Fluorescence Probes for Aqueous Solutions of Nonionic Micelles

Nicholas J. Turro* and Ping-Lin Kuo

Department of Chemistry, Columbia University, New York, New York 10027

Received August 24, 1984. In Final Form: November 15, 1984

Three fluorescence probes, pyrenecarboxaldehyde (PA), pyrene (P), and an ionic indole labeled detergent (In), have been employed to investigate nonionic (Triton) micelles of varying EO number. PA serves as a probe of the surface of micelle, P serves as a probe of the inner layer of micelles, and In serves as a probe of the inner core of micelles. Measurement of fluorescence parameters for PA, P, and In as a function of variations of surfactant structure and temperature provides direct information of the time-averaged location of the probes in nonionic micelles and indirectly provides information on the nonionic micelles' structure.

Introduction

Photoluminescence probes are capable of providing microscopic information concerning the nature of micellar aggregates in aqueous solution. To date, the majority of published papers deal with ionic micelles.[1] We report here the use (Chart I) of three fluorescence probes (pyrenecarboxaldehyde, PA; pyrene, P; and an indole detergent, In) to probe the microscopic characteristic of nonionic micelles (Triton series, C_9PhE_n). The probes were selected on the basis of previous investigations which suggest (1) that PA is a relatively polar probe that should be located on a time average near the outer surface of the hydrophilic micelle/water interface,[2] (2) that P is a less polar probe that should be located on a time average near the inner layer of the hydrophilic micelle/water interface,[3] and (3) that In is a relatively nonpolar probe that should be located on a time average near the hydrophobic micellar core.[4] These expectations are shown pictorially in Figure 1 (bottom). For each probe there is a characteristic fluorescence property which reports the polarity of its time-averaged environment. For PA the parameter is λ_F^{PA}, the fluorescence maximum, for P the parameter is I_1/I_3, the ratio of the first and third fluorescence vibrational bands, and for In the parameter is λ_F^{In}, the fluorescence maximum. In each case, λ_F^{PA}, I_1/I_3, and λ_F^{In} have been shown to faithfully report solvent polarity for homogeneous environments (ϵ's in Figure 1 are obtained from ref 5). Figure 1 shows values for these parameters near ambient temperatures in water, n-butyl alcohol, and n-dodecane. When the values for the parameters for aqueous solutions of sodium dodecyl sulfate (SDS) micelles are plotted in Figure 1, it is seen that the order of polar environments experienced by the probes is PA (most polar), P (intermediate polarity), and In (least polar). The time-average positions of PA, P, and In are, therefore, assigned to the surface, inner layer, and inner core of SDS micelles, re-

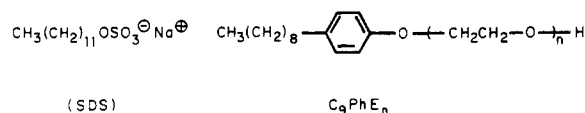## Chart I

PROBES
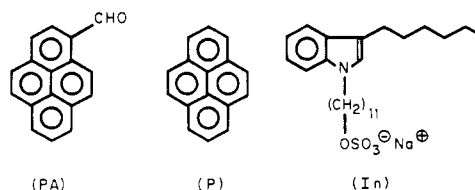
SURFACTANTS

Table I. Fluorescence Parameters for Micellar Solutions of Tritons at Ambient Temperature and Pressure

micelles or solvents	λ_F^{PA}	I_1/I_3	λ_F^{In}
$C_9PhE_{7.5}$	451	1.40	331
C_9PhE_{10}	452	1.41	330
C_9PhE_{15}	452	1.43	330
C_9PhE_{18}	453	1.46	331
C_9PhE_{20}	452	1.47	332
H_2O	468	1.90	372
SDS	454	1.22	360
$n\text{-}C_4H_9OH$	460	1.10	351
$n\text{-}C_{12}H_{26}$	415	0.60	333

spectively, as shown schematically at the bottom of Figure 1.

The experimental strategy of this report is based on the hypothesis that PA, P, and In will be faithful reporters of the polarity of micellar environments. Within the validity of this assumption, variations in micellar structure may be inferred from variations in λ_F^{PA}, I_1/I_3, and λ_F^{In}, with the three independent measurements serving as interactive tests of the consistency of the interpretation.

