

seems to occur in most of the L₂ area, down to a 20/80 T/TX ratio. It is also evident that a rapid exchange between the confinements occurs, more rapidly at high water and low toluene content. This is in qualitative accord with the self-diffusion and conductivity data, although the water molecules move faster than the bulkier solutes. The numerical values estimated for various parameters have to be regarded with caution for several reasons: the exchange mechanism is unknown, there may be an important po-

lydispersity effect, and some irregularities were observed in the n/Q and k_2 values.

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Registry No. Triton X-100, 9002-93-1; toluene, 108-88-3; water, 7732-18-5.

Pyrene Excimer Formation in Micelles of Nonionic Detergents and of Water-Soluble Polymers

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Pyrene excimer formation has been investigated in two nonionic micellar systems, one composed of water-soluble copolymers of poly(ethylene oxide-propylene oxide) (E/P 0.8) and one composed of surfactants of the Triton type (alkylphenol ethoxylate). The ratio of excimer emission intensity to monomer emission intensity (I_e/I_m) is employed to investigate the variation of certain micellar properties as a function of surfactant structure, temperature, pressure, and added electrolyte. It is proposed that variations of I_e/I_m serve as a qualitative monitor of variation in micellar properties with experimental variables. Analysis of quenching of pyrene fluorescence by nitrite ion in Triton micelles shows it to be consistent with occupancy of pyrene in the hydrophilic ethylene oxide outer core and penetration of the nitrite ion into the core.

Introduction

Pyrene excimer formation is a well-known concentration-dependent phenomenon in organic solutions.¹ However, because of the low solubility of pyrene in water (ca. 10^{-7} M), pyrene excimer formation is not observed in pure water solution. Solubilization of pyrene by micelles formed from ionic surfactants allows observation of pyrene excimer formation in aqueous solutions under proper conditions.¹ This measurement of pyrene excimer emission as a function of surfactant concentration allows the determination of aggregation numbers of micelle formed from nonionic and ionic surfactants.² We report the results of investigations of pyrene excimer formation in aqueous solutions of nonionic surfactants of the Triton type and of water-soluble polymers of the ethylene oxide/propylene oxide types.

Experimental Section

Materials. Pyrene (P, Aldrich Chemical Co.) was purified by recrystallization (3×) from ethanol. The synthesis of 1,3-di-*n*-naphthylpropane (DNP) is described in the literature.³ Sodium dodecylsulfate (SDS, Biorad, Lab.), the polyethylene glycol *n*-nonylphenyl ethers (C₉PhEO_{*n*}, *n* = 5, 10, 15, 18, 20, respectively, Tokyo Kasei Co.), the poly(ethylene oxide-propylene oxide) block copolymer with an ethylene oxide/propylene oxide ratio of 0.8 (E/P 0.8, MW 2917, Polysciences), and sodium chloride (Alfa) were used as received. Sodium nitrite (Mallinckrodt, Chem. Works) was purified by recrystallization (2×) from water.

Fluorescence Measurements. Fluorescence spectra were acquired on either a Perkin-Elmer MPF-3L or a SLM 8000 spectrometer. Fluorescence lifetimes were acquired on a PRA single photon counting apparatus.⁴ Quenching parameters were determined by Stern-Volmer analysis of fluorescence lifetimes as a function of quencher concentration. All samples were deaerated by nitrogen purging. The ratio of pyrene excimer emission (I_e , ca. 470 nm) to pyrene monomer emission (I_m , ca. 375 nm) is defined as I_e/I_m . The emissions were obtained by excitation at 332 nm. The ratio of naphthyl excimer emission (I_e^N , ca. 397 nm) to naphthyl monomer emission (I_m^N , ca. 337 nm) is defined as I_e^N/I_m^N . The emissions were excited at 290 nm. The conversion of I_e^N/I_m^N into microviscosities, η , of colloidal aggregates follows a literature method.^{5a} The ratio of pyrene monomer fluorescence intensity at 373 nm (I_1) to that at 383 nm (I_3) is defined as I_1/I_3 (intensities of the first and third vibrational bands of pyrene monomer fluorescence) and follows a literature method, ref 5b, to estimate micropolarity ϵ_m of colloidal aggregates. A stainless steel high pressure cell (Union Giken Engineering Co.) was employed for the high pressure studies.⁶ The microviscosity, η , of colloidal aggregates under pressure was estimated by fluorescence polarization methods.^{7,8} The polarization of pyrene monomer was acquired on a SLM 8000 spectrophotometer employing a two polarizer system.

