Surface and Bulk Interactions of Ionic and Nonionic Surfactants

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The fluorescence parameter I_1/I_3 of pyrene was used to detect the interaction between anionic and nonionic surfactants (SDS and C_9PhE_{10}) in the bulk solution. In addition, the change in the air–water interface was investigated by surface tension over the interaction range. In the range of [SDS] = 10^{-5}–10^{-1} M, the interaction is divided into three regions. In each region, the results from these two methods were compared and used to interpret the phenomena with each other. The foamate technique was used to estimate the change in the composition of surfactant at the air–water interface, and the trend of the change in foamate composition for several points in three regions is identical with that observed in the γ vs. [SDS] plot and supports the interpretation. Also, the comicellar composition, the activity in the comicelle, and the monomer concentration for SDS and C_9PhE_{10} were theoretically calculated. The trends of these calculated data are parallel to those of the experimental observations.

Introduction

Since micellar solutions of mixed surfactants can exhibit strikingly different physicochemical behavior from those of single surfactants, mixed surfactant systems have received considerable attention recently from both theoretical and industrial researchers.[1] These systems have been studied in the past by means of conventional techniques involving measurements of surface tension, conductivity, solubilization, etc. Recently photoluminescence techniques have been applied to colloidal systems[2] to detect the microviscosity, the local polarity, and the aggregation number of a micelle. The photoluminescence methods can provide direct information about an aggregate on the molecular level which cannot be detected by the conventional colloidal methods.

A fluorescence probe, pyrene, was successfully used to detect the interaction between surfactant and polymer in our previous work.[3] In this paper, pyrene was used to obtain the information on comicellization of ionic and nonionic surfactants in bulk solution. Corresponding changes in air–water interface was investigated by measuring surface tension and changes in surfactant composition of bulk solution during foaming. The results are correlated to understand the comicellization phenomenon.

Experimental Section

Materials. Pyrene purchased from Aldrich Chemical Co. was purified by three recrystallizations from ethanol. Sodium dodecyl sulfate (SDS; electrophoresis grade), purchased from Bio-Rad Laboratories, and the selected polyoxyethylene glycol *n*-nonylphenyl ethers (C_9PhE_n), purchased from Tokyo Kasei Co., were employed without further purification.

Fluorescence Measurements. All fluorescence measurements were recorded on a Perkin-Elmer Model MPF-3L spectrometer. The ratio of the intensity of pyrene emission at 373 nm and at 383 nm is defined as I_1/I_3.

Surface Tension Measurements. Surface tension was measured by the Wilhelmy plate method with CAHN2000 microbalance using a sandblasted platinum plate as sensor.

Foaming Tests. Fifty-milliliter samples of the desired solutions were used for the foaming experiments. Foaming was done by passing humidified air through a Büchner funnel with a sintered glass bottom of pore size 10–20 μm (POR D, Ace Glassware, N.J.). The foam was allowed to dry for 5 min, after which it was aspirated off into a tared vial. Total foamate collected was about 1.0–1.7 mL.

SDS concentration was measured by the two-phase titration technique,[4] using hexadecyltrimethylammonium bromide as the cationic surfactant, and dimidium bromide disulphine blue as the color indicator.

To determine the C_9PhE_{10} concentrations, foamate bulk and standard solutions were diluted with concentrated SDS such that

the final solution was above the cmc of SDS, and then the UV absorption at 276 nm was recorded.

Results

Figure 1 shows that both surface tensions and I_1/I_3 values track the expected cmc behavior of SDS. The I_1/I_3 values show a rapid decrease from 1.85 (aqueous environment) at [SDS] ca. 5×10^{-3} M to 1.25 (alcohol-like environment) at [SDS] ca. 1×10^{-2} M. The literature cmc for "pure" SDS is ca. 8.2×10^{-3} M.[5] Since pyrene is a deliberately added "impurity" the values of γ were measured with and without pyrene. As can be seen from Figure 1, the addition of pyrene, at a concentration comparable to that employed for the I_1/I_3 measurements, did not result in any significant modification of the γ vs. [SDS] behavior.

