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# Organization of Amphiphiles, Part 1: Evidence in Favor of Pre-micellar Aggregates through Fluorescence Spectroscopy[#]

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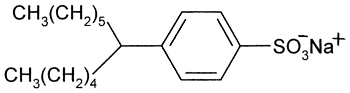
The advantage of a change in the vibrational structure of the emission spectra of pyrene as a function of the concentration of a series of polyoxyethylated alkyl ethers and alkylsulfonates has been utilized to explore the co-operative association of ionic and nonionic amphiphiles into micelles, the micropolarity of these micelles and the solubilization site of pyrene in micelles. The results indicate that the micropolarity of the environment experienced by pyrene is alcohol-like. Pyrene preferably resides in the palisade layer of a nonionic micelle, while in the interior of an anionic micelle. A multiple equilibrium model for micelle formation has been suggested and the existence of pre-micellar aggregates has been evidenced from the excimer characteristics of pyrene.

The vibronic fine structure of pyrene monomer fluorescence is characteristically susceptible to changes in the solvent polarity.[1] The ratio between the intensity of the third and first peak changes with a change in the polarity of the solvent, and is thus called the polarity parameter (PP). The PP value of pyrene is about 0.54 in acetonitrile and 1.65 in hexane.[2] In water and at low concentration of the surfactant the value is about 0.6, but above the critical micelle concentration (CMC) the ratio substantially changes,[3] thus indicating the change in the micropolarity of the medium experienced by pyrene. Chandar et al.[3] have studied the fluorescence behavior of pyrene in a sodium dodecyl sulfate solution above and below CMC. Below CMC the pyrene fluorescent spectrum corresponds to that in water with a PP value of 0.6, while at a concentration above CMC the value is 1.2. This principle was adopted here to study the aggregation behavior of a few industrially important surfactants. The PP has been measured as a function of the surfactant concentration to enlighten the solution properties of these surfactants. The main objective of the present work was to determine the critical micellar concentration of the surfactants under investigation and the micropolarity of their micelle, to locate the solubilization site of the fluorescent probe and to look for evidence in favor of the formation of pre-micellar aggregates.

## Experimental

**Materials.** Polyoxyethylated alkyl ethers surfactants (a) were obtained from Nikko Chemicals, Japan. These nonionic surfactants were BL-X(a-i), BC-X(a-ii), and BO-X(a-iii), where X represents the number of poly(oxyethylene) units. Alkene-1-sulfonate (AOS, b-i), linear alkylbenzenesulfonate (LABS, b-ii), and sodium dodecyl[poly(oxyethylene)]$_{(2.4)}$ sulfonate (SLES, b-iii) were obtained from SMZS Chemical Ltd. Pune, India. All of the surfactants were used without further purification. Triple distilled water (conductance = $1\times10^{-6}$mho) was used within seven days of its preparation.

(a) Polyoxyethylatd Alkyl Ethers
    $RO–(CH_2CH_2O)_x–H$
    (i) R = dodecyl, $x$ = 9, 21, 25 (BL-X)
    (ii) R = hexadecyl, $x$ = 15, 20, 25, 30, 40 (BC-X)
    (iii) R = 9-octadecenyl, $x$ = 15, 20, 50 (BO-X)
(b) Anionic Surfactants:
    (i) Alkene-1-sulfonate (AOS)
    $CH_3–(CH_2)_{12}–CH=CH–SO_3^-Na^+$
    (ii) Linear alkylbenzenesulfonate (LABS)



    (iii) Sodium dodecyl [poly(oxyethylene)]$_{(2.4)}$sulfonate (SLES)
    $CH_3–(CH_2)_{11}–O–(CH_2–CH_2–O)_{2.4}–SO_3^-Na^+$

**Sample Preparation.** A saturated aqueous solution of pyrene was prepared by stirring about 0.1 g of pyrene for 24 hours at room temperature (27 °C) in 2 L of triple-distilled water, followed by filtration to remove any undissolved pyrene. The concentration of pyrene, determined from its extinction coefficient in water, was $5.0\times10^{-7}$ M. Solutions of the surfactants were prepared in saturated pyrene solution. The emission spectra were recorded on a Shimadzu RF-5000 spectrofluorophotometer at 27 ± 0.1 °C by exciting the solution at the absorption maximum ($\lambda_{max}$) of pyrene in water (335nm)

## Results and Discussion

**Determination of CMC and Micropolarity of Micelles:** The emission spectra of pyrene at various concentrations of nonionic surfactants were recorded; a representative set of the spectra (in BO-20) is shown in Fig. 1. It can be seen that at

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[#] This paper has been dedicated to Prof. P. Somasundaran, Chairman, Henry Krumb School of Mines, Columbia University, New York on his sixtieth birth day.