Results

Although pyrene excimer is not observed for saturated aqueous solutions of pyrene (ca. 10^{-7} M) in water, aqueous solutions containing pyrene (10^{-4} M) and micelles of sodium dodecyl sulfate (SDS), C₉PhE₁₀, or E/P (0.8) show

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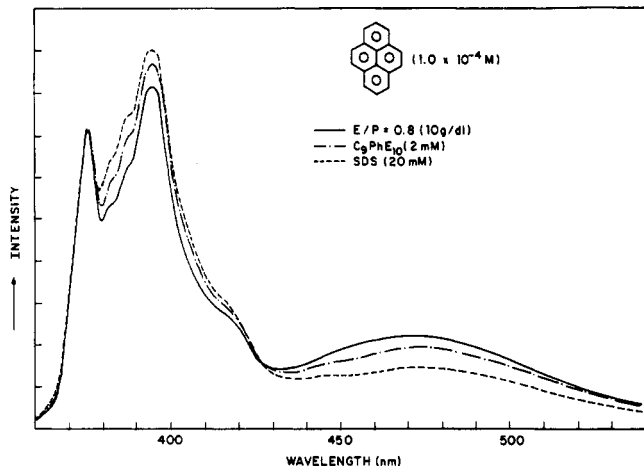


Figure 1. Excimer emission of P (1×10^{-4} M) in (—) E/P (0.8), (---) C_9PhE_{10} , and (- - -) SDS normalized at $\lambda = 373$ nm (excited at 332 nm).

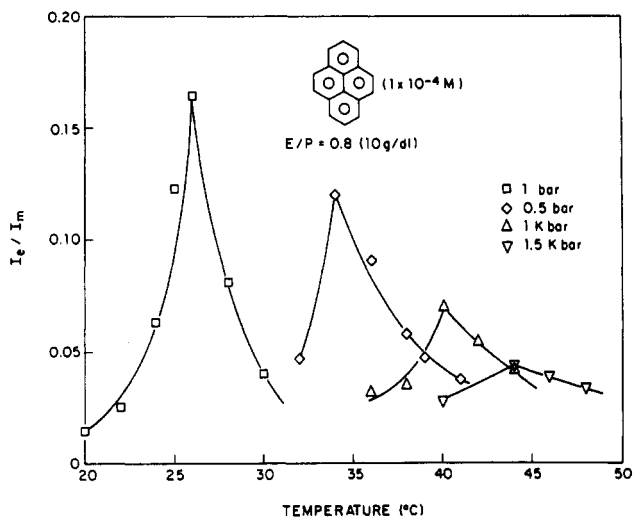


Figure 2. I_E/I_M of P in E/P (0.8) under various pressures: (□) 1 bar; (◇) 0.5 Kbar; (△) 1 Kbar; (▽) 1.5 Kbar.

significant amounts of excimer (Figure 1). The parameter I_e/I_m (ratio of intensities of excimer maximum emission to monomer maximum emission) characterizes the efficiency of excimer formation in the micellar aggregates. We have investigated the response of I_e/I_m to pressure, temperature, and added salt at fixed surfactant concentration. In the case of nonionic surfactants, C_9PhE_n , we have also studied I_e/I_m as a function of n .