Figures 2 and 3 show the results of γ and I_1/I_3 measurements as a function of [SDS] for systems containing fixed amounts (2.5 $\times 10^{-5}$ and 5.0×10^{-5} M, respectively) of the nonionic Triton detergent C_9PhE_{10}. Compared to Figure 1, the I_1/I_3 vs. [SDS] curves in Figures 2 and 3 have the same general slope but the sharp decrease in I_1/I_3 near the SDS cmc is broadened in Figure 2 and difficult to see at all in Figure 3. Compared to Figure 1, the γ vs. [SDS] curves in Figures 2 and 3 have a very different shape. For both of the latter figures after an initial decrease, γ increases, reaches a maximum, and then decreases. In both cases the maximum occurs at about 2×10^{-2} M SDS, and above 5×10^{-1} M SDS γ approaches a common limiting value of ca. 35 dyn/cm.

Figure 4 shows the results of γ and I_1/I_3 measurements as a function of [SDS] for a system containing 5.0×10^{-5} M C_9PhE_{20}. The shape of the γ vs. SDS curve in Figure 4 is similar to the corresponding curve in Figure 1. The shape of the I_1/I_3 vs. [SDS] curve in Figure 4 does not show the sharp break observed in Figure 1, but rather a monotonic but gradual decrease in I_1/I_3 up to about 1×10^{-2} M SDS, followed by an even smaller decrease at higher [SDS].

The results obtained for the SDS and C_9PhE_{10} concentrations in the foamate are given in Figure 6 as a function of the bulk concentration of SDS. As expected, SDS concentration in the foamate increases as the bulk SDS concentration is increased.

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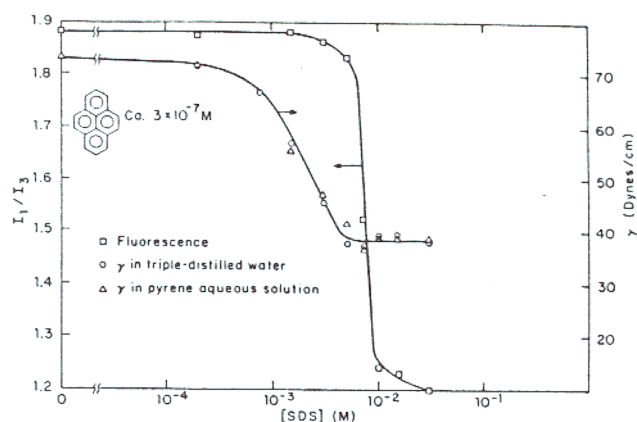
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Figure 1. Correlation between the plots of I_1/I_3 vs. [SDS] and of γ vs. [SDS] for SDS only and with pyrene.
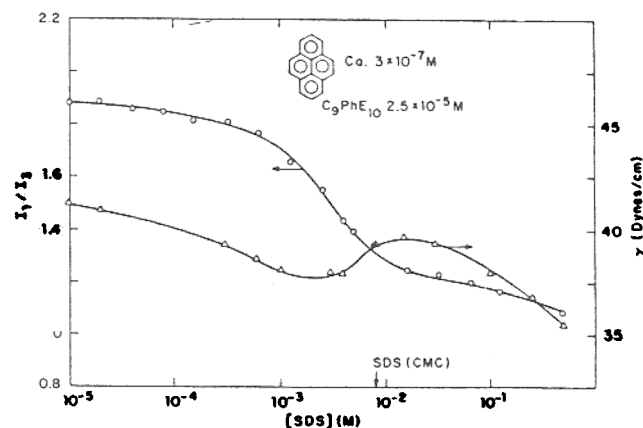

