Exit and Reentry Kinetics of Bromoacetonaphthone in Aqueous Polystyrene–Poly(ethylene oxide) Block Copolymer Micelles[1]

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ABSTRACT: Phosphorescene quenching kinetics were studied for 4-bromo-1-acetonaphthone (BAN) in water in the presence of a series of polystyrene–poly(ethylene oxide) block copolymer micelles. The quencher, $NaNO_2$, remains in the aqueous phase. We determine the exit and entry rate constants for BAN and the micelles: the former rate constant is independent of the micelle size whereas the latter increases linearly with the micelle core radius. These experiments demonstrate that BAN binds only to the surface region of the micelle where it is protected from quenching. Under our experimental conditions, we can establish that whenever BAN*[3] exits from a micelle, it essentially always reenters the same micelle.

Luminescent probe experiments have proved very powerful in the study of low molecular weight surfactant micelles.[3-5] Much of our knowledge of these systems derives from nearly two decades of fluorescence and phosphorescence studies of these systems. By contrast, there have been until recently few studies of block copolymer micelles employing fluorescence techniques[6-9] and none using phosphorescent probes. Block copolymer micelles are in many ways more interesting to study than normal surfactant micelles because one can vary the block lengths in a systematic way and examine the consequences on micelle structure and dynamics.

In this paper we describe phosphorescence quenching experiments on 4-bromo-1-acetonaphthone (BAN) in water in the presence of block copolymer micelles.[10] The micelles are self-assembled spherical structures composed of polystyrene–poly(ethylene oxide) (PS–PEO) diblock or PEO–PS–PEO triblock copolymers. They possess a core of an essentially pure PS phase surrounded by a water-swollen corona of PEO chains.[11] One anticipates that the properties of the corona resemble those of typical nonionic PEO-based surfactants. The major differences derive from the composition of the core. The core is much larger for block copolymer micelles, leading to larger aggregation numbers, and is almost certainly less fluid.

We examine seven block copolymer samples, four triblocks and three diblocks. The micelles themselves have been fully characterized by a combination of static and dynamic light scattering experiments.[11] In each case, spherical micelles are formed with a very narrow size distribution. Critical micelle concentrations (cmc) for these samples are very small, on the order of 1–4 mg/L, as determined by pyrene fluorescence probe experiments.[8] The various characteristics of the polymers and their micelles are presented in Table I.

Our phosphorescence quenching experiments with BAN follow the protocol of the classic paper by Almgren, Grieser, and Thomas[5] (AGT), who examined the phosphorescence of 1-bromonaphthalene (BN) and other aromatic molecules in the presence of sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) micelles. Our objective is to compare the behavior of phosphorescent dyes in the larger and nonionic block copolymer micelles with that described by AGT for normal ionic surfactants.

Table I
Block Copolymer and Micelle Properties

sample	M_n[a]	wt % PEO	cmc[b] (mg/L)	R_H[c] (nm)	$\langle n \rangle$[c]
		Diblock			
JLM5	8 500	80	2.8	9	64
R41	23 500	84	4.0	19	120
R23	28 700	61	<1.0	22	290
		Triblock			
R51	20 000	91	2.0	9	67
R19	13 100	68	1.0	12	130
JLM6	18 000	80	2.5	13	120
JLM11	25 900	81	2.5	18	150

[a] M_n(PS) from gel-permeation chromatography; PEO content from ^{1}H NMR. See ref 11. [b] See ref 8. [c] R_H from dynamic light scattering (DLS); $\langle n \rangle$ from DLS in combination with static light scattering. See ref 11.

Kinetic Analysis

In its simplest conception, a micellar solution represents a two-state system in which an electronically excited dye can be located in either the aqueous or micellar phases. If the lifetime τ of the dye exceeds its residence time within the micelle, then the emission of the dye will be sensitive to its partitioning dynamics. The most useful experiments are those in which one adds to the solution a quencher Q located exclusively in the aqueous phase and monitors the changes in τ which result. These processes are summarized in Scheme I.

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Scheme I

$$MP^* \underset{k_+}{\overset{k_-}{\rightleftharpoons}} M + P^* \quad (1)$$

$$P^* \xrightarrow{k_w} h\nu + P \quad (2)$$

$$P^* + Q \xrightarrow{k_q} [Q] \quad (3)$$

$$MP^* \xrightarrow{k_m} h\nu + MP \quad (4)$$

MP refers to the micelle-bound phosphorescent molecule, which is denoted P when it is free in aqueous solution. The corresponding triplet excited-state species are denoted MP* and P*, respectively. The (diffusion-controlled) entry rate is described by the second-order rate constant k_+. The exit rate coefficient is k_-, and the triplet decay rates in water and in the micellar phase are described by the first-order rate constants k_w and k_m, respectively. We assume that P and MP absorb light with the same probability at the excitation wavelength.