The influence of pressure and temperature on the value of I_e/I_m for the E/P (0.8) systems is shown in Figure 2. At any of the selected pressures from 1 to 1500 bar, a maximum is observed as the temperature is increased. The maximum became less pronounced as the applied pressure is increased. The influence of added salt (NaCl) on the I_e/I_m for the E/P (0.8) system at 1 bar is shown in Figure 3. The maxima are shifted to lower temperatures as NaCl is added, but the maxima remain as pronounced in the presence as in the absence of salt. The effect of pressure and added NaCl thus have opposite effects on I_e/I_m for the E/P (0.8) systems. For example, as the pressure is increased from 1, to 500, to 1000, and to 1500 bar, the temperature at which maxima of I_e/I_m occurs shifts from 26, to 34, to 40, and to 44 °C, respectively. It was also observed that the total intensity of both monomer and excimer emission decreased significantly as pressure and temperature are increased. At any given pressure, the decrease in the excimer emission is less pronounced than the decrease in monomer emission. In the case of added

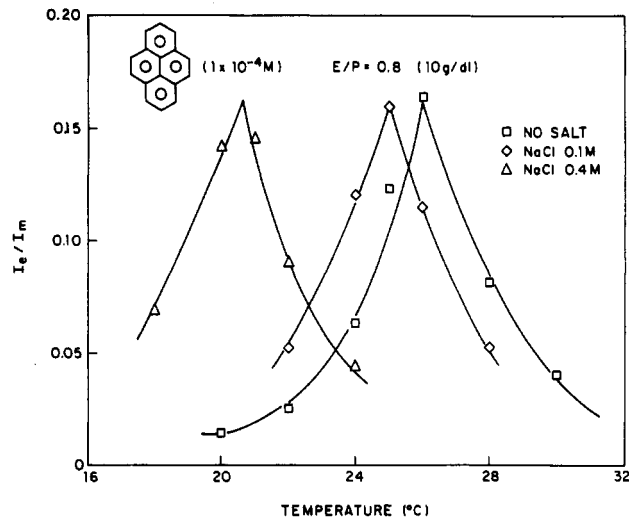


Figure 3. I_E/I_M of P in E/P (0.8) in the presence of NaCl: (□) no NaCl; (◇) 0.1 M NaCl; (△) 0.4 M NaCl.

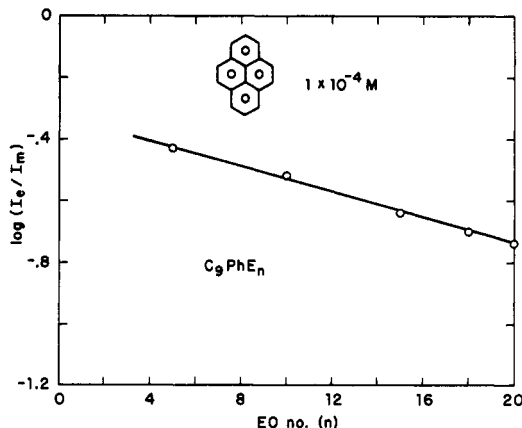


Figure 4. Relationship between I_E/I_M of P and n for C_9PhE_n .

NaCl, the maximum in I_e/I_m shifts from 26 to 25 to 21 °C in the presence of 0.1 M NaCl and 0.4 M NaCl, respectively.

The influence of surfactant structure on I_e/I_m was examined by investigating the variation of I_e/I_m as a function of n for the series C_9PhE_n ($n = 5, 10, 15, 18, 20$). The results are shown in Figure 4. The value of I_e/I_m is found to decrease as n is increased, at 1 bar and 25 °C. The surfactant C_9PhE_{10} was selected for a detailed examination of the effect of pressure and temperature on I_e/I_m (Figure 5). In contrast to the situation observed for E/P (0.8), at a fixed pressure I_e/I_m increases monotonically with increasing temperature. At a fixed temperature I_e/I_m decreases monotonically with increasing pressure. Addition of NaCl slightly increased the monomer emission and slightly decreased the excimer emission. For example, at 25 °C, the value of I_e/I_m decreased from 0.40 to 0.36 upon addition of NaCl.