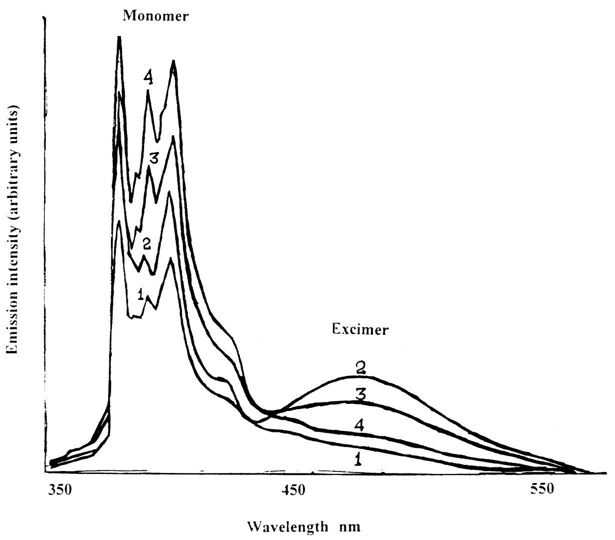

Fig. 1. Emission spectra of pyrene in presence of various concentration of BO-20 surfactant: (1) $10^{-6}$ M, (2) $4\times10^{-5}$ M, (3) $2\times10^{-4}$ M, (4) $6\times10^{-4}$ M.

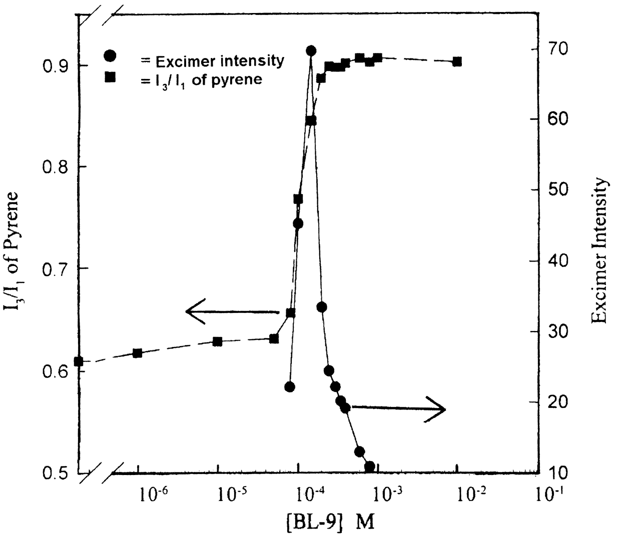

Fig. 2. Plot of polarity parameter ($I_3/I_1$) and excimer intensity of pyrene at various concentration of BL-9.

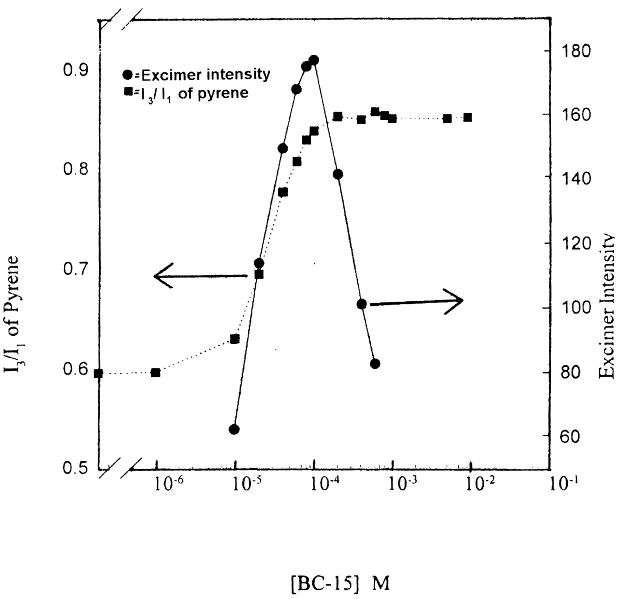

Fig. 3. Plot of polarity parameter ($I_3/I_1$) and excimer intensity of pyrene at various concentration of BC-15.

