Fluorescence Probes for Critical Micelle Concentration

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The utility of pyrene and pyrene-3-carboxaldehyde as fluorescence probes for determining the critical micelle concentration (cmc) of nonionic (Tergitol 25-L-9, Tergitol 15-S-40, Neodol 91-8), anionic (sodium decyl sulfate), and cationic (cetyltrimethylammonium bromide) surfactants was investigated. The probes were dissolved in trace amounts ($<10^{-6}$ kmol/m^3) in a series of aqueous solutions of these surfactants. Results obtained indicated that the surfactant concentration at which a marked decrease in the λ_{max} parameter of pyrene-3-carboxaldehyde occurs corresponds to the cmc determined by surface tension. In contrast, the customarily used parameter, I_1/I_3, of pyrene undergoes a reduction at concentrations close to, but consistently lower than, the accepted cmc values of the surfactant. Thus, it appears that pyrene-3-carboxaldehyde is the more reliable probe for cmc determination. Surface tension results show, furthermore, that the probe molecules at the levels used to determine the cmc by fluorescence do not noticeably affect the surfactant properties, viz., surface tension, nor the surface tension derived cmc value.

Introduction

The fluorescence probe technique is becoming increasingly popular in the study of surfactant micellization/adsorption,[1–5] polymer–surfactant interactions,[6–8] microemulsions,[9] etc. This method involves the use of a hydrophobic fluorescence dye which exhibits different fluorescence characteristics depending upon the properties of the solubilizing medium. For example, fluorescence probes such as pyrene and pyrene-3-carboxaldehyde which are sensitive to the polarity of the solubilizing medium will exhibit different fluorescence behavior in micellar and nonmicellar solutions. Such changes of behavior as a function of surfactant concentration have been used to determine the critical micelle concentration (cmc) and other micelle characteristics of certain surfactants. It is, however, necessary in such applications to ensure the absence of any influence of the probe molecule itself on the specific property in question. In this paper, a comparative evaluation of the performance of two probes, namely, pyrene and pyrene-3-carboxaldehyde, in determining the cmc of selected nonionic, cationic, and anionic surfactants, is presented. The influence of the probe molecule on the surfactant solution behavior has been tested by determining the surface tension behavior of selected surfactant systems in the presence and absence of the probe.

Experimental Section

Materials. The nonionic surfactants included two detergent-range primary and secondary Tergitol ethoxylates from Union Carbide Corporation. Another is Neodol 91-8 obtained from Shell Development Corporation. Properties of these surfactants are given in Table I. A laboratory synthesized and purified sample of sodium decyl sulfate was used as the anionic surfactant. The cationic cetyltrimethylammonium bromide purchased from Fluka Chemical Corporation was used as received. All surfactants chosen for this work exhibited no minimum or virtually no minimum in their surface tension concentration plot. The fluorescence probes, pyrene and pyrene-3-carboxaldehyde, were purchased from Aldrich Chemical Co. and purified by three crystallizations from ethanol.

Methods. Fluorescence characteristics of pyrene and pyrene-3-carboxaldehyde were determined by using two different Perkin-Elmer fluorescence spectrophotometers, viz., Models MPF-3L and LS 5. Emission spectra of pyrene and pyrene-3-carboxaldehyde were obtained by exciting the samples at 332 and 380 nm, respectively. All the surfactant solutions were prepared

Table I. Structural Properties of Nonionic Surfactants

surfactant	hydrophobe	hydrophile
Tergitol 25-L-9	1° alcohol (C_{12}–C_{15})	9 EO
Tergitol 15-S-40	2° alcohol (C_{11}–C_{15})	40 EO
Neodol 91-8	1° alcohol (C_9–C_{11})	8 EO

using water previously saturated with pyrene or pyrenecarboxaldehyde (concentration of the probes $<10^{-6}$ kmol/m^3).

Surface tension measurements were conducted by use of the Wilhelmy plate technique with a filter paper rectangle or platinum plate as the sensor.