The degree of polarization, p , of emitted fluorescence is given by eq 1, where I_{11} and I_1 are the intensity of

$$p = \frac{I_{11} - I_1}{I_{11} + I_1} \quad (1)$$

emission parallel and perpendicular to the incident beam, respectively. The microviscosity^{7,8} η of a fluorescence probe may be estimated from measured values of p by use of eq 2, where p_0 is the limiting value of p (in a medium of

$$\frac{1/p - 1/3}{1/p_0 - 1/3} = 1 + \frac{kT\tau}{\eta V} \quad (2)$$

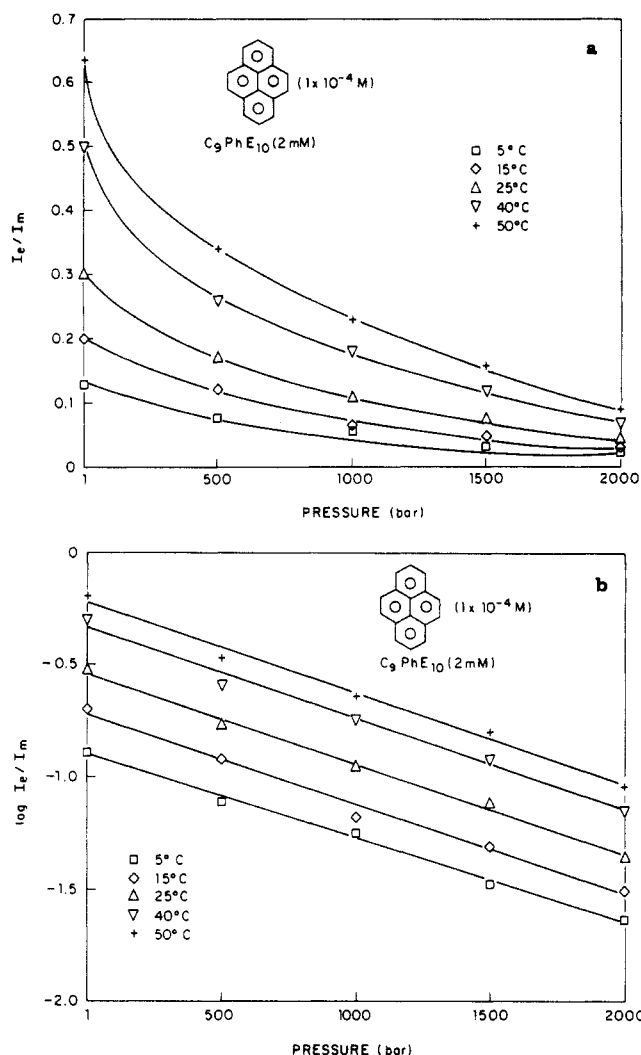


Figure 5. I_E/I_M of P under various pressures: (\square) 5 °C; (\diamond) 15 °C; (Δ) 25 °C; (∇) 40 °C; (+) 50 °C. (a) Plotted in usual scale; (b) plotted in semilog scale.

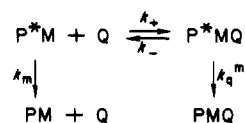
"infinite" viscosity), V is an effective volume characterizing the size of the probe, τ is the measured fluorescence lifetime of the probe, η is the average microviscosity experienced by the probe during its lifetime, T is the temperature, and k is the Boltzmann constant. Inspection of eq 2 reveals that if V and τ are constant, then η increases with increasing p , i.e., the greater the value of p , the greater the value of η at constant T . For pyrene as a fluorescence probe in both E/P (0.8) and in C_9PhE_{10} , p is found to increase with either increasing temperature or decreasing pressure; i.e., $p = 2.0$ and 7.4 for E/P (0.8) and 1.9 and 4.8 for C_9PhE_{10} at 5 and 50 °C, respectively; $p = 2.5$ and 1.0 for E/P (0.8) and 2.0 and 1.5 for C_9PhE_{10} at 1 and 2000 bar pressure (25 °C), respectively.

The lifetimes of P excimer and monomer in the E/P (0.8) system are of the order of 150 and 220 ns, with the lifetimes slightly increasing when NaCl is added. The lifetimes of P excimer and monomer in the C_9PhEO_{10} and C_9PhEO_{20} systems are of the order of 150 and 200 ns and are unaffected by added NaCl.

