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ORIGINAL RESEARCH ARTICLE

Efficiency of single and mixed dimeric surfactants micelles on solubilization of polycyclic aromatic hydrocarbons

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ABSTRACT

The solubilization of polycyclic aromatic hydrocarbons (PAHs) such as naphthalene, phenanthrene and pyrene by single and mixed anionic dimeric surfactants was investigated and correlated with micellar properties of these surfactants. The surface and micellar properties of single and binary mixed combinations of anionic dimeric surfactants have been studied through surface tension as well as conductivity measurements at 300 K. The associations between their micelle properties and solubilizing efficiency towards PAHs have been quantified and discussed in terms of the molar solubilization ratio (MSR), micelle-water partition coefficient (K_m) and standard free energy of solubilization (ΔG^0_S).The negative value of ΔG^0_S exhibits spontaneously the solubilization process. The MSR values increase with the order "pyrene < phenanthrene < naphthalene". The current study provides significant information for the selection of mixed dimeric surfactants for solubilizing water-insoluble compounds.

Keywords: Anionic Dimeric Surfactants; Polycyclic Aromatic Hydrocarbons; Solubilization

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1. Introduction

The contamination of soil and water by hydrophobic organic compounds (HOCs) are a universally widespread environmental problem. HOCs are found in the priority list of hazardous substances as listed by the agency for toxic substances and disease registry of USA[1]. Among these compounds, polycyclic aromatic hydrocarbons (PAHs) are more hazardous compounds to human health due to their mutagenic and carcinogenic nature[2,3]. PAHs constitute a class of hazardous organic compounds consisting of two or more fused benzene rings in linear, angular or cluster arrangements. These hydrophobic pollutants are byproducts of the incomplete combustion of organic matter. The major sources of PAHs are the wastes from the combustion of fossil fuel, incineration of industrial waste and petroleum products viz., coal tar, crude oil, creosote, vehicle emissions, etc.[4] These organic pollutants defile sea water, sediments and soil and also remain in the atmosphere for a long time due to their low solubility in water. Because of their higher hydrophobicity and poor solubility in water, the removal of PAHs from the contaminated sites becomes excessively difficult. Advancement of desorption and removal of these organics from soil is challenge to researchers and technologists.

It is well known that surfactants can enhance the aqueous solubility of hydrophobic compounds by incorporating them into the hydrophobic cores of micelles. This process is called solubilization[5]. Micelle-enhanced solubilization of hydrophobic compounds is clearly one of the primary applications of surfactants in liquid media. It has been reported that the solubility of PAH increases linearly with surfactant concentration above the critical micelle concentration (CMC)[6–8]. However, most of the previous studies related to solubilizing of PAHs on the use of conventional surfactants having single monomers with a single hydrophobic tail and a single hydrophilic head group[9,10]. A more modern and advanced surfactant to aid the removal of contaminants from soil dimeric surfactant, differently from conventional surfactant, dimeric surfactant consisting of two hydrophobic tails and two hydrophilic head groups connected by a spacer group[11]. Their surface active properties are better to corresponding conventional surfactants with the same chain length. Therefore, they have much lower CMC values and are more capable in lowering the surface tension of water[12]. Recently, dimeric surfactants were shown to be of great interest in industrial and scientific application due to their efficient solubilization capabilities[13,14]. As the dimeric surfactants form larger micelles than the conventional surfactants, it should have a superior solubilizing capacity.

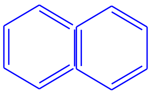
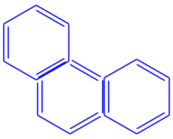
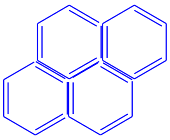
The specific objectives of the present study are to explain how partitioning of PAHs are influenced by the micelles of anionic dimeric surfactants and to have the idea about the synergistic solubilization by their equimolar mixed surfactant systems. In this study, we have studied water solubilization enhancement of three PAHs such as naphthalene, phenanthrene and pyrene, having different polarity by anionic dimeric surfactants (CADs, s = 12 and 16). The molar solubilization ratio (MSR), micelle-water partition coefficient (K_m) and standard free energy of solubilization (ΔG^0_S) towards PAHs have been determined.