Results and Discussion

The fluorescence spectrum of pyrene in water exhibits five predominant peaks and that of pyrene-3-carboxaldehyde a single peak at 469 nm. It has been shown (1) in the case of pyrene that the ratio of intensity of the first (I_1 at 373 nm) and third peaks (I_3 at 384 nm) is a sensitive parameter characterizing the polarity of the probe's environment. For example, I_1/I_3 in hydrocarbon solvents has a value of about 0.6, in ethanol about 1.1, and in water about 1.8. In the case of pyrenecarboxaldehyde the position of the maximum has been shown to be the parameter that correlates with the solvent polarity:[2,3] the dielectric constant, D, of the medium is related to the position of the peak maximum (λ_{max}) by the equation[2,3]

$$\lambda_{max} = 0.52D + 431.5$$

In the sections to follow, the dependence of the above mentioned parameters on surfactant concentration is presented and the utility of the probes is discussed.

The dependence of I_1/I_3 of pyrene and λ_{max} of pyrenecarboxaldehyde on the concentration of Neodol 91-8 is illustrated in Figure 1. Both I_1/I_3 and λ_{max} remain constant up to a certain surfactant concentration and decrease sharply above it. The first break points in the fluorescence

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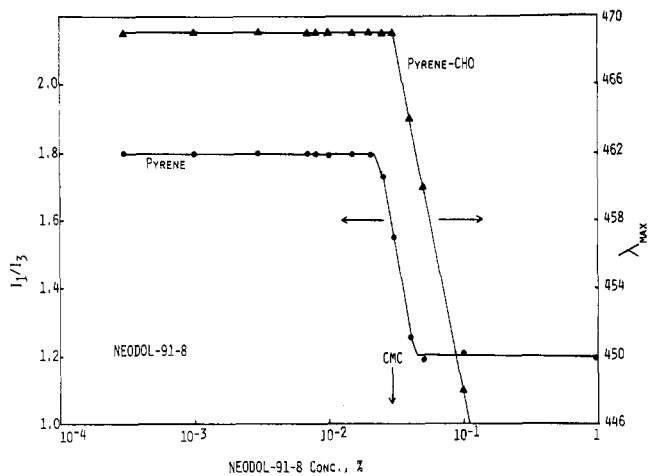
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Figure 1. Change in the fluorescence characteristics of pyrene and pyrenecarboxaldehyde as a function of Neodol 91-8 concentration.
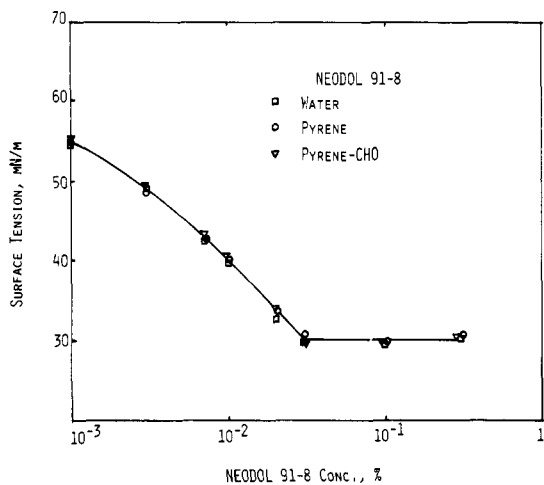

Figure 2. Effect of pyrene and pyrenecarboxaldehyde on the surface tension behavior of Neodol 91-8 solutions.
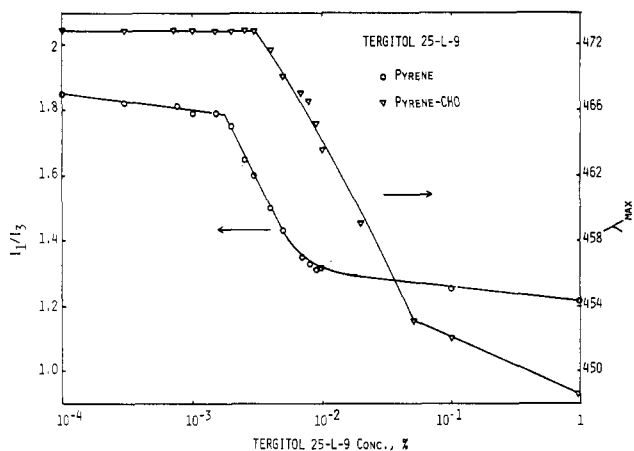

Figure 3. Change in the fluorescence characteristics of pyrene and pyrenecarboxaldehyde as a function of Tergitol 25-L-9 concentration.