Discussion

The formation of pyrene excimers in micellar aggregates depends on several factors: The occupancy number of pyrene molecules in a given micelle, the mobility (which is related to microviscosity) of an excited pyrene molecule in a micelle, and lifetimes of an excited pyrene molecule in a micelle. Excited pyrene molecules in singly occupied

Scheme I



micelles are incapable of forming excimers because the lifetime of P^* is much shorter than the time of exit of P^* from a micelle. For example, a typical exit time⁹ for P^* from detergents in ca. 10^{-3} s, where its fluorescence is ca. 10^{-7} s. These considerations require that excimer formation can only occur in multiply occupied micelles. In order to experimentally determine the dynamics of P^* exit and entrance into and out of nonionic micelles, quenching by the water-soluble species NO_2^- was investigated.

Since the solubility of pyrene in water (ca. 3×10^{-7} M) is much smaller than that in aqueous solutions of C_9PhE_n (>10 M), for the latter all pyrene is assumed to be solubilized in micellar aggregates of C_9PhE_n . The quenching of pyrene emission by $NaNO_2$ is thus assumed to occur by penetration of NO_2^- into the micelle aggregates. On the basis of these assumptions, Scheme I is used as the basis for analysis of the Stern-Volmer quenching data. In Scheme I, P^*M is micellized, excited pyrene M is a C_9PhE_n micelle, Q is $NaNO_2$, k_m and k_q^m are the decay constant and quenching constants in the micelle, and k_+ and k_- are the entrance and escape rate constants of the quencher, respectively.

The kinetic eq 3 and 4 follow from Scheme I. Equation

$$-\frac{d[P^*M]}{dt} = (k_m + k_+[Q])[P^*M] - k_-[P^*MQ] \quad (3)$$

$$-\frac{d[P^*MQ]}{dt} = (k_q^m + k_-)[P^*MQ] - k_+[P^*M][Q] \quad (4)$$

5 follows from the steady-state assumption for $[P^*MQ]$.

$$[P^*MQ] = \frac{k_+[P^*M][Q]}{k_q^m + k_-} \quad (5)$$

Equation 6 follows from substitution of eq 6 into eq 3.

$$-\frac{d[P^*M]}{dt} = (k_m + k_+[Q])[P^*M] - \frac{k_-k_-[P^*M][Q]}{k_q^m + k_-} \quad (6)$$

The experimental, observed rate constant, k_{obsd} , and observed lifetime, τ_{obsd} , are given by eq 7 in terms of the

$$k_{obsd} = \tau_{obsd}^{-1} = k_m + \frac{(k_+ + k_q^m)[Q]}{k_-k_q^m} \quad (7)$$

defined rate constants of Scheme I and the quencher concentration. The formal quenching rate constant, k_q , is given by eq 8 in terms of the defined rate constants of Scheme I.

$$k_q = \frac{k_+ + k_q^m}{k_-k_q^m} \quad (8)$$

Equation 7 predicts a linear relationship between k_{obsd} and $[Q]$ whose slope is k_q and whose intercept is k_m . Figure 6 shows that the data can be fit to the linear relationship of eq 7 for the quenching of pyrene monomer fluorescence lifetimes in C_9PhE_{10} and C_9PhE_{20} (with a deviation of $\pm 5\%$ and $\pm 4\%$ in slope, respectively). Figure 7 shows similar data for the quenching of pyrene monomer fluorescence