2. Experimental procedures

2.1 Materials

The anionic dimeric surfactants with carboxy late head group, CADs, were synthesized in our laboratory, according to our recently reported method[15,16]. The molar ratio of reactants i.e., fatty amine (N-methyldodecylamine or N-methylhexadecylamine) and EDTA dianhydride was 2:1 and the mixture was refluxed in methanol for 20 h at 50 ℃. The purification and characterization of synthesized compound was done as discussed previously[15]. Naphthalene (Naph), phenanthrene (Phen) and pyrene (Py) were used as polycyclic aromatic hydro carbon in the present work and were also procured by sigma Aldrich. The formulas and aqueous properties of PAHs are listed in **Table 1**. Surfactant solutions were prepared in double distilled water.

Table 1. Showing water solubility of the selected PAHs[17]

Compound	**Molecular structure**	**Molecular weight (g/mol)**	**Water solubility at 25 ℃ (mg/L)**
Naphthalene		128.2	34.4
Phenanthrene		178.2	1.0
Pyrene		202.3	0.16

2.2 Methods

2.2.1 Solubility measurements

The solubility measurement was similar to described elsewhere[18]. The solubility of PAHs i.e., naphthalene, phenanthrene and pyrene, were measured in CADs solutions. Surfactant solutions were placed in 25 ml flasks at concentrations higher than CMC. An amount of each PAH in excess of its apparent solubility was added to each flask. Extra amount of PAHs was added to ensure maximum solubility in surfactant solution. These samples are then agitated on magnetic stirrer and allowed to stand for about 24 h. After this, the sample was collected and then centrifuged at 5000 rpm to settle down the excess amounts of PAHs. The determination of PAHs concentration was done by UV spectrophotometer (Elico SL 210). 1 ml of the supernatant surfactant solution taken and diluted to 10 ml in flask with 1 ml methanol and rest with the corresponding surfactant-water solution. Naphthalene, phenanthrene and pyrene in the solutions were analyzed at the wavelengths of 220 nm, 254 nm and 334 nm, respectively. All experiments were performed at room temperature (22–26 ℃).

2.2.2 Surface tension measurements

The CMC of the pure and mixed surfactant systems were determined by the surface tension measurement. The surface tension was determined using the Du Noüy tensiometer (Jencon, India) by the platinum ring detachment method. The tensiometer was calibrated through double-distilled water, and the platinum ring was perfectly cleaned and dried prior every observation. The surface tension values were measured until constant surface tension values indicated that equilibrium had been reached. The accuracy of the measurements was within ±0.1 mNm^{-1}.

3. Results and discussion

3.1 CMC of the single and equimolar binary CADs surfactants

Solubilization is closely related to the solution properties of the surfactant micelles. Therefore, to better understand the solubilization power, we have studied the micellar properties of selected single dimeric surfactants and their equimolar mixtures. The CMC values of single as well as of binary surfactant mixtures ($CAD_{12\text{-}16}$) were examined on the basis of tensiometric measurements. Surface tension decreases as the concentration of the CADs increases. The CMC values of the single and binary surfactant systems are tabulated in **Table 2**, which were determined from the **Figure 1**. The CMC values of CAD_{12} and CAD_{16} were observed following order $CAD_{16} < CAD_{12}$. The surfactant's chain length is main driving factor for micellization as well as hydrophobic interactions. As the hydrophobic chain length of dimeric surfactant increases, much water molecules are released, bringing about more entropy increase, and micellization of anionic dimeric with longer hydrophobic tail becomes at lower concentration.