Figure 2. Correlation between the plots of I_1/I_3 vs. [SDS] and of γ vs. [SDS] with C_9PhE_{10} fixed at 2.5×10^{-5} M.
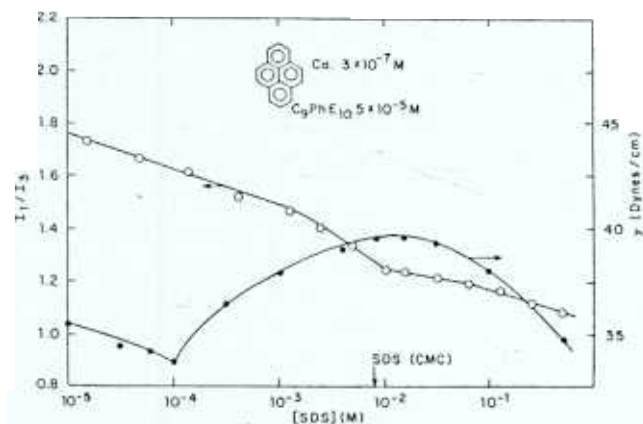

Figure 3. Correlation between the plots of I_1/I_3 vs. [SDS] and of γ vs. [SDS] with C_9PhE_{10} fixed at 5.0×10^{-5} M.

C_9PhE_{10} concentration in the foamate, on the other hand, is found to undergo very little change until about 7×10^{-4} M SDS and then an apparent increase followed by a clear decrease above bout 5×10^{-3} M. Above about 2×10^{-2} M SDS, the C_9PhE_{10} concentration in the foamate changes very little.

Discussion

The interpretation of the data in Figure 1 is straightforward and conventional. Near the cmc, SDS begins to form micelles in the bulk aqueous phase. As a result, at or above the cmc a further increase in SDS monomers produces very little decrease in the surface tension. Until micelles are formed, the value of I_1/I_3 reflects the pyrene dissolved in the bulk aqueous phase. As soon as micelles are formed, the pyrene is preferentially solubilized in the micelle aggregates and is mostly removed from the aqueous phase. Because the micelles provide a less polar environment for
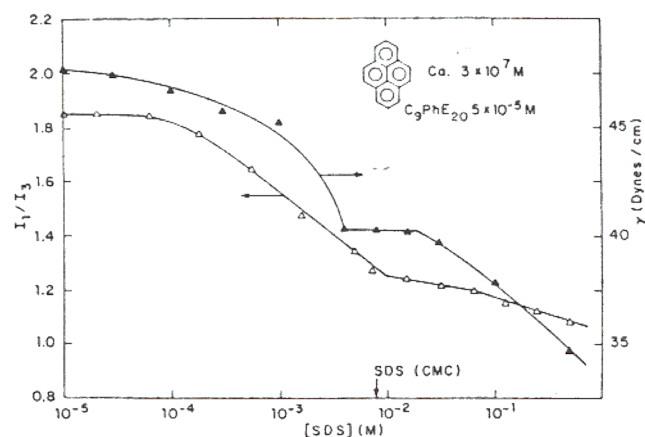

Figure 4. Correlation between the plots of I_1/I_3 vs. [SDS] and of γ vs. [SDS] with C_9PhE_{20} fixed at 5.0×10^{-5} M.
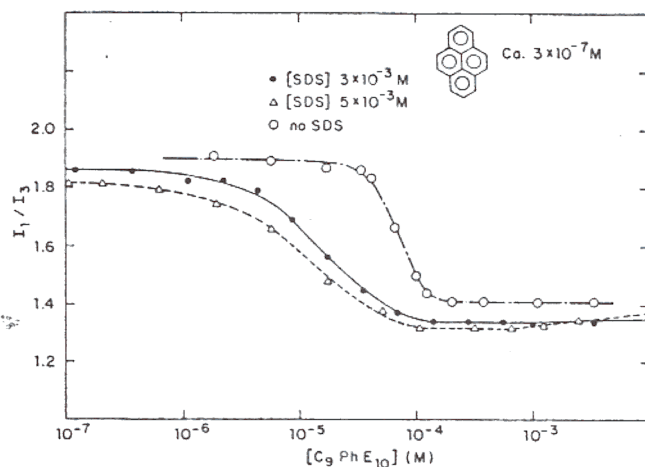

