S_{exp}^{phenanthrene}$;(- - - -) $S_{calc}^{phenanthrene}$. The error bars do not exceed the size of the symbols.

considering independent activity of the surfactants (Eq. (4)) are also shown in Fig. 3.

The comparison of the slopes obtained experimentally under the conditions shown in Fig. 3 with those calculated for the ideal mixture, considering additivity for both surfactants, indicates that for phenanthrene practically no synergistic effect is observed. The ratio between the experimental and calculated MSR is close to 1. On the other hand, the same comparison for naphthalene, indicates synergism for its solubilization at one constant concentration of sodium laurate (from Fig. 3, $R = 2.21$). The study of the variation of total surfactant concentration at two different molar fraction of non-ionic surfactant in the mixture ($X_{Tween\ 80} = 0.2$ and 0.6) presents the same effect as that previously observed, indicating synergism in that mixture for that pollutant (data not shown). The ratios between the experimental and calculated values for the ideal mixing were higher than 1 in both cases (1.16 and 1.44 respectively). The effect of the change in the composition of the mixture was analysed at several molar fractions at constant total surfactant concentration of 2.5×10^{-2} M. As can be observed in Fig. 4 the synergistic effect is produced under all conditions studied. A small addition of sodium laurate to Tween 80 increases considerably the solubilization of naphthalene and the effect decreases slightly when the fraction of Tween 80 increases. The same experiments done with phenanthrene shows that an inhibitory effect is exerted, i.e., R is smaller than 1 at $X_{Tween\ 80} = 0.4$, 0.6 and 0.8 (data not shown).

The change in the chain length of the fatty acid by adding two further carbons (sodium miristate, SM) causes a similar effect on the solubilization of naphthalene. The ratio between experimental and calculated values for a molar fraction of Tween 80 = 0.6 in the mixture with SL is 1.44; with SM it is 1.68.

On the other hand, the mixture of SL or SM with other nonionic surfactants such as Brij-35 or Triton X 100 ($C_8H_{17}C_6H_4O(CH_2CH_2O)_{9.5}H$) does not manifest synergism in the solubilization of naphthalene since the values of R were very close to 1 at $X_{nonionic} = 0.6$.

The differences found in the behaviour of phenanthrene and naphthalene in mixed systems may be explained in terms of different solubilization sites for both compounds. Morisue et al. (1994) found that in aqueous micellar solution of dodecylammonium trifluoroacetate there is a change in the site of solubilization for PAHs with the increment in the number of carbon atoms. The values of dielectric constant determined for the microenvironments of several PAHs in micelles indicate that the microenvironment of anthracene and pyrene are less polar than that for naphthalene,
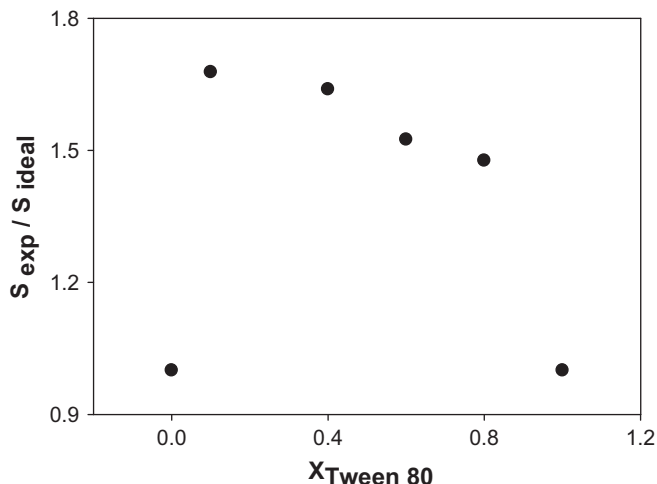
and much less polar than that for benzene; i.e., as the compound becomes bigger, it sits more in the interior of the micelle, compared with the smaller one. A similar situation is probably occurring here with naphthalene and phenanthrene.