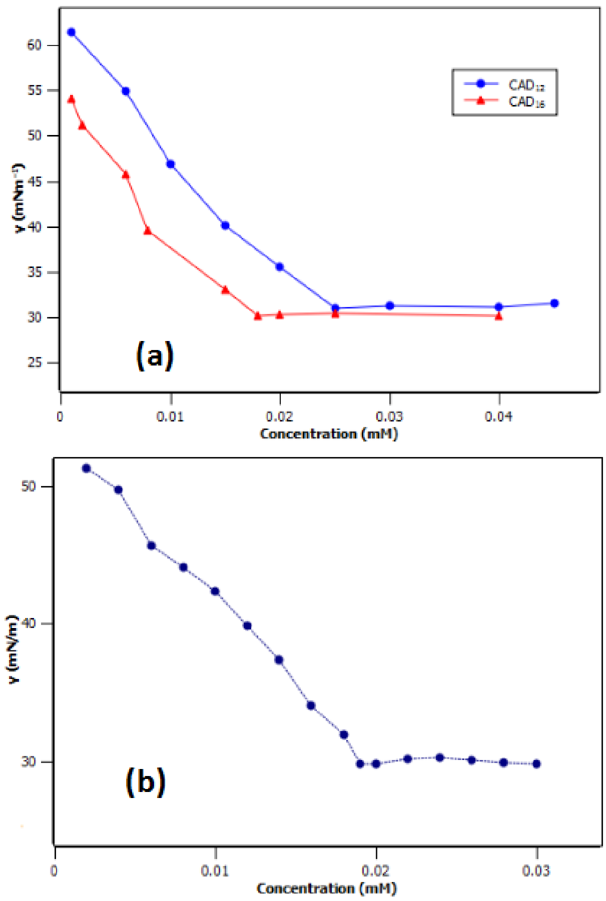


Figure 1. Plots of the surface tension (ɣ) vs. concentration of the single; CAD_{12} and CAD_{16} **(a)** and binary dimeric surfactant combinations; $CAD_{12\text{-}16}$ **(b)**, at 25 ℃**.**

Table 2. Micellization properties of single and mixed dimeric surfactant systems at 25 ℃

Micellization parameters	**CAD_{12}**	**CAD_{16}**	**$CAD_{12\text{-}16}$**
CMC_{exp} (mM)	0.025	0.018	0.021
CMC_{ideal} (mM)	-	-	0.019
γ_{cmc} (mN/M)	31.0	30.1	29.8
Π_{cmc} (mN/M)	41.0	41.9	42.2
$\Gamma_{cmc} \times 10^{10}$ (mol/cm^2)	4.09	4.67	4.71
A_{cmc} (nm^2 × 10^2/molecule)	40.6	35.6	36.1

3.2 Interfacial parameters

Various surface properties such as, surface excess or adsorption (Γ_{cmc}), occupied area per molecule (A_{cmc}) and surface pressure at the CMC (Π_{cmc}) of individual as well as equimolar binary surfactant systems were determined, which is given in **Table 2**. The adsorption efficacy of selected surfactants and their mixtures at the air/solution interface were calculated by Gibbs equation[19].

$$\Gamma_{cmc} = \left(-1/2.303nRT\right)\left(d\gamma / d\log C\right)_T \qquad (1)$$

where R and T are the ideal gas constant and temperature, respectively, and n is a constant, which depends on the number of species constituting the surfactant. Γ_{cmc} values were used to calculate the minimum area per surfactant molecule (A_{cmc}) at the air/water interface using the equation[19]:

$$A_{cmc} = 1/N_A \Gamma_{cmc} \tag{2}$$

Where, N_A is Avogadro's number. The values of the surface pressure at the CMC (Π_{cmc}) were determined from the following equation[19]:

$$\Pi_{cmc} = \gamma_0 - \gamma_{cmc} \tag{3}$$

Where, γ_0 and γ_{cmc} are the surface tension of the solvent and surface tension of the mixture at the CMC, respectively.

3.3. Interaction of the mixed micelles systems

For the equimolar binary mixed solutions, the interactions between the surfactant molecules (synergism or antagonism) can be explained by various parameters and equations. For ideal mixing of dimeric surfactants system, the ideal CMC value was calculated using the Clint equation[20].

$$\frac{1}{C_i} = \frac{\alpha}{C_1} + \frac{(1-\alpha)}{C_2} \tag{4}$$

Where, C_1 and C_2 are the CMC and the mole fraction of component 1 and 2 in mixed surfactant systems and α stands for the stoichiometric molar fraction. **Table 2** indicates that obtained CMC values (CMC_{exp}) was lower than ideal CMC values (CMC_{ideal}), as signified in the formation of mixed micelles, which demonstrate a negative deviation with respect to ideal mixture for binary mixed systems. It is expressed that the mixing effect of CADs surfactant system is more reliable than expected in the ideal state due to the two tails of dimeric surfactant allowing the micellar molecules even more hydrophobic.