Figure 4. Change in the fluorescence characteristics of pyrenecarboxaldehyde as a function of Tergitol 15-S-40 concentration.

Figure 5. Effect of pyrene and pyrenecarboxaldehyde on the surface tension behavior of Tergitol 25-L-9 solutions.

Figure 6. Surface tension behavior of Tergitol 15-S-40 solutions.

behavior of pyrene and pyrenecarboxaldehyde occur, respectively, at $(2.2 \times 10^{-2})\%$ and $(3 \times 10^{-2})\%$ Neodol 91-8. A lowering of the value of I_1/I_3 or λ_{max} is an indication of the solubilization of the probes in a more hydrophobic environment than water—in this case surfactant micelles. Therefore the concentration at which the first break occurs should correspond to the critical micelle concentration (cmc). A comparison of the first break points with the cmc
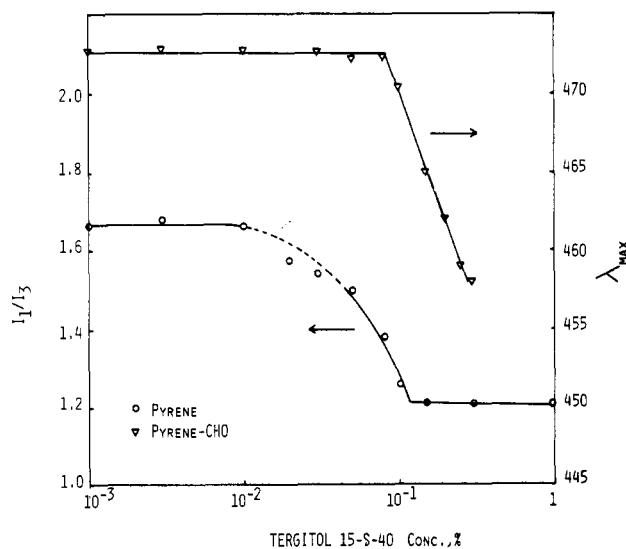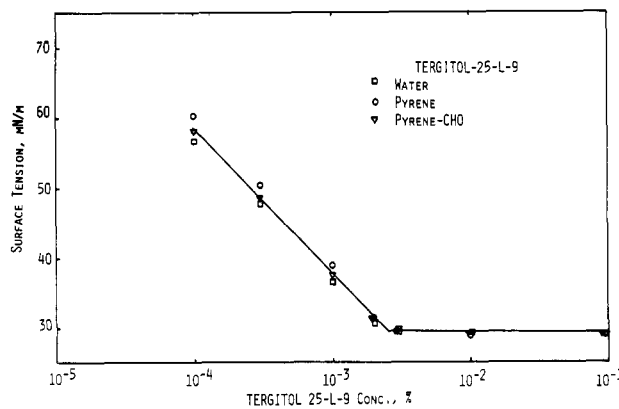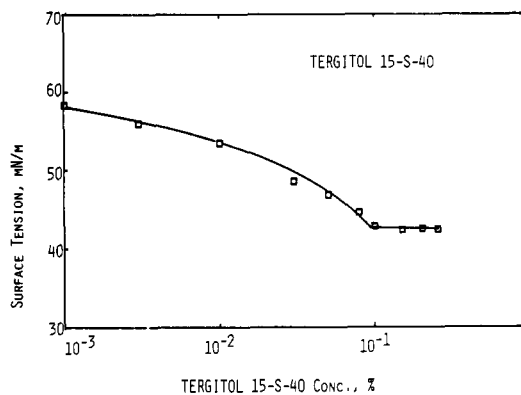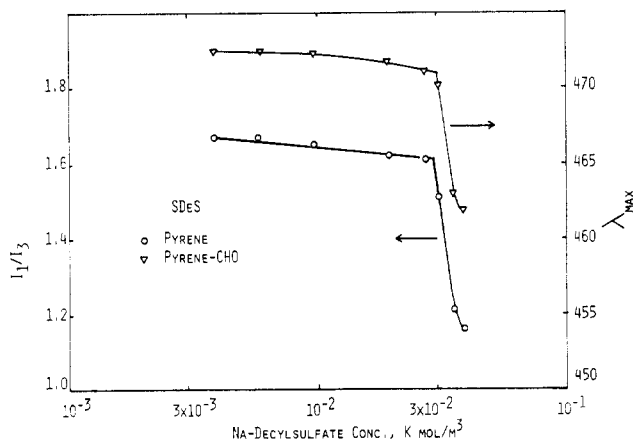
$[(3 \times 10^{-2})\%]$ determined from surface tension measurements (see Figure 2) shows that the value indicated by pyrenecarboxaldehyde fluorescence change is closer to the actual cmc. Possible reasons for this behavior are examined in a later section. Interestingly, the surface tension results obtained in the presence and absence of the probes do not indicate any significant effect of the latter themselves on the cmc.