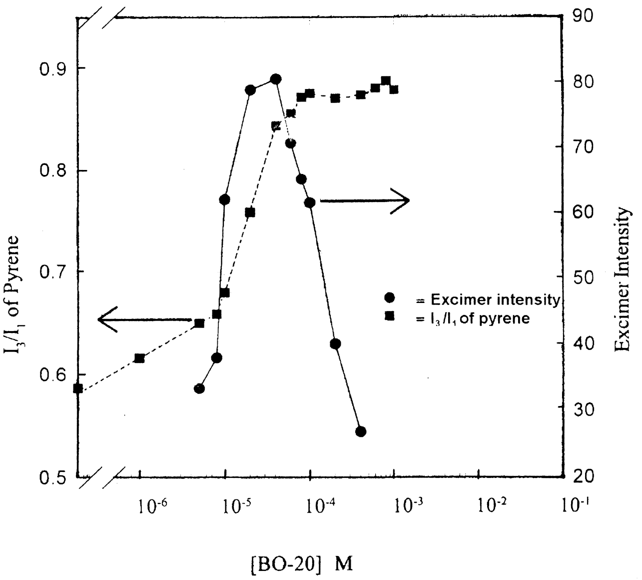

Fig. 4. Plot of polarity parameter ($I_3/I_1$) and excimer intensity of pyrene at various concentration of BO-20.

low concentrations of the surfactant in aqueous solutions the spectrum of pyrene has the characteristics monomer emission, and is identical to that obtained in water in the absence of a surfactant.[4] The ratio of the intensities between the third peak (380 nm) and the first peak (370 nm) of pyrene is found to be 0.6, which is the same as that in water. This ratio undergoes a gradual increase with an increase in the concentration of surfactant (Figs. 2 to 7). Plots of PP versus the surfactant concentration are sigmoidal in nature. The PP value changes from 0.6 to 0.83–1.05, attaining a plateau at higher concentrations of the surfactants. The constant value beyond a certain concentration (different for different surfactants) indicates a constant polarity experienced by pyrene. The appearance of a plateau in the PP versus [surfactant] curve has been attributed to the consequence of micelle formation; the concentration at the onset of plateau of this curve is considered to be CMC (Table 1). The CMC values of T-X-100 and BC-20 measured by this method compare well with those obtained from the literature[5,6] (Table 1).

Upon examining the CMC values in the BL series, it is observed that CMC increases with an increase in the poly(oxyethylene) unit ($CH_2$–$CH_2$–O, abbreviated as POEO hereafter) in the surfactant which, in turn, indicates that the tendency to form micelles decreases with an increase in number of POEO units. This phenomenon could be attributed to a partial dehydration of the poly(oxyethylene) chain during the formation of micelles resulting in an increase in the free energy of micelle formation.[7,8] The probability of solubility of the surfactant in water also increases with an increase of POEO units, since the

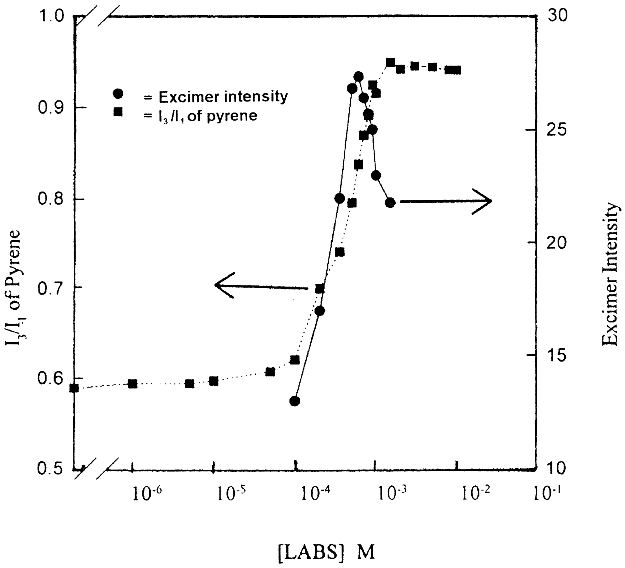

Fig. 5. Plot of polarity parameter ($I_3/I_1$) and excimer intensity of pyrene at various concentration of LABS.