The existence of mixing effect on the solubilization of both PAHs (synergism or inhibition) is an indication that some interaction takes place among the surfactant components, leading to a non-ideal behaviour of the mixed micelles (Rosen and Zhou, 2001; Matsubara et al., 2001). With the aim of gaining new insights into the interactions between surfactants in the mixtures, we characterized the mixed micelles formed by Tween 80/SL by spectrofluorimetry using pyrene as probe, and with surface tension measurements.

3.4. CMC and interaction of surfactants in mixed micelles of Tween 80/LS

The CMC values of single as well as mixed surfactant systems formed by Tween 80 and SL were determined measuring pyrene fluorescence. Pyrene is a fluorescent probe widely used to determine CMC, aggregation number, micropolarity, etc. of mixed micellar systems (Nakano et al., 2002; Asakawa and Miyagishi, 1999). The fluorescence intensity ratio of the first (I_1) and third (I_3) vibronic peaks of pyrene is well known to be sensitive to solvent polarity (Kalyanasundaram, 1988). The higher hydrophobic environment gives the higher I_3/I_1 ratio, as was reported for n-hexane (1.65) > 1-butanol (0.98) > methanol (0.75) > acetonitrile (0.57) (Kalyanasundaram and Thomas, 1977).

The values of I_3/I_1 ratio (I_1 was determined at 374 nm and I_3 at 385.0 nm) were measured at several surfactant concentrations in pure and mixed solutions. The I_3/I_1 ratio increases as the total surfactant concentration also increases, reaching a maximum value at each surfactant composition. There is no unified method to obtain the CMC values from the plots of pyrene I_3/I_1 (or I_1/I_3) ratio vs. surfactant concentration; different authors seem to adopt diverse criteria for choosing this point (Kalyanasundaram and Thomas, 1977; Aguiar et al., 2003). We carried out the analysis of the systems according to Aguiar et al. (2003) as was previously reported (Torres et al., 2010) and the inflection point of the sigmoid plot was taken as the CMC, whose values are shown in Table 2. The CMC values obtained in this way were compared with those from surface tension measurements (Table 2). It can be seen that these values are similar, therefore with both values at each molar fraction, the CMC averages were calculated and included in Table 2 too.

For ideal mixing in multicomponent systems, the ideal CMC values, CMC_{calc}, were calculated using the Clint equation (Eq. (5)) (Clint, 1975).

$$\frac{1}{CMC_{1,2}} = \frac{X_1}{CMC_1} + \frac{X_2}{CMC_2} \tag{5}$$

where $CMC_{1,2}$, CMC_1 and CMC_2 are the critical micelle concentration of mixed surfactant and individual pure components 1 and 2, respectively; X_1 and X_2 are the mole fraction of components 1 and 2 in mixed surfactant solutions, respectively.

However, due to the interaction between the components of the mixed micelle, the experimental CMCs of mixed surfactant usually differ from the theoretical CMCs. The differences between the experimental and calculated values of Tween 80/LS mixed system are subtle and practically zero at $X_{Tween\ 80}$ higher than 0.4, indicating their almost ideal behaviour for mixed micelle formation under those conditions. At lower molar fractions, $X_{Tween\ 80} = 0.1$ and 0.2, major differences between the experimental and calculated values are observed. At these molar fractions the observed CMC values were found to be lower than the ideal values, indicating negative deviation from ideal behaviour for mixed micelle formation.

Fig. 4. Solubility of naphthalene as a function of the solution composition in Tween 80/SL mixtures, [Surfactant]$_{total}$ = 2.5×10^{-2} M, pH = 9.16.

Table 2
CMC values determined for the mixture Tween 80/SL.