Experimental Section

Materials. Pyrene (P) and pyrene-3-carboxaldehyde (PA) were purchased from Aldrich Chemical Co. and were purified by three crystallizations from ethanol. The preparation of sodium 11-(3-hexyl-1-indolyl)undecyl sulfate (In) has been reported.[4] Sodium dodecyl sulfate (SDS), electrophoresis grade, was purchased from Bio-Rad Laboratories and was employed without further purification. The selected poly(ethylene glycol) n-nonylphenyl ethers

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(2) (a) Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 279. (b) Kalyanasundaram, K.; Gratzel, M.; Thomas, J. K. *J. Am. Chem. Soc.* **197j**, *96*, 7869. (c) Singer, L. A. "Solution Behavior of Surfactants", Mittal, L. K., Fendler, E. J., Eds.; Plenum: New York, 1982; Vol. 2, p 91.

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(4) (a) Schore, N. E.; Turro, N. J. *J. Am. Chem. Soc.* **1978**, *97*, 2488. (b) Turro, N. J.; Tanimoto, Y.; Gabor, G. *Photochem. Photobiol.* **1980**, *31*, 527.

(5) Weast, R. C., Ed. "Handbook of Chemistry and Physics", 57th ed.; Chemical Rubber Publishing Co.: Cleveland, OH, 1976; p E55.
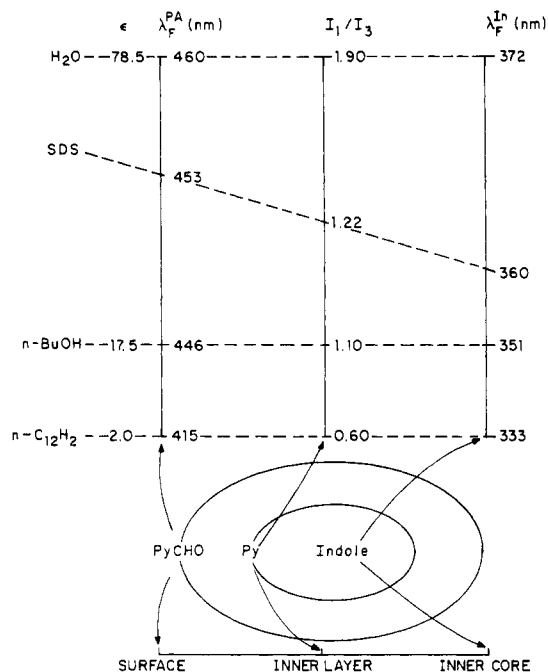
Figure 1. Values for λ_F^{PA}, I_1/I_3, and λ_F^{In} in water, n-butyl alcohol, n-dodecane, and SDS. The values of ϵ are taken from ref 5.

(C_9PhE_n) were purchased from Tokyo Kasei Co., Japan, and were employed without further purification.

Fluorescence Measurements. All fluorescence measurements were recorded on a Perkin-Elmer Model MPF-3L spectrometer.

Results and Discussion

The values of λ_F^{PA}, I_1/I_3, and λ_F^{In} at 25 °C for micellar aqueous solutions of C_9PhE_n are listed in Table I, where a comparison of the probe parameters in SDS is given. The values of λ_F^{PA} for the C_9PhE_n systems (ca. 453 nm) are similar to those for SDS micelles (454 nm), whereas the I_1/I_3 values are larger (ca. 1.45) than for SDS micelles (1.2) and the λ_F^{In} values (ca. 332 nm) are much lower than for SDS micelles (360 nm). The polarity experienced by the probe is expected to be related to the time-average water content of the probe environment. With this attitude as a basis, the nonionic C_9PhE_n micelles appear to have water content at their surface that is comparable to SDS micelles but to have a higher water content than SDS in their inner layers and less water content in their inner cores. These conclusions are consistent with the more polar nature of the hydrated EO groups (relative to SDS) that form the composition of the inner layer of the C_9PhE_n micelles.