From an analysis of Scheme I one obtains two coupled differential equations:

$$-d[P^*]/dt = k_+[P^*][M] + k_w[P^*] + k_q[Q][P^*] - k_-[MP^*] \quad (5)$$

$$-d[MP^*]/dt = k_-[MP^*] + k_m[MP^*] - k_+[M][P^*] \quad (6)$$

The complete solution to eq 5 and 6 gives expressions for [P*] and [MP*] in terms of sums and differences of exponentials. Since P* and MP* emit at the same wavelength and the emission from MP* is much more intense than that from P*, there are not sufficient data to evaluate the kinetics without further assumptions.

In the AGT experiments,[5] all measured decays were exponential. These signals were due to micelle-bound chromophore. Under their conditions, the competing emission from P* was too short-lived and too weak to be detected. To proceed, they assumed steady-state conditions for P*. The implicit argument behind this assumption is that directly excited P* makes a negligible contribution to the measured signal. What one observes are the consequences on [MP*] due to the *exit* and *reentry* processes, eq 1. Thus they arrive at the expression

$$k_{obs} = \frac{1}{\tau_{obs}} = k_- + k_m = \frac{k_-k_+[M]}{k_q[Q] + k_w + k_+[M]} \quad (7)$$

Experimental Section

BAN was prepared by reaction of 1-bromonaphthalene with acetyl chloride in the presence of $AlCl_3$ and purified by repeated recrystallization from hexanes, mp 47–48 °C (lit.[12] mp 47–47.5 °C). Micelle solutions were prepared by dissolving known amounts of the block copolymer, with or without probe, in glass-distilled tetrahydrofuran (THF), adding it to a round-bottom flask, and evaporating completely the THF. Deionized distilled water (Milli-Q grade) was added, and the mixture was heated at 60 °C for 20 min and allowed to cool slowly overnight. Typical BAN concentrations were 1×10^{-5} M and that of the polymer was 0.1 g/L.

The block copolymers were prepared by anionic polymerization in THF as described previously.[13] Table I lists composition and molecular weight characteristics of the polymers as well as the micellar properties for these polymers in water.

Steady-state emission spectra were measured with a Fluorolog 112 spectrometer equipped with a DM 3000 data system. For some samples, spectra were obtained with a pulsed lamp and gated detection. Emission decay profiles were obtained as described previously,[14] with samples excited at 355 nm with ca. 15-ns pulses of a Spectra Physics DCR-3 Nd:YAG laser. All samples, in square Pyrex cells, were purged by bubbling with Ar gas for 20 min prior to the measurement. The optimum degassing conditions were determined by a series of experiments in which BAN*[3] emission intensity was monitored as a function of purge time.

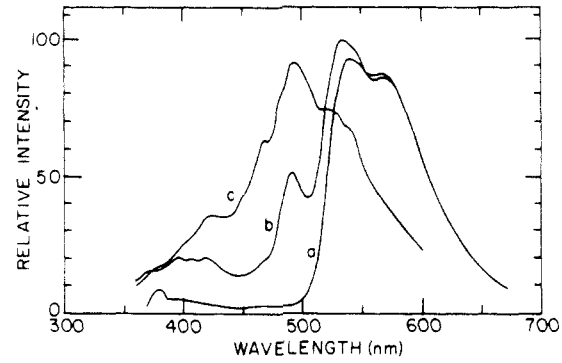

Figure 1. Luminescence spectra of BAN (1×10^{-5} M) in deoxygenated media: (a) in water; (b) in water in the presence of PS–PEO block copolymer; (c) in a film of semicrystalline PEO. Note that the emission spectrum of BAN in a PS film strongly resembles curve a.