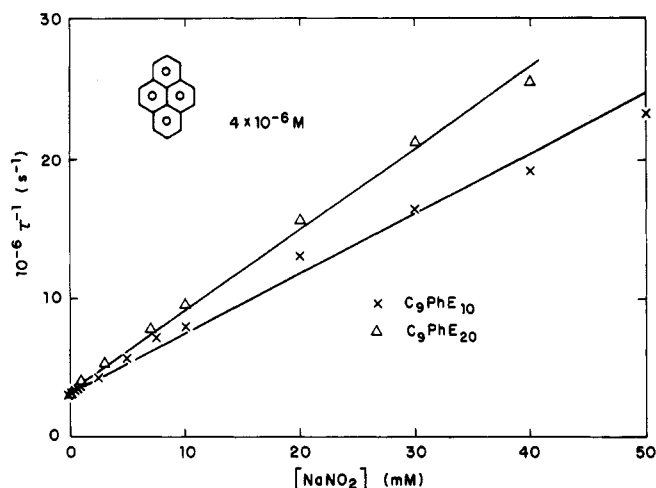


Figure 6. Linear relationship between $1/\tau$ and quencher concentration in the solution of C_9PhE_{10} and C_9PhE_{20} .

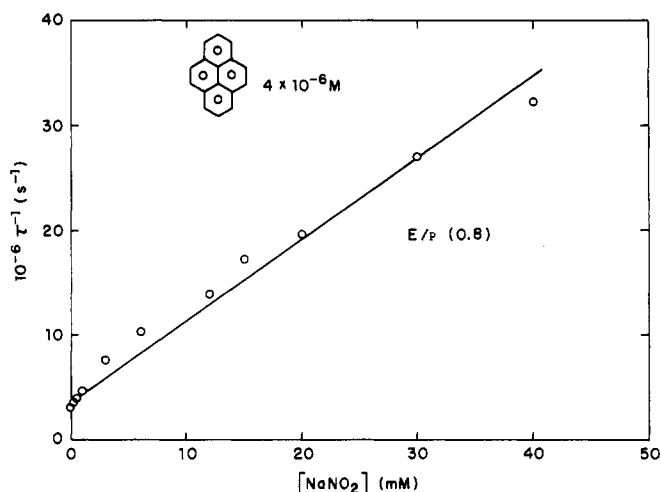


Figure 7. Linear relationship between $1/\tau$ and quencher concentration in the solution of E/P (0.8).

by nitrite in E/P = 0.8 micelles. These observations confirm the validity of the assumptions of Scheme I.

The I_1/I_3 value (1.5) reveals that the pyrene microenvironment in C_9PhE_{20} aggregates is slightly more polar than that (1.4) in C_9PhE_{10} aggregates. These values can be compared with I_1/I_3 values for water (1.9) and butanol (1.4). The value of k_q ($5.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) is higher than that ($4.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) for C_9PhE_{10} aggregates. Thus the more hydrophilic aggregate yields a k_q value closer to that found for quenching of pyrene fluorescence lifetimes in water ($k_q = 5.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). Both I_1/I_3 and k_q values are consistent with pyrene "seeing more water" (i.e., being in a more hydrophilic environment on a time average) in C_9PhE_{20} aggregates than in C_9PhE_{10} aggregates. The polarity of ethanol (ϵ 24.6) and methanol (ϵ 32.7) corresponds to I_1/I_3 values of 1.40 ± 0.02 and 1.29 ± 0.02 , respectively. Thus, the difference in I_1/I_3 values between C_9PhE_{10} (1.41 ± 0.02) and C_9PhE_{20} (1.47 ± 0.02) is significant. Also the difference in τ of pyrene at high quencher concentration for the C_9PhE_{10} and C_9PhE_{20} systems under comparable conditions is sufficient to distinguish these two systems. As a result, the k_q values obtained are experimentally differentiable. The differences in I_1/I_3 values and in k_q values for the same systems are much smaller than those for, say, C_9PhE_{10} and SDS or between C_9PhE_{10} and H_2O .

If a micelle is doubly occupied, an excited pyrene must diffuse in the micelle and contact a ground-state pyrene to form an excimer. The *P lifetime and its diffusional characteristics in the micelle thus determine the efficiency

of excimer formation in a doubly occupied micelle. Of course, the probability of excimer formation increases as the number of pyrene molecules in a micelle increases. Since other studies⁶ have shown that micellar microviscosity is significantly (factor of 3 or so) affected by temperature, pressure, or salt for the systems studied, we conclude that the major factors influencing I_e/I_m are the microviscosity and the occupancy number of pyrene molecules in a micelle. We now seek an empirical quantitative relationship between the value of I_e/I_m and aggregation numbers.