The Influence of EO Number on the Time-Averaged Probe Position in Nonionic Micelles. The values for λ_F^{PA}, I_1/I_3, and λ_F^{In} for aqueous solutions containing micelles of C_9 (n = 7.5, 10, 15, 18, and 20) are listed in Table I. The value of λ_F^{PA} is essentially unchanged (452 ± 1 nm) in the systems studied. The average value of λ_F^{PA} for the nonionic detergents is very close to that for SDS micelles (454 nm), suggesting that PA sees a similar relatively hydrophilic region of each nonionic micelle. In analogy to SDS, the time-averaged position is assigned to the surface or outer layer of the nonionic micelles. The value of I_1/I_3 increases monotonically with increasing EO number. The range of values (1.40–1.47) is in all cases higher than for P in SDS micelles (1.22) where P resides in the inner layer portion of the micelle. Thus, P experiences a more hydrophilic enrivonment, which is attributed to the higher degree of water associated with the hydrated EO chains forming the inner layer of the nonionic
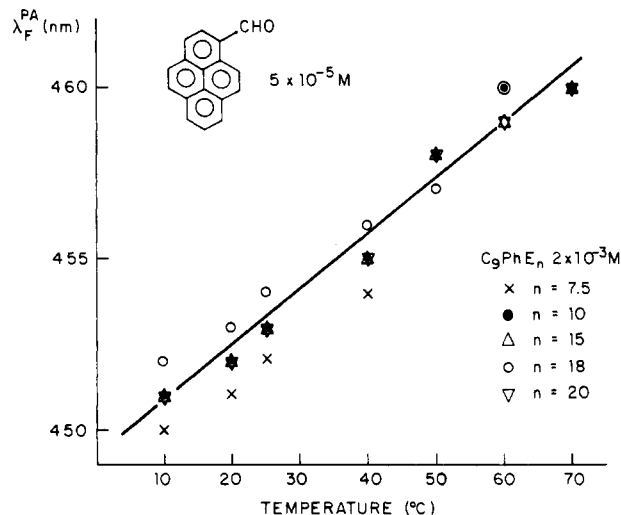

Figure 2. Temperature effects on λ_F^{PA} in C_9PhE_n: n = 7.5 (X), 10 (●), 15 (▲), 18 (○), and 20 (▽).
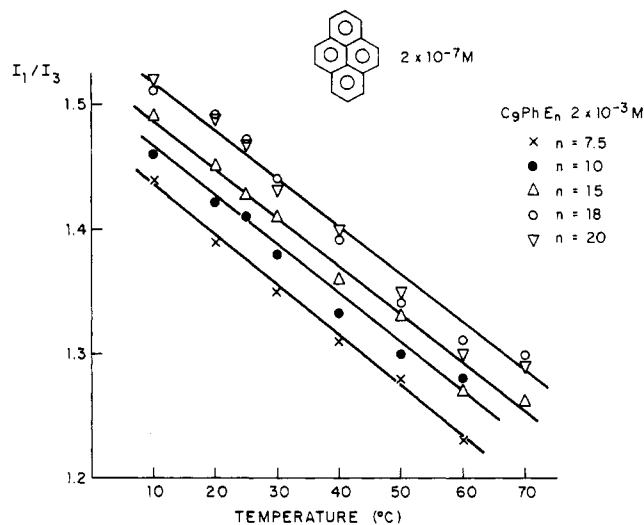

Figure 3. Temperature effects on I_1/I_3 in C_9PhE_n: n = 7.5 (X), 10 (●) 15 (▲), 18 (○), and 20 (▽).

micelles. The increasing polarity seen by P with increasing EO number may be attributed to a loosening of the EO chains and increasing hydration which accompanies the larger EO chain.[6] The values of λ_F^{In} are significantly different (ca. 330 nm) from that of SDS (360 nm) for the systems studied and correspond to a highly hydrophobic and relatively water-free environment for In.

In general, the conclusions to be reached are that the nonionic micelles formed from C_9PhE_n possess similar hydrophilic surfaces and hydrophobic cores but that the degree of hydration of the inner layer increases with increasing EO number.

Influence of Temperature on Time-Averaged Probe Position in Nonionic Micelles. Figures 2–4 show the response of λ_F^{PA}, I_1/I_3, in λ_F^{In}, respectively to variation in temperature for aqueous solutions of three C_9PhE_n detergents. Between 10 and 70 °C there is a significant change in λ_F^{PA} from ca. 451 nm to ca. 460 nm. For homogeneous solvents this change would correspond to an *increase* in polarity. However, the variation in λ_F^{PA} over this temperature range for homogeneous solvents is within experimental error (±1 nm). For the same temperature range I_1/I_3 decreases from ca. 1.49 to 1.20 (e.g., C_9PhE_{15}),