Figure 5. I_1/I_3 vs. $[C_9PhE_{10}]$ with [SDS] fixed at 3 or 5 mM.
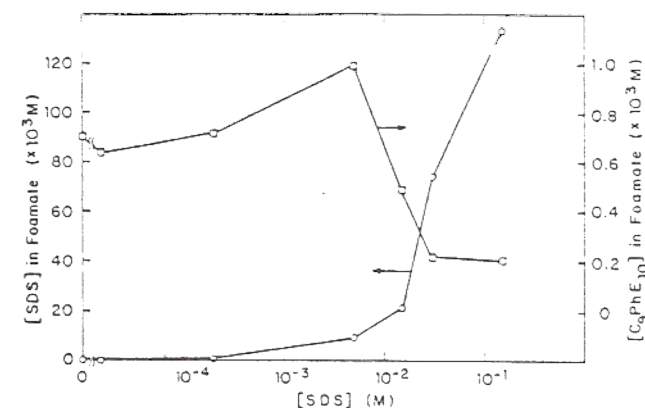

Figure 6. Foamate concentrations of SDS and C_9PhE_{10} as a function of [SDS].

the pyrene molecules, near cmc, I_1/I_3 decreases sharply until all of the pyrene molecules are solubilized in micelles. At that point the value of I_1/I_3 undergoes a much smaller decrease with increasing [SDS].

The shapes of the γ vs. [SDS] curves in Figures 2 and 3 are drastically different from that of Figure 1. However, the shapes of the curves in Figures 2 and 3 are reminiscent of those observed when "impurities" are present in surfactant solutions. We can interpret the γ vs. [SDS] curves in terms of the nonionic detergent as a deliberately added impurity as follows. The nonionic C_9PhE_{10} detergent is a more surface active material than SDS.[5-7] At the

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TABLE I: Calculated Parameters of the Comicelles with Different Combinations of SDS and C_9PhE_{10}[a]

no.	[SDS], 10^{-3} M	[C_9PhE_{10}], 10^{-3} M	C^*, 10^{-3} M	X_1	X_2	f_1	f_2	C_1^M, M	C_2^M, M	β
1	150.0	0.025	6.2	0.83	0.17	0.91	0.10	7.5×10^{-3}	1.6×10^{-9}	-3.4
2	30.0	0.025	4.3	0.70	0.30	0.75	0.19	6.1×10^{-3}	1.8×10^{-8}	-3.3
3	15.0	0.025	3.4	0.64	0.36	0.64	0.25	5.3×10^{-3}	5.7×10^{-8}	-3.4
4	5.0	0.025	2.4	0.56	0.44	0.52	0.36	4.2×10^{-3}	7.7×10^{-6}	-3.3
5	0.2	0.025	0.39	0.27	0.74	0.16	0.79	2.0×10^{-4}	2.0×10^{-5}	-3.4
6	5.0	0.5	0.45	0.28	0.72	0.18	0.76	1.3×10^{-3}	6.7×10^{-6}	-3.4

[a] The cmc's for SDS (surfactant 1) and C_9PhE_{10} (surfactant 2) measured from the plot of I_1/I_3 vs. [surfactant] (8.2×10^{-3} and 7.5×10^{-5} M, respectively) are very close to those measured by surface tension and conductivity methods.[5,20]

concentrations employed, C_9PhE_{10} does not form a saturated monolayer on the surface, so that initial addition of SDS reduces the value of γ as added SDS monomers fill unsaturated sites on the surface. At values of ca. 1×10^{-3} M SDS and ca. 1×10^{-4} M SDS for the lower and higher initial C_9PhE_{10} concentrations, respectively, the value of γ ceases to decrease and begins to increase. The increasing trend is similar to those observed in the systems of binary micelles[8,9] or those containing impurities.[5,10] We interpret this reversal in the behavior of γ to be due to the removal of C_9PhE_{10} molecules from the surface as a result of formation of comicelles of C_9PhE_{10} and SDS in the bulk aqueous phase. At the same time, added SDS monomers are being deposited on the surface, in competition with formation of comicelles.

At ca. 2×10^{-2} M the removal of C_9PhE_{10} molecules from the surface is nearly complete and the value of γ begins to decrease again as SDS monomers fill the unsaturated sites on the surface. At [SDS] = 1×10^{-1} M, the value of γ approaches the value for pure SDS solutions.