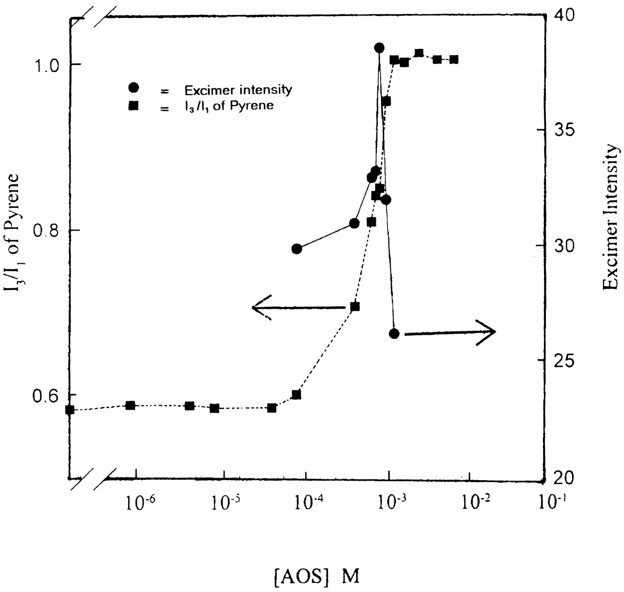

Fig. 6. Plot of polarity parameter ($I_3/I_1$) and excimer intensity of pyrene at various concentration of AOS.

presence of this unit enhances the extent of hydrogen bonding with water. Ravey et al.[9] have also observed a similar trend in the CMC values along with an increase in the number of POEO units.

However, in contrast to the BL series, the CMC values of the BC and BO series are found to be independent of the POEO chain length. This is because in these surfactants the hydrocarbon chain lengths are sufficiently long (C = 16 and 18) to dominate over the effect of the hydrophilic group. It has also been reported earlier that the changes in the hydrophilic part of the amphiphiles do not have any significant role on CMC.[10] The CMC values depend much more on the hydrocarbon chain length than on the corresponding hydrophilic part.[11]

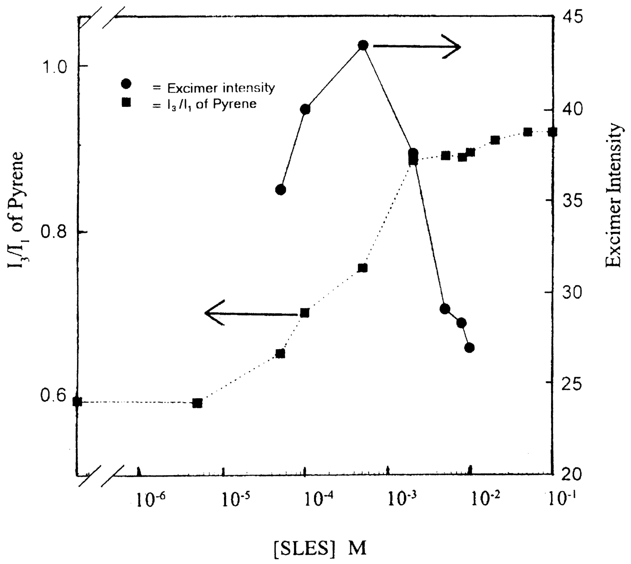

Fig. 7. Plot of polarity parameter ($I_3/I_1$) and excimer intensity of pyrene at various concentration of SLES.