The changes in I_1/I_3 and λ_{max} as a function of the concentrations of two other nonionic surfactants, namely, Tergitol® 25-L-9 and Tergitol® 15-S-40, are given in Figures 3 and 4. Surface tension plots are included in Figures 5 and 6. For Tergitol 25-L-9, the break point in the presence

Table II. Comparison of the Cmc Values Determined from Surface Tension and Fluorescence Measurements

	cmc		
surfactant	pyrene I_1/I_3	pyrene-3-carboxaldehyde λ_{max}	surface tension
Tergitol 25-L-9	$(1.7 \times 10^{-3})\%$	$(3 \times 10^{-3})\%$	$(2.5 \times 10^{-3})\%$
Tergitol 15-S-40	(10^{-2})–$(5 \times 10^{-2})\%$	$(8.5 \times 10^{-2})\%$	$(9 \times 10^{-2})\%$
Neodol 91-8	$(2.2 \times 10^{-2})\%$	$(3 \times 10^{-2})\%$	$(3 \times 10^{-2})\%$
sodium decyl sulfate	2.95×10^{-2} kmol/m^3	3.0×10^{-2} kmol/m^3	3.0×10^{-2} kmol/m^3
cetyltrimethylammonium bromide	5.5×10^{-4} kmol/m^3	8×10^{-4} kmol/m^3	8×10^{-4} kmol/m^3