We can define three regions and two transitions for the γ vs. [SDS] of Figures 2 and 3. In region I, the value of γ decreases with added [SDS] and in region II the value of γ increases with added [SDS]. The value of [SDS] for transition from I → II is smaller for the higher starting concentration of the nonionic additive (ca. 5×10^{-3} M SDS for 2.5×10^{-5} M C_9PhE_{10} and ca. 1×10^{-4} M SDS for 5×10^{-5} M C_9PhE_{10}). This result is consistent with the removal of nonionic surfactant at the surface because of displacement by SDS and formation of comicelles, since comicelles will form at a lower [SDS] as the initial concentration of the cosurfactant is increased.

Although the value of [SDS] required for the transition from region I → II depends on the initial concentration of C_9PhE_{10}, the value of [SDS] required for the transition from region II → III is independent of the initial concentration of C_9PhEO_{10}. These results are consistent with the formation of SDS micelles becoming the controlling factor in the value of γ; i.e., region II is one that is rich in SDS micelles.

The variation of I_1/I_3 with [SDS] can now be viewed in terms of the above interpretion. Region I corresponds to the formation of low concentrations of comicelles or small micellar aggregates and concurrent solubilization of the pyrene in the comicelles. The transition I → II is broad in Figure 2. During this transition the values of I_1/I_3 decrease rapidly, while the value of γ remains nearly constant. These data are consistent with the lowering of the cmc of SDS by the added nonionic surfactant.[8,11] The transition region II → III in the γ vs. [SDS] curve corresponds to a break in the slope of the I_1/I_3 vs. [SDS] curve. This coincidence of transitions is in agreement with the completion of the SDS monomer–micelle phase transition. Further increase in [SDS] simply increases the concentration of SDS micelles.

In Figure 3, the transition from region I → II is sharp in the γ vs. [SDS] curve but not perceptible in the I_1/I_3 vs. [SDS] curve. At higher initial concentrations of C_9PhEO_{10}, formation of co-micelles begins at lower concentrations of SDS and continues to

form until [SDS] reaches a value of ca. 2×10^{-2} M at which point SDS micelles and SDS-rich comicelles dominate the behavior of the colloid system.

From Figure 4 it is seen that for C_9PhE_{20}, which is not as effective a surfactant as C_9PhE_{10} as gauged by its ability to reduce the surface tension,[7] the γ vs. [SDS] curve does not display a maximum, i.e., no region corresponding to region II of Figures 2 and 3. The graph of I_1/I_3 vs. [SDS] has a similar shape to that in Figures 2 and 3. The absence of region II behavior is ascribed to the poorer surfactant ability of C_9PhE_{20} relative to C_9PhE_{10} and its poorer ability to form comicelles. Comparison of the initial portion of region I of Figures 3 and 4 shows it is consistent with a poorer ability of C_9PhE_{20} to form micelles since the I_1/I_3 value is found to remain initially constant for the larger surfactant as the [SDS] is increased.

Figure 5 shows the behavior of I_1/I_3 as a function of [C_9PhE_{10}] in the absence of SDS and in the presence of 3×10^{-3} and 5×10^{-3} M SDS. The curves have the shapes of typical cmc profiles, with the pure surfactant having the sharper break at the cmc (the value of which from Figure 5 is ca. 8×10^{-5} M; the literature value is 7.5×10^{-5} M[12]); the limiting value of I_1/I_3 in C_9PhE_{10} micelles is 1.35, a value higher than 1.2 for SDS micelles, suggesting a more open, hydrated structure for the nonionic micelles.

The qualitative conclusions concerning comicelle formation can be put on a more quantitative basis by use of a formulation proposed by Rubingh (eq 1).[13] Rubingh's model differs from the ideal mixing models developed by Lange[11] and Clint[8b] in that it incorporates a regular solution approximation to describe the activity coefficients of the components in the mixed micelle. The ideal mixing theory is found to adequately describe cmc, monomer concentrations, and micelle composition for the systems where ideal mixing might be expected, i.e., homologus series of surfactants. It however fails to predict cmc and micelle composition for systems that deviate from ideality such as surfactants with widely differing head groups. The regular solution theory in this context provides a reasonable mathematical approach by incorporating an interaction parameter β which can be obtained from experimental cmc data. This approach was found to be applicable to a variety of anionic, cationic, and nonionic surfactant mixtures almost all of which exhibited negative deviations from ideality. The relevant equations from Rubingh's derivation used in the present treatment to calculate monomer and micelle compositions are discussed below.