$X_{\text{tween 80}}$	CMC_{fluor}, 10^{-4} M[a]	CMC_{st}, 10^{-4} M[b]	CMC_{aver}, 10^{-4} M[c]	CMC_{calc}, 10^{-4} M[d]
0.0	164	164	164	164
0.1		0.64	0.64	1.15
0.2	0.36	0.39	0.37	0.58
0.4	0.33		0.33	0.29
0.6	0.26	0.16	0.21	0.19
0.8	0.14		0.14	0.14
1.0	0.09	0.12	0.10	0.10

[a] The *CMC* were calculated from the variation of I_3/I_1 vibronic bands of pyrene against total surfactant concentration at each molar fraction.
[b] Calculated from measurements of surface tension.
[c] Average values from the *CMC* determined by fluorescence and surface tension.
[d] Calculated using Eq. (5). SL: sodium laurate.

The regular solution theory has been proven to be successful in modelling the nonideal behaviour of mixed surfactants. According to this theory, the deviation of the experimental *CMC*s from the theoretical *CMC*s in mixed surfactant can be expressed with the interaction parameter β, which represents the interaction of the components, and can be calculated with Eqs. (6) and (7) (Holland and Rubingh, 1983).

$$1 - \frac{(x_1)^2 \ln(X_1 CMC_{12}/x_1 CMC_1)}{(1-x_1)^2 \ln[(1-X_1)CMC_{12}/(1-x_1)CMC_2]} = 0 \qquad (6)$$

$$\beta = \frac{\ln(X_1 CMC_{12}/x_1 CMC_1)}{(1-x_1)^2} \qquad (7)$$

In Eqs. (6) and (7), considering individual pure components 1 and 2, X_1 is the stoichiometric fraction of the nonionic surfactant in the mixed solution ($X_{\text{Tween 80}}$), CMC_1 and CMC_2 represent the experimental *CMC* of pure surfactants, x_1 is the molar faction of nonionic surfactant in the mixed micelle, β is the interaction parameter, and CMC_{12} is the *CMC* experimentally determined for the mixture at each X_1. From these equations β values of -6.3 and -6.0 were calculated for the solutions of mixed surfactants at $X_{\text{Tween 80}} = 0.1$ and 0.2 respectively.

Since the value of the β parameter is proportional to the free energy of mixing of the system, a negative value of β suggests that the attractive interaction between the two different surfactants is stronger than that between the two individual surfactants with themselves, and/or that the repulsive interaction between the two different surfactants is weaker than the self repulsion of the two individual surfactants. It can be assumed that the headgroups of ionic surfactants will cause electrostatic self-repulsion and that the bulky groups in the non-ionic surfactants will cause steric self-repulsion in the micelles of the pure compounds. In mixed systems these two effects are weakened by dilution effects after mixing, and the electrostatic self-repulsion of the anionic surfactants is replaced by the attractive ion–dipole interaction between the hydrophilic groups of the both surfactants. That is the reason why the formation of mixed micelles is favoured in this kind of mixtures (Zhou and Rosen, 2003).

4. Conclusions

The solubilities of naphthalene and phenanthrene were measured in solutions of different pure surfactants and in mixtures of nonionic–anionic surfactants. All the amphiphilic systems solubilize higher concentrations of pollutants than pure water. The best single systems were the nonionic surfactants and among them, Tween 80 was the most effective one for increasing the solubility of naphthalene and phenanthrene in water. The micelle–water partition coefficients were determined for the contaminants in all single systems correlating well with the respective octanol–water partition coefficients of the two pollutants.

We can establish that the amphiphilic Mod-β-CD studied in this work does not form mixed micelles with nonionic surfactants, probably due to the strong intermolecular interactions in the cyclodextrin aggregates. These interactions are absent in fatty acids which mixed with Tween 80, are the systems that showed better performance. In these mixtures, synergistic effect for the solubilization of naphthalene was obtained; however it was not found for phenanthrene. These results could be attributed to the different solubilization sites of the substrates in the mixed micelles.

These data can be used together with additional information on surfactants and contaminants sorption on soil, to estimate PAH solubilization in soil–water–surfactant systems and in this way we continue working.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2011.04.073.

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