Figure 7. Change in the fluorescence characteristics of pyrene and pyrenecarboxaldehyde as a function of sodium decyl sulfate concentration.
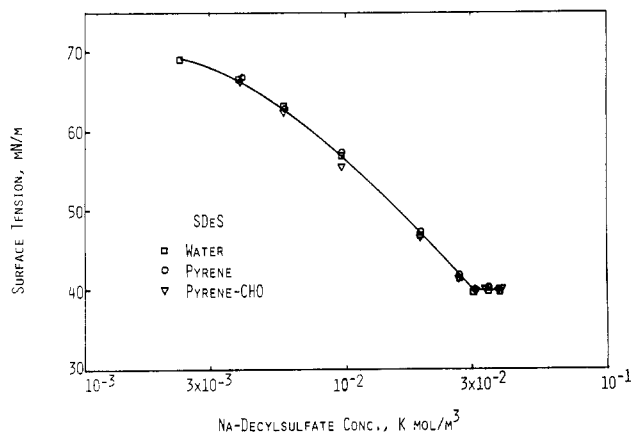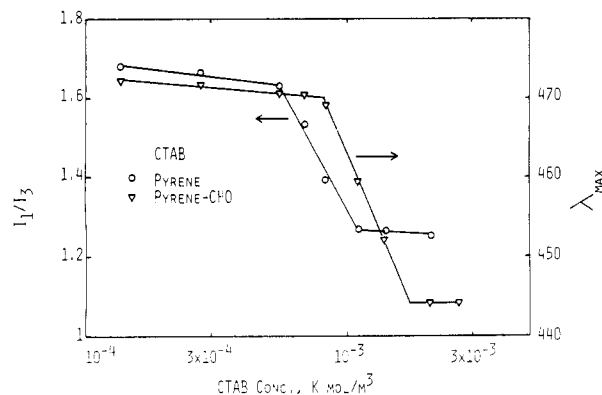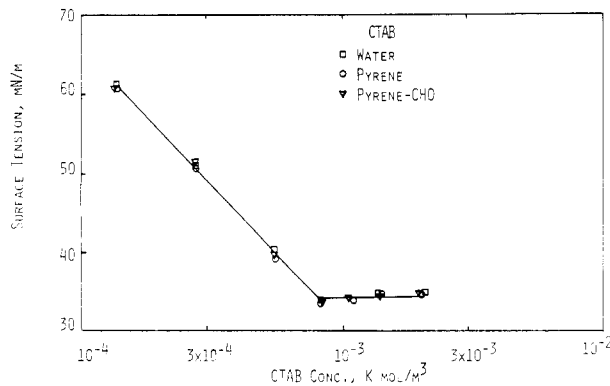

Figure 8. Effect of pyrene and pyrenecarboxaldehyde on the surface tension behavior of sodium decyl sulfate solutions.

of pyrenecarboxaldehyde $[(3.0 \times 10^{-3})\%]$ is again close to the cmc $[(2.8 \times 10^{-3})\%]$ determined from surface tension measurements whereas the break point in the pyrene-fluorescence plot is significantly lower. While the λ_{max} values for pyrenecarboxaldehyde are constant below the cmc of Tergitol 25-L-9, a slight but steady drop in I_1/I_3 value is evident in the corresponding pyrene system.

A comparison of the surface tension and fluorescence results of Tergitol 15-S-40 shows that the pattern broadly repeats itself. Evidently pyrene-3-carboxaldehyde reliably predicts the cmc of this surfactant also, which has a different structure, i.e., based on a random secondary alcohol, whereas pyrene does not.

The results presented so far have been for nonionic surfactants. We have determined the fluorescence behavior of pyrene and pyrenecarboxaldehyde in typical anionic (sodium decyl sulfate, SDeS) and cationic (cetyltrimethylammonium bromide, CTAB) surfactants also. For SDeS the cmc indicated by the λ_{max} plot of pyrenecarboxaldehyde $(3.0 \times 10^{-2}$ kmol/m$^3)$ is in excellent agreement with the cmc $(3.0 \times 10^{-2}$ kmol/m$^3)$ obtained from surface tension measurements (see Figures 7 and 8). The I_1/I_3 plot for pyrene also indicates a cmc $(2.95 \times 10^{-2}$ kmol/m$^3)$ in good agreement with the "surface tension" cmc in this case.

The surface tension results for SDeS given in Figure 8 show that the probe molecules have no measurable effect on the surface tension behavior of the system. Evidently, the probe molecules at the tested levels do not interfere with the surfactant aggregation behavior.

Fluorescence behavior of the two probes in CTAB solutions is shown in Figure 9. As in previous examples, the sharp decrease in the λ_{max} of pyrenecarboxaldehyde (8.0 $\times$ 10^{-4} kmol/m^3) is in excellent agreement with the cmc derived from surface tension measurements (8.0 $\times$ 10^{-4} kmol/m^3; see Figure 10). The I_1/I_3 plot of pyrene, on the other hand, indicates that the "cmc" lies in the range (5.5–6.8) $\times$ 10^{-4} kmol/m^3 which is substantially lower than the "surface tension" cmc. Surface tension results, in this case again, confirm that the probes do not have any sig-

Figure 9. Change in the fluorescence characteristics of pyrene and pyrenecarboxaldehyde as a function of CTAB concentration.