Results and Discussion

Spectroscopy. The limiting solubility of BAN in water is 1.1×10^{-4} M at 22 °C. In the UV, it has a broad peak (λ_{max} = 308, ϵ_{max} = 7380 M^{-1} cm^{-1}) extending out to 360 nm. In organic solvents, it shows a typical naphthalene phosphorescence with characteristic maxima at 540 and 570 nm. In water these peaks broaden and become less distinct. Emission spectra are shown in Figure 1 for aqueous and micellar media. In each case there is a weak prompt fluroescence at 400–450 nm accompanying the phosphorescence. This fluorescence has been reported previously[15] but has never been properly attributed. Another feature of BAN*[3] spectroscopy which we are still unable to explain is the blue shift of the phosphorescence in the presence of block copolymer. We tentatively assign this shift to BAN in a PEO-rich environment, since BAN in films of pure PEO has a phosphorescence centered at 480 nm. We have been unable to discern a difference in phosphorescence lifetime over the wavelength range of 480–600 nm.

In deoxygenated water, BAN phosphorescence decays exponentially with a lifetime (τ_w) of 400 μs. In the presence of block copolymers the phosphorescence decay curves of BAN show two resolvable exponential components. The shorter component corresponds to the decay time of BAN*[3] in water, and we attribute the longer decay time τ_m to the micellar species.

$$I_p(t) = A_w \exp(-t/\tau_w) + A_m \exp(-t/\tau_m) \quad (8)$$

One anticipates the prefactors to be sensitive to the fraction of BAN incorporated into the micelles. We find for example, with a BAN concentration of 1.0×10^{-5} M, that A_m/A_w is approximately 1:10 with a micelle concentration (sample TB19) of 5.9×10^{-8} M. Increasing the micelle concentration by a factor of 5 increases A_m/A_w to 1:2.

In our system, where BAN is present at 1.0×10^{-5} M and the concentration of block copolymer micelles is 5.9×10^{-8} M, the ratio of BAN molecules to micelles is 170. This is very different from the situation for low molecular weight surfactants studied by luminescence techniques. There, the number of micelles is commonly larger than the number of probe molecules, and most of the probes are solubilized in the micelles. Here, most of the BAN molecules are in the water phase. We can estimate the fraction of the BAN in the micellar phase as $A_m/(A_w$

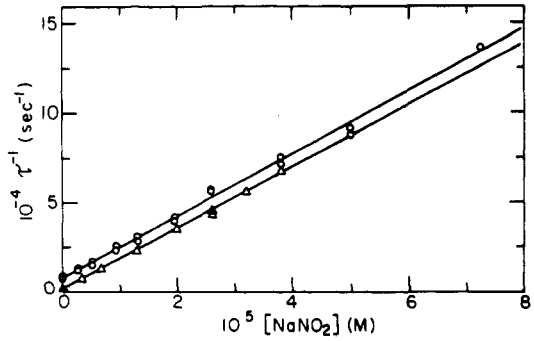

Figure 2. Stern–Volmer plot of $NaNO_2$ quenching BAN phosphorescence: (Δ) plot of $1/\tau$ vs $[NO_2^-]$ for BAN in water; (O) plot of $1/\tau_w$ vs $[NO_2^-]$ for BAN + block copolymer (R41) in water.

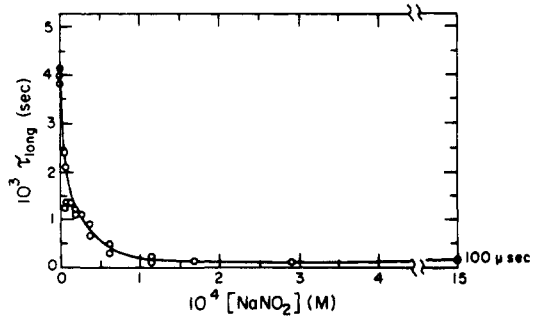

Figure 3. Plot of τ_{long} vs $[NaNO_2]$ for BAN in water in the presence of PS–PEO block copolymer (R41) micelles.

$+ A_m) = 9.0 \times 10^{-2}$. Under these conditions there are, on average, just under two BAN molecules in each block copolymer micelle. Concentration quenching effects are not observed. Even with substantial changes in micelle or BAN concentrations, no significant lifetime variations are observed.

We can estimate the equilibrium constant for binding, K_{eq}, from the A_w and A_m values in eq 8.

$$K_{eq} = \frac{[MP]}{[P][M]} = \frac{A_m}{A_w[M]} \tag{9}$$

and obtain a value of $1.7 \times 10^5\ M^{-1}$.

Quenching Experiments. BAN phosphorescence in water is quenched by NO_2^-. A plot of the data according to the expression

$$\frac{1}{\tau} = \frac{1}{\tau_w} + k_q[Q] \tag{10}$$

is linear (Figure 2) and yields a k_q value of $1.7 \times 10^9\ M^{-1}\ s^{-1}$. This compares with a value obtained by AGT[5] of $5.1 \times 10^9\ M^{-1}\ s^{-1}$ for the quenching of BN*[3] by NO_2^- in water.