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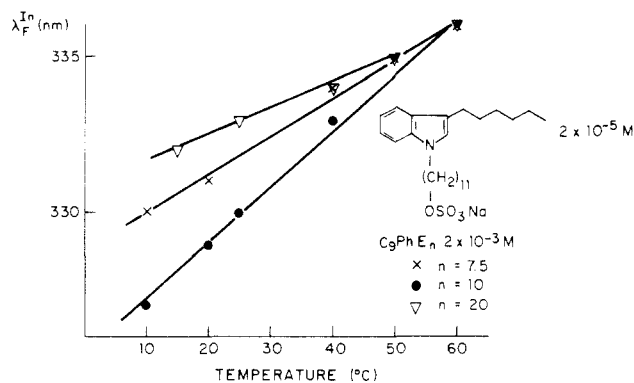
Figure 4. Temperature effects on λ_F^{In} in C_9PhE_n: n = 7.5 (X), 10 (●), and 20 (▽).

corresponding to a *decrease* in polarity experienced by P in a homogeneous environment. Finally, λ_F^{In} *increases* with increasing temperature, corresponding to an increase in polarity. As for λ_F^{PA}, neither I_1/I_3 nor λ_F^{In} undergoes significant variation in the temperature range 10–70 °C in homogeneous solvent. Thus, we attribute the observed variation in Figures 2–4 to changes in the probes location in the micelle. Although quantitative differences can be noted from among different members of the C_9PhE_n family, the trends are the same for each probe in micelles of each member: (1) The surface probed by PA becomes more polar with increasing temperature; (2) the inner layer probed by P becomes less polar with increasing temperature; (3) the inner core becomes more polar with increasing temperature.

If we interpret increased polarity as increased water in the time-averaged environment, then the PA and In probes "see" more water during their lifetimes, whereas P and In see less.

The aggregation number of micelles of nonionic surfactants tends to increase with increasing temperature, a result that has been related to the dehydration and tighter coiling of the poly(oxyethylene) chain.[7,8] The PA probe, being in the outer hydrophilic layer, evidently is "pushed out" further with increasing temperature into a more aqueous time-averaged environment. The P probe, being in the inner layer, evidently sees less water with increasing temperature because of the tighter coiling of the EO chains. The In probe, which resides in the inner core, sees a slightly more polar environment with increasing temperature, which could be due to thermal scrambling of the EO group into the core.

The cloud point (temperature at which turbidity appears) is an important characteristic of nonionic surfactants.[9] Above the cloud point, the resulting turbidity of a solution of C_9PhE_n surfactants is regarded as resulting from the decreased hydration of the poly(oxyethylene) chain. The question arises as to the existence and nature of nonionic micelles above the cloud point. It was found that I_1/I_3 decreases and the value of λ_F^{PA} increases above the cloud point (20 °C) of $C_9PhE_{7.5}$ in the same manner as it does for clear solutions for other members of the family. Furthermore, the value of λ_F^{In} for $C_9PhE_{7.5}$ above the cloud point is ca. 334 nm, quite different from the value for water. Several authors believe that the separation of surfactant-rich phase occurs above cloud point but have not presented evidence for the existence of micelles for that phase.[8] Our results provide evidence for the existence of micelles above the cloud point. Furthermore, on the basis of the above interpretation of the temperature effects, we conclude that the aggregation numbers of C_9PhE_n micelles continue to increase and that increased thermal scrambling of the EO groups into the inner core occurs for micelles above the cloud point.

Conclusions

The three fluorescence probes PA, P, and In appear to be viable probes of the surface, the inner layer, and the inner core of nonionic micelles. Measurement of the fluorescence parameters λ_F^{PA}, I_1/I_3, and λ_F^{In} as a function of surfactant structure and of temperature provide direct information on the time-average probe position in the micelle and indirect information on the micelle structure. Further investigations are required before the range of validity, the probe method for other nonionic micelles, can be evaluated, but it appears that the method provides a convenient qualitative guide to the properties of nonionic micelles containing various solubilized substrates.

As usual, when one is dealing with probes of micelles, one must consider the possibility that the native micelle structure has been perturbed. Our results are consistent with recent investigations of Triton systems which suggest that micelles of these detergents possess a relatively "dry" and nonpolar central core consisting of phenyl group and aliphatic chains and a relatively "wet" and polar outer sheath of partially hydrated ethylene oxide units.[10]

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