The probability of finding x pyrene molecule in a micelle is given by the Poisson expression¹⁰ (eq 9):

$$P(x) = \frac{S^x}{x!} [\exp(-S)] \quad (9)$$

where S is the ratio of [pyrene] to [micelles]. $P(x)$ is clearly a function of [micelles] as shown in eq 10. As N increases, for fixed [pyrene], S increases.

$$[\text{micelles}] \approx [\text{surfactant}]/N \quad (10)$$

Physically, as the micelle aggregation number increases, the number of micelles decreases, so that a fixed [pyrene] the probability of finding multiply occupied micelles increases.

At the concentrations of ca. 10% E/P (0.8) employed, this surfactant forms micelles composed of E/P polymolecules.¹¹ The hydrophilic ethylene oxide units serve as the outer core and the propylene oxide units serve as the inner core of these micelles. From our quenching experiments and other reports,¹² pyrene molecules have been shown to mainly occupy the outer core of ethylene oxide chains. As temperature is decreased^{13,14} or as pressure is increased,¹⁵ the hydration of the outer core is enhanced. As a result, it is expected and generally found that the aggregation number, N , decreases as temperature is decreased¹⁶ or as the pressure is increased.¹⁵ Since a decrease in N will lead to an increase in [mic] at fixed surfactant concentration, it is expected that I_e/I_m will decrease with decreasing temperature or increasing pressure. Since a maximum is observed in the profile of I_e/I_m with temperature (at fixed pressure), more than one factor must be operating. It would appear that in the lower temperature portion of each profile the value of N decreases as T decreases, thereby causing I_e/I_m to decrease.

In order to investigate the influence of temperature on the microviscosity and on the values of I_e/I_m we employed an intramolecular excimer probe 1,3-di- α -naphthylpropane (DNP).⁵ We find that increasing temperature causes an increase in the microviscosity for E/P (0.8). DNP reports an increase in the microviscosity of E/P (0.8) micelles from ca. 46 cP at 10 °C to ca. 87 cP at 30 °C at 1 bar. In the higher temperature branch of Figure 2 (at a given pressure), this effect of increasing microviscosity will cause the rate of excimer formation to decrease, thereby decreasing I_e/I_m . The competing influence of increasing N and in-

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creasing microviscosity rationalizes the maxima observed in Figure 2.

For the C_9PhE_{10} system, the value of I_e/I_m increases with increasing temperature. This result is consistent with a decrease in [mic] with increasing temperature. Indeed, since the aggregation number of C_9PhE_n series increases with increasing temperature,¹⁶ the [mic] is expected to decrease with increasing temperature. The solubility of nonpolar molecules in nonionic micelles generally increases with temperature.¹⁷ Since the concentration of P in the aqueous phase is very small (ca. 10^{-7} M), compared to the bulk P concentration (ca. 10^{-4} M), shifts in the equilibrium concentration of micelle-solubilized P with temperature will not be significant in influencing I_e/I_m .

The increasing temperature causes an increase in the microviscosity surrounding pyrene in C_9PhE_{10} according to our polarization data. This result is confirmed by an independent measurement of the microviscosity of C_9PhE_{10} micelles by the DNP method (ca. 48 cP at 25 °C, and ca. 69 cP at 50 °C). The increase in microviscosity with increasing temperature is probably related to a smaller water-polymer interaction causing the aggregates to "tighten up" their structure. The results (Figure 5), however, show that the I_e/I_m increases as temperature increases. This suggests that the increased microviscosity is overcome by the concurrent factor of decreased [mic] upon increasing temperature. Similarly, increasing pressure decreases the microviscosity surrounding pyrene in C_9PhE_{10} and also decreases I_e/I_m . This suggests that the effect of the increased [mic] upon increasing pressure¹⁵ dominates the opposing factor of microviscosity.