Table 1. The CMC of Various Surfactants (Temp = 27 °C)

| Surfactant | CMC M |
|---|---|
| BL-9 | $2.0\times10^{-4}$ |
| BL-21 | $3.5\times10^{-4}$ |
| BL-25 | $4.0\times10^{-4}$ |
| BC-15 | $9.0\times10^{-5}$ |
| BC-20 | $8.0\times10^{-5}$ |
| | $7.7\times10^{-5}$ (Ref. 5) |
| BC-25 | $8.0\times10^{-5}$ |
| BC-30 | $1.0\times10^{-4}$ |
| BC-40 | $9.0\times10^{-5}$ |
| BO-15 | $9.0\times10^{-5}$ |
| BO-20 | $8.0\times10^{-5}$ |
| BO-50 | $8.0\times10^{-5}$ |
| AOS | $1.5\times10^{-3}$ |
| LABS | $9.0\times10^{-4}$ |
| SLES | $2.0\times10^{-3}$ |
| T-X-100 | 0.54 vol% |
| | 0.54 vol% (Ref. 6) |

To see the effect of methylene units in hydrophobic tail of the surfactant on the CMC values, the results of BC-20, BO-20 and BL-21 are considered. It is seen that there is a substantial decrease in the CMC values of BO-20 and BC-20 compared to that of BL-21. This happens because each $-CH_2-$ unit contributes about 0.5 unit to the hydrophobicity,[12] and CMC decreases along with an increase in hydrophobicity. However, there is no significant difference in the CMC values in the BC and BO series with the same poly(oxyethylene) number (Table 1). This may possibly be due to a coiling of the chains for the surfactant having an alkyl group longer than sixteen carbons.[13]

The CMC of three of the anionic surfactants with the same functional head group are found to be in almost the same order. The CMC of AOS is about seven-times lower than sodium dodecyl sulfonate ($9.8\times10^{-3}$ M).[5] This is due to the presence of one additional $-CH_2$ group, which contributes to the hydrophobic interaction and the presence of the $-CH{=}CH-$ group adjacent to the hydrophilic moiety. Because the point charge of the sulfonate ion is conjugated to the C=C bond, it becomes delocalized. This results in reduction of the partial ionic character of the sulfonate ion, thereby decreasing the electrostatic interaction and, hence, resulting in aggregation at a lower concentration. The large decrease of LABS compared to sodium dodecyl sulfonate with the same hydrophilic head group is attributed to larger hydrophobic contribution from the hydrophobic moiety. The CMC of SLES in which the hydrophilic head and hydrophobic tail are sandwiched by a poly(oxyethylene) $(CH_2CH_2O)_{2.4}$ spacer, is about five-times lower than that of sodium dodecyl sulfonate. The point charge on sulfonate ion becomes dispersed over a wider surface due to an inductive effect of oxygen atoms on the POEO unit and, hence, weakens its ionic character. This reduces electrostatic interaction in the molecule, and hence aggregation occurs at a lower concentration.

The emission spectrum of pyrene in the presence of all ethoxylated surfactants under study has a general tend, the ratio $I_3/I_1$ being around 0.6 at very low concentrations of the surfactant, remains constant for a small range of concentrations, and then increases to a plateau value of 0.83–1.05 (Figs. 2 to 7). The molecular organization of micellar systems is a consequence of electrostatic repulsion between the hydrophilic head groups and the attractive interaction between the hydrophobic tails. In case of the nonionic surfactants, since the hydrophilic groups do not contain any point charge, like ionic surfactants and the hydrophobic interaction is not sufficient enough to hold the bulky surfactant molecule into the micelle, the formation of micelles takes place in a step-wise manner. The monomeric surfactants are packed into micelles via association through the aggregates of a different number of surfactants. The pyrene molecule experiences a gradual decrease in the polarity of the solvent systems, as indicated by the gradual increase in the $I_3/I_1$ value in the middle arm of the sigmoidal curve (Figs. 2 to 7). The polarity of the SDS micelle, as estimated by the $^{14}$N hyperfine coupling constants of the indicator, is reported to decrease along with an increase in the micelle size.[14] Hence, a gradual increase in the $I_3/I_1$ values (which increases with an increase of the nonpolarity of a medium[2]) in the present case is due to an decrease in the polarity of the pyrene environment, which may be due to a gradual increase in the micellar size. The value becomes constant with the completion of micelle formation. Thus, micelles are formed in a step-wise manner, and micelle formation is only a part of a progressive aggregation process. This supports a multiple equilibrium model for the formation of micelles applied to nonionic surfactant systems.[15] The step-wise growth of micelles can be represented as follows (Scheme 1).

$$M_1 \quad + \quad M_1 \rightarrow M_2$$

$$M_2 \quad + \quad M_1 \rightarrow M_3$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$M_1 \quad + \quad M_{n-1} \rightarrow M_n \quad , n=2, 3, 4, 5,..$$

Scheme 1.