Adding small concentrations of $NaNO_2$ to aqueous solutions containing block copolymer plus BAN causes significant quenching of the short-time component of the BAN*[3] decay, with relatively little effect on the long-lived component. One sees in Figure 2 that essentially identical plots are obtained for $1/\tau$ (BAN in water) and $1/\tau_{short}$ (BAN + block copolymer in water) vs $NaNO_2$ concentration. This result confirms that the short component in the BAN*[3] decay in the presence of micelles is due to BAN in water at the moment of sample excitation.

The lifetime of the longer component does in fact decrease as the $NaNO_2$ concentration is raised. The dependence of τ_{long} on $[NaNO_2]$ is shown in Figure 3. Once this concentration exceeds 1×10^{-4} M, the $I_p(t)$ profile can be fit to a single exponential, with a decay time of 100 μs that is invariant with additional quencher concentration.

The behavior observed for τ_{long} in Figure 3 is exactly that predicted by eq 7. Setting $\tau_{long}^{-1} = k_m + k_-$ yields a value of $9.1 \times 10^3\ s^{-1}$ for k_-. For bromonaphthalene, AGT found k_- values of $3.3 \times 10^4\ s^{-1}$ for SDS micelles and $4.1 \times 10^3\ s^{-1}$ for CTAB micelles.

Table II
Experimental Data Related to Entry and Exit Rates

sample	R_H (nm)	R_c[a] (nm)	10^8[micelle][b]	$10^{-5}k_+$[M][c]	$10^{-12}k_+$	$10^{-3}k_-$[c]
JLM5	9	3.4	18	2.6	1.4	9.4
R51	9	3.6	7.3	2.2	3.1	7.7
R19	12	5.9	5.9	2.8	4.9	9.4
JLM6	13	5.5	4.5	2.5	5.5	7.1
R41	19	5.5	3.5	2.4	6.8	6.7
JLM11	18	6.5	2.5	2.2	8.4	5.0
R23	22	10.7	1.2	2.8	23.8	8.3

[a] Radius of the PS core, calculated from $\langle n \rangle$ and composition assuming a dense-packed PS core of density 1.04. [b] The micelle concentration for each experiment, calculated from $\langle n \rangle$. [c] Estimated error in k_- is ± 10% and in k_+[M] is ±20%.

In the case of surfactant micelles, k_- values depend primarily on the solubilities of the dye in water and in the micelle.[5] The core of a block copolymer micelle is much larger than a surfactant micelle. One could easily imagine a situation where diffusion of the dye to the surface of the micelle was rate limiting. This would occur, for example, if the lumophore were distributed throughout the core of a large micelle and the core could be described as a viscous liquid-like phase. Under these circumstances, k_- would be a function of the micellar radius.

This situation is exactly analogous to the kinetics of quenching of a lumophore diffusing within a spherical liquid droplet, where quenching occurs when the excited species reaches the surface of the droplet. For this situation, recently examined by Duhamel et al.,[16] the general solution to the emission decay profile following δ-pulse excitation is given by the expression

$$I(t) = I(0)\left(\frac{6}{\pi^2}\right)\exp(-t/\tau_m)\sum_{n=1}\frac{1}{n^2}\exp(-n^2\pi^2 D_m t/R_c^2) \tag{11}$$

where D_m is the diffusion coefficient of the lumophore in the droplet of radius R_c. An initially fast decay will become exponential at times such that $(\pi^2 D_m t/R_c^2) \geq 1$

$$\tau_{long}^{-1} = k_m + \frac{\pi^2 D_m}{R_c^2} \tag{12}$$

The spherical diffusion model predicts that the decay of MP* will be exponential at long times for concentrations of NO_2^- sufficient to quench P* completely, that τ_{long} will be independent of $[NO_2^-]$, and that τ_{long}^{-1} should be proportional to R_c^{-2}.

In fact, we obtain k_- values which are essentially independent of micelle size and independent of whether the micelle is formed from a diblock or triblock copolymer. We do obtain sample-to-sample variation of k_- values (Table II) which, with one exception, vary from 7×10^3 to $9 \times 10^3\ s^{-1}$. These show no pattern with changes in core radius. From these results we draw the interesting conclusion that the BAN moclecules must reside near the core surface so that diffusion through the core is not necessary for micellar exit. Note that if some BAN molecules were buried in the core and could not exit, they would contribute an unquenchable long-lived component to the phosphorescence decay. This is never observed.