The mole fraction of a given surfactant (x_1 for SDS) in a comicelle containing two surfactants 1 (SDS) and 2 (C_9PhE_{10}) can be estimated from knowledge of the cmc's of the individual surfactants (C_1, C_2), the cmc of the mixed surfactant system (C^*), and the mole fraction of surfactant 1 in the total mixed solute (α) by eq 1.

$$1 = \frac{x_1 \ln (C^* \alpha / C_1 x_1)}{(1 - x_1)^2 \ln [C^*(1 - \alpha)/C_2(1 - x_1)]} \qquad (1)$$

Solutions of mixed surfactants of known α value were successively diluted with the water solution of pyrene, so that a series of solutions of constant pyrene concentration and constant α but

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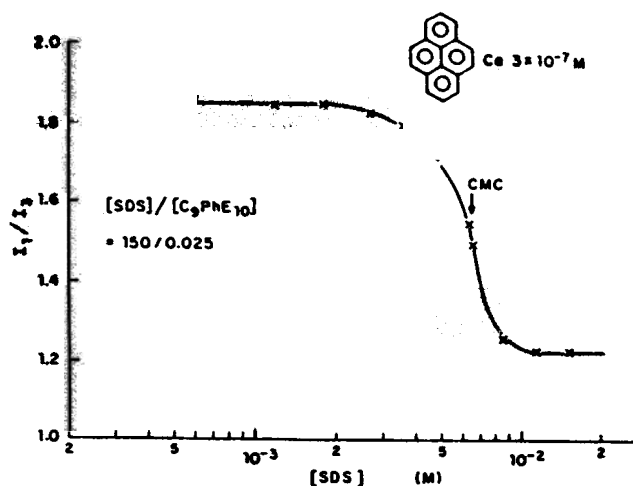
Figure 7. cmc for the system of mixed SDS/C_9PhE_{10} with the mole ratio fixed at 150/0.025.

varying overall surfactant concentration were prepared. The I_1/I_3 values for three solutions are plotted against the concentration of SDS in the solution as shown in Figure 7 for No. 1 in the Table I. The inflection point is observed which corresponds to the point at which micelles of this mixed system are formed. C^* is obtained by adding the concentration of C_9PhE_{10} and SDS which are present in the solution at the inflection point.

From the x_1 value, it is convenient to calculate the following parameters β, f_1, and f_2 as given by eq 2, 3, and 4, respectively,

$$\beta = \ln (C^*\alpha/C_1 x_1)/(1 - x_1)^2 \tag{2}$$

$$f_1 = \exp \beta(1 - x_1)^2 \tag{3}$$

$$f_2 = \exp \beta x_1^2 \tag{4}$$

on the basis of the calculated x_1 value obtained from eq 1. β is the interaction parameter, and f_1 and f_2 are the activity coefficients of surfactants 1 and 2 in the comicelle, respectively.

The concentration of monomer surfactant 1 or 2 (C_1^M or C_2^M, respectively) at a given total surfactant concentration of 1 and 2 (C_t), in turn, can be calculated from

$$C_1^M = \frac{-(C_t - \Delta) + [(C_t - \Delta)^2 + 4\alpha C_t \Delta]^{1/2}}{2(f_2 C_2/f_1 C_1 - 1)} \tag{5}$$

$$C_2^M = (1 - C_1^M/f_1 C_1)f_2 C_2 \tag{6}$$

where $\Delta = f_2 C_2 - f_1 C_1$.

From the eq 5 and 6, values of the mole fraction of SDS and of C_9PhE_{10} were calculated (Table I) for several points employing the data from the figures. The results allow the conclusion that for the regions in which comicelles exist in significant concentration (up to the II → III transition), an increase in [SDS] causes an increase (1) in the activity of SDS in the comicelle, (2) in the SDS monomer concentration, and (3) in the fraction of SDS monomers in the comicelle. The abrupt decrease in C_2^M and f_2 from 5 × 10^{-3} M to 1.5 × 10^{-2} M corresponds to the increase in γ.