The slow increase in $I_3/I_1$ of anionic surfactants (Figs. 5, 6 and 7) can also be attributed to the step-wise growth of these aggregates. Sivkumar et al.[16] during their studies on the adsorption behavior of alkylxylenesulfonates on alumina have seen a relatively slower increase of the $I_3/I_1$ values due to bulky surfactants, compared to the present anionic surfactants.

In order to determine the micropolarity experienced by pyrene, the $I_3/I_1$ ratio of pyrene in various organic solvents were determined, and plotted against the $E_T(30)$ value.[17] The $E_T(30)$ value[18] of a solvent is the energy of the intermolecular charge-transfer band in kilo joules per mole of 1-ethyl-4-carbomethoxy pyridinium iodide when dissolved in that solvent ; these values are reflexive of the polarity of the medium. The plot is a linear one with a correlation coefficient ($r$) value of 0.995 (Fig. 8). This is used as a calibration curve to predict the $E_T(30)$ value of the environment experienced by pyrene in surfactant systems. $E_T(30)$ values are given in Table 2. These results indicate that polarity of the pyrene environment in the micelles are in between water and hexane.

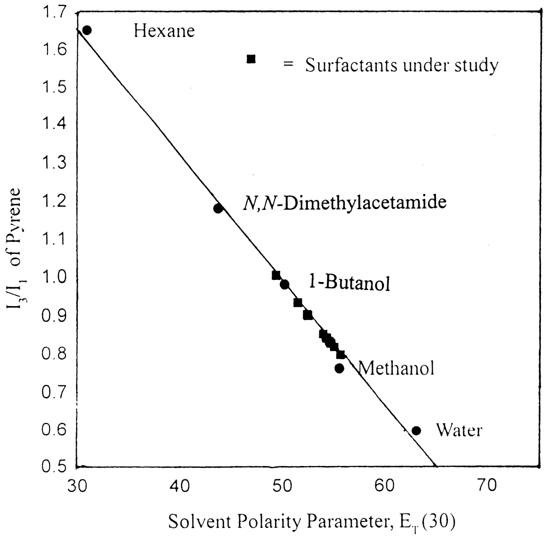

Fig. 8. Plot of ($I_3/I_1$) of pyrene versus solvent polarity [$E_T(30)$] parameter of some of the selected solvents and extrapolated values of the surfactants under study.

Table 2. $I_3/I_1$ of Pyrene and Solvent Polarity. $E_T(30)$ in Presence of the Surfactant System

| Surfactant | Polarity Parameter, $I_3/I_1$ | Solvent polarity, $E_T(30)$/kJ mol$^{-1}$ |
|---|---|---|
| BL-9 | 0.900 | 52.47 |
| BL-21 | 0.816 | 55.01 |
| BL-25 | 0.840 | 54.28 |
| BC-15 | 0.851 | 53.95 |
| BC-20 | 0.839 | 54.31 |
| BC-25 | 0.832 | 54.52 |
| BC-30 | 0.825 | 54.73 |
| BC-40 | 0.827 | 54.67 |
| BO-15 | 0.828 | 54.61 |
| BO-20 | 0.796 | 55.61 |
| BO-50 | 0.842 | 54.22 |
| AOS | 1.003 | 49.35 |
| LABS | 0.933 | 51.47 |
| SLES | 0.903 | 52.38 |