3.4. Solubilization of PAHs by individual and mixed dimeric surfactants

Prior to measure the solubilization power of binary mixtures of CADs, single systems were first studied to understand the efficiency of anionic dimeric surfactants. Plots for the variations of solubility of PHAs with concentration of single dimerics CAD_{12} and CAD_{16} are shown in **Figure 2** and **3**. All the figures show that with the increasing of concentration of CADs, concentration of dissolved PHAs is also increasing, or solubility increases with the increasing concentrations of dimerics above the CMC. This phenomenon demonstrates that solubilization is closely associated to micellization.

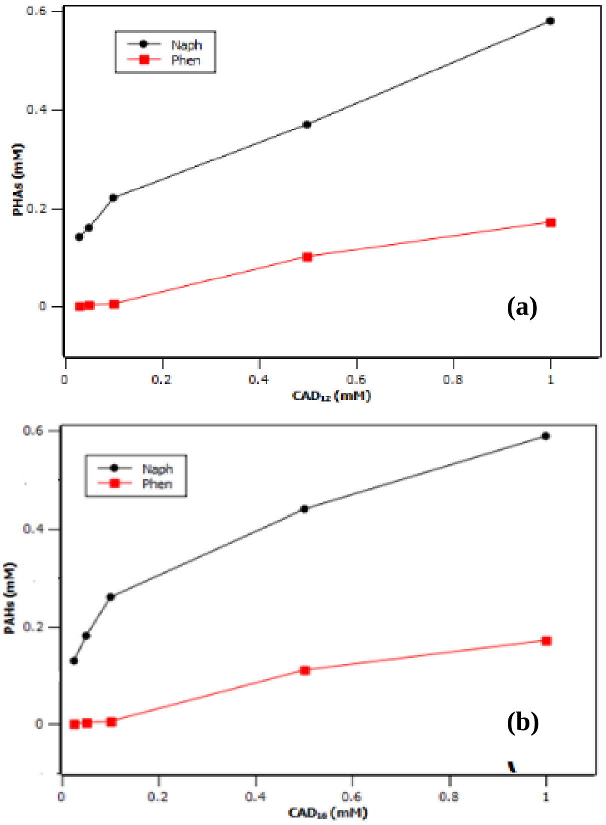


Figure 2. Variation of the solubility of PHAs with surfactant concentration CAD_{12} **(a)** and CAD_{16} **(b).**

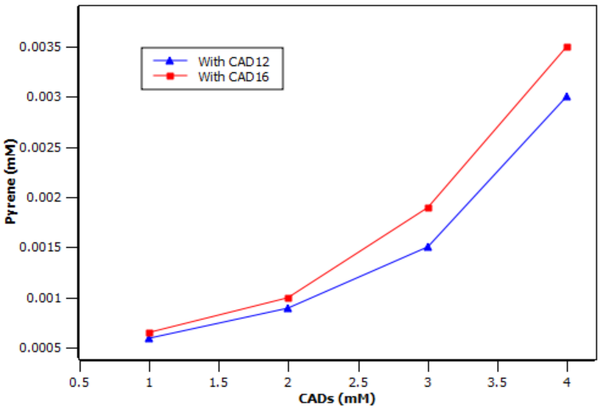


Figure 3. Variation of the solubility of pyrene with surfactant concentration CAD_{12} (■) and CAD_{16} (▲).

Therefore, water solubility of selected PHAs by equimolar binary mixed systems of $CAD_{12\text{-}16}$ was further to be determined. The apparent solubility of PHAs increases linearly with equimolar binary mixed surfactant combinations (**Figure 4** and **5**). This process showing the formation of mixed micelles and their potential ability to increase the solubility of PHAs in water.

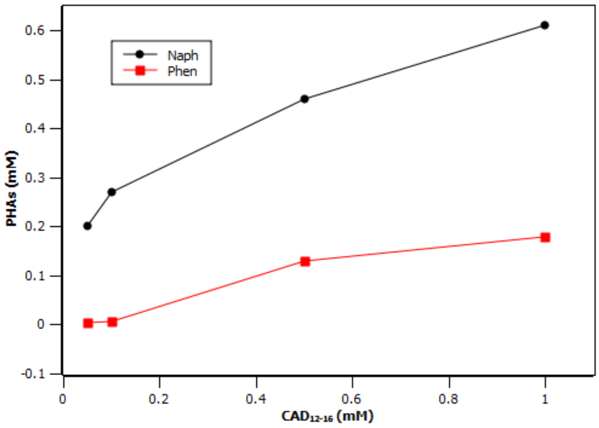


Figure 4. Solubilization of PAHs in CAD_{12-16} mixed surfactants.