Figure 10. Effect of pyrene and pyrenecarboxaldehyde on the surface tension behavior of CTAB solutions.

nificant effect on the surfactant behavior.

A compilation of all the cmc values obtained from fluorescence and surface tension measurements is given in Table II. The cmc values estimated from the fluorescence characteristics of pyrene-3-carboxaldehyde can be seen to be consistently closer to the accepted "surface tension" cmc values of surfactants.

Note that in all the cases reported here, cmc values indicated by pyrene are lower than those indicated by pyrenecarboxaldehyde and in some cases the discrepancy is substantial. Pyrene and pyrenecarboxaldehyde, because of differences in hydrophobic/hydrophilic nature, can be expected to be located in different parts of the micelle (pyrenecarboxaldehyde is probably located closer to the periphery of the micelle[2,11,12]) and so could influence the micellization process to different extents. The surface tension results, however, show that the probes do not sensibly affect the surfactant behavior and the cmc values derived therefrom. Thus, the reasons for the observed decreases in I_1/I_3 at concentrations below the cmc are not clear at present.

It is possible that at concentrations well below the cmc small premicellar aggregates exist in the system.[13,14] A possibly relevant observation in this regard is our finding that in surfactant systems with small amounts of surface-active impurity (as detected by the presence of a minimum in the surface tension vs. log concentration plot), the I_1/I_3 plot departed from linearity at concentrations substantially lower than the cmc and exhibited significant curvature. This would imply that pyrene, in fact, is an extremely sensitive probe. On the contrary, such premicellar aggregation itself may have been brought about by

the presence of pyrene. This aspect needs to be examined further and is beyond the scope of the present investigation. In any case, from the point of view of cmc determination, pyrene-3-carboxaldehyde is a more reliable probe than pyrene.

Conclusions

The use of the fluorescence characteristics of two widely used probes, namely, pyrene and pyrene-3-carboxaldehyde, has been investigated as a means to determine the cmc of selected nonionic, anionic, and cationic surfactants. The influence of the probe molecule itself on the surfactant behavior was tested by measuring the surface tension behavior of surfactants in the presence and absence of the probe. Results obtained show that the surfactant concentration at which a sharp decrease in the λ_{max} parameter of pyrenecarboxaldehyde occurs corresponds closely to the cmc determined from surface tension measurements. In contrast, the cmc indicated by pyrene was in general lower than the latter values and in some cases the discrepancy was serious. Evidently, pyrene-3-carboxaldehyde is a more reliable probe than pyrene for cmc determination. It is of interest that the surface tension results further show that the probe molecules at levels required to determine the cmc do not noticeably affect the surface behavior of the surfactants.

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Laser Heating and Particle Temperature Measurement in an Electrodynamic Balance[†]

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The laser heating of a 10–50-μm-diameter particle suspended in an electrodynamic balance to temperatures of 500 K and above is examined theoretically and experimentally. The average particle temperature is described by a lumped-parameter model, and comparison is made with more advanced models. The transient response has a $1/e$ time constant of between 0.5 and 20 ms. The needed light flux ranges upward from 10 MW/m². The measurement of particle temperature by multicolor infrared pyrometry is experimentally demonstrated above 500 K.

Introduction

The motivation for this research is the study of the kinetics of gas–solid reactions. For fast reactions (characteristic reaction time of a second or faster), present methods are either mass-transfer limited (e.g., thermogravimetric analyzers) or unable to measure weight or temperature in a continuous fashion (e.g., laminar-flow furnaces). What is needed is a means of suspending a

submillimeter particle in a gas, introducing a step change in either the temperature or concentration, and continuously measuring the weight and temperature. This paper reports on progress to date to meet these goals.

Theory

Particle Dynamics. Wuerker et al. in 1959[1] developed an electrode configuration that permitted stable containment of a charged particle. Their chamber used an AC

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