**Solubilization Site of Pyrene :** Mishra et al.[19] have mapped the polarity pocket with varied $E_T(30)$ values for the localization of some tailor-made cyanine dyes having varied hydrophobicity. The dyes were cationic in nature and they found a polarity gradient between 55.5 to 63.0, ranging from the inner surface of the micelle, and extending to the bulk water. However, in the present study, the $I_3/I_1$ values of pyrene in a micelle correspond to $E_T(30)$ values of 49.0 to 55.0. Pyrene, being hydrophobic, chooses a hydrophobic environment as its localization site.[1,20] Had it been incorporated into the innermost core of the Hartley micelle,[21] having a hexane-like environment, the $E_T(30)$ would have been around 30. However, the $E_T(30)$, being closer to that of alcohol indicates that pyrene resides in a relatively polar environment. This result can be well explained by considering the Menger micellar model where some parts of the hydrocarbon tails of the surfactants are exposed to water forming hydrophobic patches.[22,23] The nonionic surfactants under study have many poly(oxyethylene) units which can drag water molecules to the interior of the micelle through hydrogen bonding, thereby facilitating the penetration of water deep into the micelle and thus increasing the probability of the interaction of water with hydrophobic patches. Kalyansundaram and Thomas have also discussed the change in the fluorescence intensity of pyrene in terms of a deep penetration of water into the micelle,[1] and have suggested the solubilization site of pyrene to be the interior of the micelle. In the case of anionic surfactants the results can be similarly explained with the help of a Menger micelle. The difference in $I_3/I_1$ for different surfactants suggests that the pyrene is localized at various distances from the interface of micelles depending on their structure. A typical solubilization site of pyrene on hydrophobic patches of a micelle can be represented as shown in Fig. 9.

A comparison of the $E_T(30)$ values of nonionic with anionic micelles reveals that the micropolarity experienced by pyrene in an anionic micelle is less than that in a nonionic micelle. This can be attributed to the fact that the interface of an anionic micelle contains point charges, whereas the interface of a nonionc micelle contains induced charges. Besides, the presence of a –CH$_2$–CH$_2$– group in POEO unit makes the interface of a nonionic micelle relatively hydrophobic compared to an anionic micelle. Thus, pyrene, being hydrophobic, stays closer to the interface of a nonionic micelle. However, in order to avoid an unfavorable interaction with point charges, pyrene shrinks itself away from the interface, and hence moves deeper into an anionic micelle.

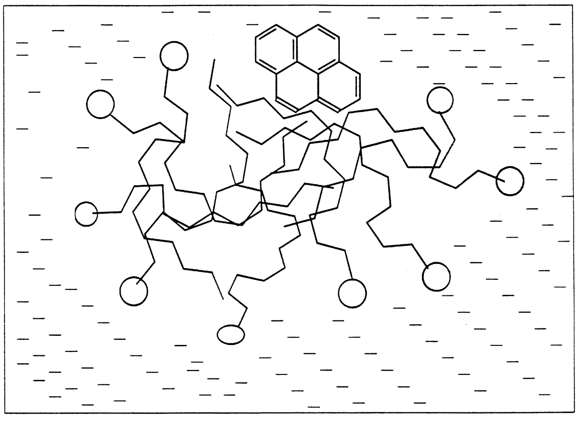

Fig. 9. Schematic representation of solubilization of pyrene in hydrophobic patches of a Menger micelle: the exposure of hydrophobic tail to water results in formation of hydrophobic patches at the micellar surface.

**Evidence in Favor of Existence of Pre-micellar Aggregates:** In the lower arm region of the PP-[surfactant] curve the pyrene molecules are proposed to remain in a monomeric state, as indicated by their characteristics monomer emission. Similarly, in the upper-arm region the pyrene molecules remain as monomer and are partitioned into the micelle as evidenced from the appearance of a monomer emission spectrum and the $I_3/I_1$ values (Figs. 1 to 7). However, in the transition zone, where pyrene starts partitioning from the aqueous region to the micellar domain, an additional emission peak at 480 nm appears. The absorption spectrum of pyrene is not modified upon the addition of surfactant to saturated pyrene water, thereby precluding the formation of ground-state dimer or pyrene-surfactant aggregates in the solution. The appearance of the band at 480 nm is therefore attributed to the formation of an excimer.[16,24] From fluorescence-quenching study, Kusumoto et al.[25] have also proposed a surfactant-pyrene complex in a pre-micellar region of sodium dodecyl sulfate, and have seen a new peak. Olivera et al.[26] have shown that within the concentration range of $6–7\times10^{-3}$ of SDS, a reduction of the pyrene derivative monomer peak has resulted along with the appearance of a band at 480 nm and turbidity in solution. They have attributed this result to the formation of surfactant-pyrene derivative aggregates. Sanz-Medel et al.[27] have reported the formation of dye-surfactant premicellar aggregates which exist below CMC.