The value of I_e/I_m in the C_9PhE_n series decreases with increasing size of the EO chain. At 25 °C and 1 bar, there is a linear relationship between $\log(I_e/I_m)$ and n (EO no.) (Figure 4) and given in eq 11.

$$\log(I_e/I_m) = A - Bn \quad (11)$$

The value of I_e/I_m for C_9PhE_{10} was found to decrease with increasing pressure, at constant temperature, and to follow eq 12 (Figure 5b). The constants in eq 12 are A'

$$\log(I_e/I_m) = A' - B'P \quad (12)$$

$= -0.52$ and $B' = 0.00042$. Meanwhile, the constants in eq 11 are $A = -0.33$, and $B = 0.021$. From eq 11 and 12 the following derivative quantities (eq 13 and 14) are obtained.

$$\left[\frac{\partial \log(I_e/I_m)}{\partial n} \right]_P = 0.021 \quad (13)$$

$$\left[\frac{\partial \log(I_e/I_m)}{\partial P} \right]_n = 0.0042 \quad (14)$$

The effect on $\log(I_e/I_m)$ of increasing the polyoxyethylene chain by 1 EO unit is equivalent to an increase in pressure of 50 bar. The change in n mainly changes the aggregation number of C_9PhE_n , but the change in P not only influences the aggregation number but also affects

the microviscosity of micelles.

The influence of added salt on I_e/I_m for the C_9PhE_{10} and C_9PhE_{20} systems is small. Since nonionic surfactants are not electrolytes, addition of salt does not significantly alter the aggregation numbers or [mic]. This result is consistent with that found for PyS (sodium pyrene-3-sulfonate), for which the corresponding value (I_e'/I_m') increases with added salt.¹⁸ The latter result was interpreted to result from "salting out" of the PyS from the aqueous phase to the micellar phase. Pyrene is insignificantly soluble in water so that the "salting out" mechanism cannot cause significant transfer of P from the aqueous phase.

Summary

Pyrene has been employed as a useful fluorescence probe for ionic micelles. Our studies demonstrate that the intensity ratio I_e/I_m for pyrene is a useful probe of aggregation number and microviscosity of nonionic micelles. At fixed concentrations of pyrene and surfactant, an increase in aggregation number causes an increase in I_e/I_m because the number of micelles decreases as the aggregation number increases. An increase in microviscosity has the reverse effect on I_e/I_m . The microviscosity of nonionic micelles could be estimated independently by employing DNP as a fluorescence probe.

The I_e/I_m ratio was found to exhibit a maximum for E/P (0.8) as the temperature is increased. The temperature at which this maximum was found to occur is a function of pressure and added electrolytes. The maximum is interpreted to result from competing factors of increasing aggregation number (which tends to increase I_e/I_m) and increasing viscosity (which tends to decrease I_e/I_m). Increasing pressure decreases I_e/I_m and increasing temperature increases I_e/I_m , while increasing temperature increases I_e/I_m for nonionic surfactants. These results are interpreted in terms of decreasing aggregation number with increasing pressure but increasing aggregation number with increasing temperature. The quenching of pyrene fluorescence by $NaNO_2$ in C_9PhE_{10} micelles or in E/P (0.8) micelles shows a linear relationship between $1/\tau$ and $[NaNO_2]$, indicating that pyrene moves rapidly about the micelle during its lifetime and becomes time averaged with respect to its micellar position before quenching occurs. It is concluded that the pyrene exists in the palisade layer of the nonionic micelles.

A linear relationship exists between $\log(I_e/I_m)$ and occupancy number, n (eq 11). In addition, a linear relationship exists between $\log(I_e/I_m)$ and pressures (eq 12). These two linear relationships are combined to correlate the effect of pressure and n on I_e/I_m .

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Registry No. P, 129-00-0; DNP, 14564-86-4; SDS, 151-21-3; NO_2^- , 14797-65-0; poly(ethylene oxide-propylene oxide), 9003-11-6; polyethylene glycol *n*-nonylphenyl ether, 9016-45-9.

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(18) Turro, N. J.; Kuo, P. L., manuscript in preparation.