In the past foaming has been used to separate surface active components, such as in the purification of SDS,[14] the fractionation of other alkyl sulfates,[15] and the separation of closely related fatty acids.[16] The foaming experiment here has been used to analyze
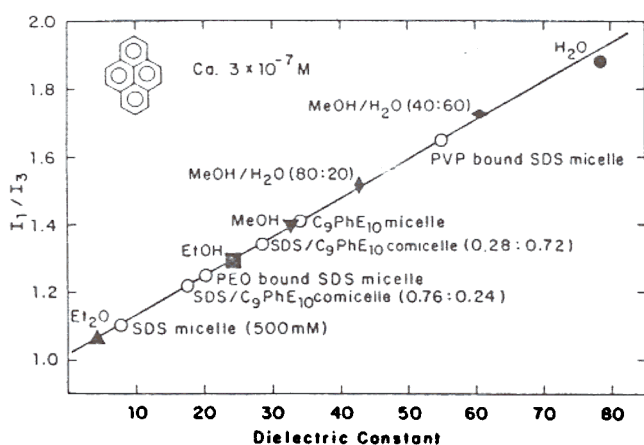

Figure 8. Linear relation between I_1/I_3 and dielectric constant for a series of solvents (dark symbols). Several micelle and comicelle systems are correlated with this straight line from their I_1/I_3 values (empty circles).

the surface concentration of C_9PhE_{10} and SDS.

The data obtained here for the foaming tests (Figure 6) are interpreted as follows: C_9PhE_{10} exists at its equilibrium concentration at the surface for low [SDS]; as [SDS] is increased, C_9PhE_{10} is solubilized at the surface and hence $[C_9PhE_{10}]_{foamate}$ increases. At ca. 5 × 10^{-3} M SDS however, competition with SDS for surface sites and the formation of suitable C_9PhE_{10}-solubilizing micelles pull the nonionic surfactant from the surface into bulk and thus $[C_9PhE_{10}]_{formate}$ decreases. The trends observed here in $[SDS]_{formate}$ and $[C_9PhE_{10}]_{foamate}$ vs. [SDS] are similar to those in C_1^M and C_2^M shown in Table I.

The I_1/I_3 of pyrene changes with the polarity (dielectric constant, ϵ) of the solvent encountered,[17] and a linear relationship exists between I_1/I_3 and ϵ; a calibration line was done with the solvents ether, ethanol, methanol, water, and the mixture of water and methanol using our experimental condition (Figure 8). The relationship between I_1/I_3 and ϵ (reference data)[18,19] can be expressed with equation

$$\epsilon = (I_1/I_3 - 1.25)86.2 + 20 \tag{7}$$

Therefore, from eq 7 the apparent dielectric constants of pure SDS micelle (ϵ_{SDS} = 19.1 at 30 mM), pure C_9PhE_{10} micelle ($\epsilon_{C_9PhE_{10}}$ = 33.8), and the comicelle ($\epsilon_{com,app}$) can be calculated from I_1/I_3 values.

Alternatively, the dielectric constant of a comicelle also can be estimated by eq 8 ($\epsilon_{com,calcd}$) from the knowledge of ϵ_{SDS}, $\epsilon_{C_9PhE_{10}}$, and the composition of the comicelle.

$$\epsilon_{com,calcd} = x_1\epsilon_{SDS} + x_2\epsilon_{C_9PhE_{10}} \tag{8}$$

where x_1 and x_2 can be obtained from Table I. The $\epsilon_{com,calcd}$ of the comicelle formed from SDS (5 × 10^{-3} M) and C_9PhE_{10} (5 × 10^{-4} M) (flat part in Figure 5) by eq 8 is 28.5, close to the $\epsilon_{com,app}$ (26.0, calculated from eq 7 with I_1/I_3 = 1.32). This suggests that the calculation for the micellar compositions of the mixed micelle in this paper is reasonable.

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