The plot of the excimer intensity at 480 nm with [surfactant] is a sine curve having maximum at a concentration just below of CMC of the surfactant (Figs. 2 to 7). The excimer vanishes as the plateau is reached. This indicates that excimer formation starts below the onset of the plateau of the curve. Lewis et al.[28] have proposed excimer formation for a pyrene derivative in a restricted environment, like a DNA medium. They have reported a decrease in the ratio of the pyrene monomer/excimer fluorescence upon duplex formation of nucleic acid. Thomas has also reported the yield of excimer to be high at low concentrations of the surfactant.[29] In fragmented media[30,31] composed of micelles or other smaller aggregates in which pyrene becomes solubilized, the probability of the excited singlet of pyrene to leave one micelle and interacting with a ground-state pyrene from another micelle during its excited lifetime is very low. The exit of pyrene from micelles occurs on the millisecond scale,[32] whereas fluorescence is on the nanosecond scale. Hence, excimer formation is essentially an intramicellar process. Only those micelle/aggregates which contain more than one pyrene at the instant of flash excitation can give rise to excimer formation. In the present study excimer formation was observed during the progress of micelle formation; hence, the involvement of pre-micellar aggregates can be assumed. Due to the low concentration and smaller size of the pre-micellar aggregates, the probability of aggregates containing more than one probe at a suitable distance to form excimers becomes

Table 3. The Concentration of Various Surfactants Where Excimer has Maximum Intensity

| Surfactant | Concentration M |
|---|---|
| BL-9 | $1.5\times10^{-4}$ |
| BL-21 | $3.0\times10^{-4}$ |
| BL-25 | $3.0\times10^{-4}$ |
| BC-15 | $1.0\times10^{-4}$ |
| BC-20 | $5.0\times10^{-5}$ |
| BC-25 | $2.0\times10^{-5}$ |
| BC-30 | $4.0\times10^{-5}$ |
| BC-40 | $6.0\times10^{-5}$ |
| BO-15 | $4.0\times10^{-5}$ |
| BO-20 | $6.0\times10^{-5}$ |
| BO-50 | $3.0\times10^{-5}$ |
| AOS | $5.0\times10^{-5}$ |
| LABS | $5.0\times10^{-5}$ |
| SLES | $5.0\times10^{-5}$ |

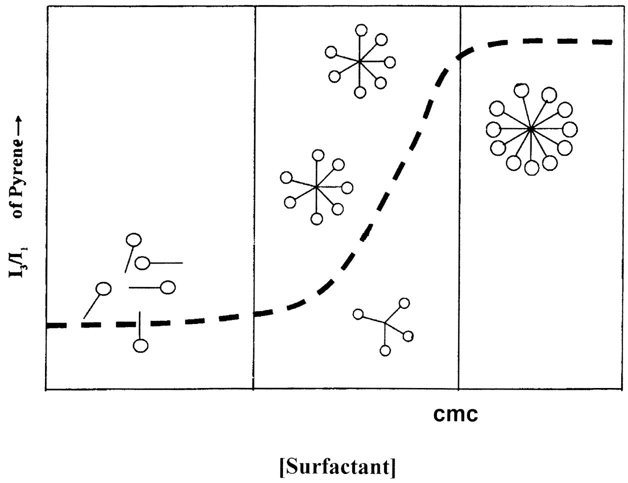

Fig. 10. Schematic representation of the formation of micelle.

greater. Hence, a fraction of the aggregates will contain two or more probes, resulting in an increase in the probability of excimer formation. But, with an increase in the surfactant concentration, the formation of excimers is less probable, since the effective concentration of pyrene for excimer formation decreases along with an increase in the size of the aggregates. However, the rising arm of the curve has a different slope for different surfactant systems, which indicates that the extent of formation of pre-micellar aggregates and their size at a particular concentration is different for different surfactants (Figs. 2 to 7, Table 3). The whole phenomenon can be represented schematically as given in Fig. 10.

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