Micelle Reentry. According to the Smoluchowski model of diffusion-controlled reactions,[17] we expect a value for k_+ which can be calculated from the expression

$$k_{diff} = 4\pi N_A' D_w R_c \tag{13}$$

where N_A' is Avogadro's number per millimole. D_w, the diffusion coefficient of BAN in water, is estimated to be

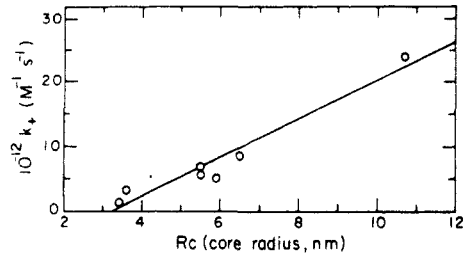

Figure 4. Plot of k_+ vs R_c, the radii of the PS cores of the block copolymer micelles.

5×10^{-6} cm^2 s^{-1}, and in this approximation we let the capture radius equal that of the core of the micelle, ca. 50 Å. This yields a value of $k_{diff} = 1.9 \times 10^{10}$ M^{-1} s^{-1} and a value of k_{diff}[M] $= 1.14 \times 10^3$ s^{-1}. In other words, the characteristic entry time for BAN molecules located in the aqueous phase at the moment of sample excitation is ca. 870 μs.

The value 870 μs is longer than τ_w and much longer than τ_{short} for BAN*[3] in the presence of micromolar $NaNO_2$. From this exercise we learn that BAN excited in the aqueous phase makes almost no contribution to τ_{long}. At higher micelle concentrations, the fraction of BAN in the aqueous phase is diminished. While the mean entry time for these BAN molecules would decrease, their contribution to the $I_p(t)$ signal would become undetectably small. Our experimental situation strongly resembles that of AGT,[5] and we are justified in treating the two decay terms in eq 8 as due to two independent populations of BAN.

Equation 7 can be rearranged to give

$$k_+[M] = \frac{(k_w + k_q[Q])(k_- + k_m - k_{obs})}{k_{obs} - k_m} \qquad (14)$$

Since each of the terms on the right-hand side of eq 14 is known, we can use the $\tau_{long} = k_{obs}^{-1}$ data to calculate k_+[M] for each sample. These values are presented in Table II. These values are constant for all samples, 2.5×10^5 s^{-1}. These values are 250 times larger than that prediced above for k_{diff}[M] using eq 13 to calculate k_{diff}. If one unthinkingly equated k_+ with k_{diff} and used these values to calculate k_{diff}, one would find values for this second-order rate constant on the order of $(2\text{–}20) \times 10^{12}$ M^{-1} s^{-1}! These are the appropriate values of k_+, but as we explain below, k_+ and k_{diff} have different meanings.

The important point to be drawn from these data is that these experiments measure the rate of reentry of a BAN*[3] molecule into the *same micelle it occupied when it was initially excited.* Most of our experiments were carried out at a block copolymer concentration of 0.1 g/L. The molar concentration of micelles varies with the molecular weight of the polymer and the aggregation number of the micelle (cf. Table II). For TB19 at [M] = 6×10^{-8} M, the micelles are on average 3000 Å apart. The residence time of a BAN*[3] molecule in the aqueous phase after it exits a micelle is too short for it to have a significant chance to encounter a second micelle.

It is significant that the k_+ values in Table II increase with increasing micelle size. As shown in Figure 4, k_+ is proportional to R_c. This is the behavior expected for a diffusion-controlled capture process, eq 13. If we plot k_+ vs k_{diff} calculated from eq 11 for each of the various micelles, we obtain a straight line with a slope of 250. This indicates that a BAN*[3] molecule newly emerged into solution experiences a "local effective micelle concentration" some 250 times larger than the bulk micelle concentration.

Summary

Phosphorescence quenching experiments on aqueous solutions of 4-bromo-1-acetonaphthone (BAN) in the presence of block copolymer micelles provide quantitative information on the exit and reentry rates of the chromophore out of and into the micelle. Two particularly interesting results are obtained. The first, from the independence of the exit rate on micelle size, one learns that BAN must be located exclusively near the surface of the micelle core. The second, from the reentry kinetics, establishes that under our experimental conditions, BAN*[3] molecules always reenter the *same micelle* which they had departed to enter the aqueous phase.

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References and Notes

(1) Paper no. 6 on the study of block copolymer micelles.

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