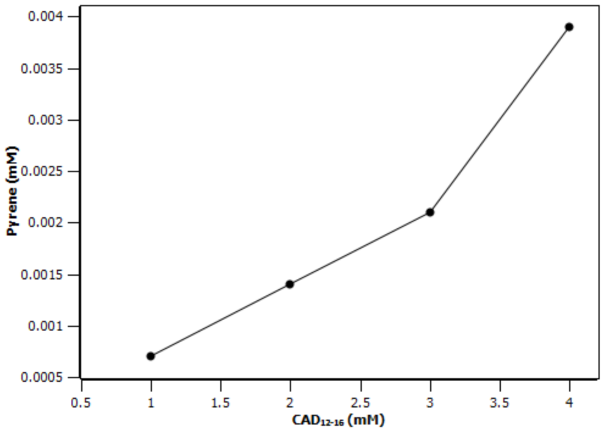


Figure 5. Solubility of pyrene with CAD_{12-16} mixed surfactants.

To measure the effectiveness of CADs in solubilizing, molar solubilization ratio (MSR) has been determined. The MSR is characterized as the number of moles of compound solubilized by 1 mol of micellized surfactant, which is given by Edwards *et al.*[21] and Wei J *et al.*[18].

$$MSR = \frac{S_{ac} - S_{cmc}}{C_{ac} - CMC} \tag{5}$$

where, S_{ac} is the apparent solubility of a PAH compound at the surfactant concentration greater than the CMC; C_{ac} is the surfactant concentration, at which S_{ac} is measured; and S_{cmc} is the PAH solubility at the CMC. The MSR may be obtained from the slope of the variation of solubilizate concentration against surfactant concentration and obtained values are listed in **Table 3**.

In addition to MSR, the effectiveness of solubilization, the partition coefficient K_m was also calculated, which is defined as distribution of the mole fraction of PAHs between surfactant micelles and the aqueous phase has been obtained as following[21]:

$$K_m = \frac{S_{ac} - S_{cmc}}{(C_{ac} - CMC + S_{ac} - S_{cmc})(V_w S_{cmc})} \tag{6}$$

where, V_w is the molar volume of water (1.8×10^{-2} l/mol at 25 ℃[21].

Table 3. Molar solubilization ratios (MSR) of PHAs in individual and mixed surfactant systems at room temperature

Surfactant system	**MSR**		
	Naph	**Phen**	**Py**
CAD_{12}	0.027	0.018	0.0006
CAD_{16}	0.035	0.028	0.0007
CAD_{12-16}	0.031	0.021	0.00067

Thus, an expression for K_m can be rearranged by substituting MSR to produce:

$$K_m = \frac{55.4 \times MSR}{S_{cmc}(1 + MSR)} \tag{7}$$

From the thermodynamic point of view, solubilization behavior of binary surfactant systems can be measured by the standard free energy of solubilization (ΔG_S^o) calculated by the following equation[22]. The obtained values of K_m and ΔG_S^o are given in **Table 4**.

$$\Delta G_S^o = -RTInK_m \tag{8}$$

Table 4. log K_m and in equimolar mixed dimeric surfactants

(8) **PAHs**	**log K_m**	**(kJ/mol)**
Naph	5.46	−31.21
Phen	5.38	−29.87
Py	4.49	−25.61

4. Conclusion

Water solubility enhancements of PAHs in single anionic dimerics and their equimolar binary mixed systems have been measured. The associations between their micelle properties and solubilizing efficiency single and binary surfactant systems for naphthalene, phenanthrene and pyrene are expressed in terms of MSR and other parameters. The MSR values increase with the order "pyrene < phenanthrene < naphthalene". The current study gives significant information for the selection of mixed dimeric surfactants for solubilizing water-insoluble compounds. The experimental results of this study will be useful to know the solubilization properties of mixed anionic dimeric surfactant systems and significant to provide statistical proof for exploring novel surfactant systems for practical soil and water remediation.

Conflict of interest

The authors declare that they have no conflict of interest.

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