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Aggregation of Poly(ethylene oxide)–Poly(propylene oxide)–Poly(ethylene oxide) Triblock Copolymers in the Presence of Sodium Dodecyl Sulfate in Aqueous Solution

Mats Almgren,* Jan van Stam, Cecilia Lindblad,

Department of Physical Chemistry, Uppsala University, Box 532, S-751 21 Uppsala, Sweden

Puyong Li, Peter Stilbs,

Department of Physical Chemistry, The Royal Institute of Technology, S-100 44 Stockholm, Sweden

and Pratap Bahadur

Department of Chemistry, South Gujarat University, Surat 395007, India (Received: June 18, 1990)

NMR chemical shift measurements and fluorescence quenching have been combined in a study of the aggregation behavior and the aggregate properties of two poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (EPE) triblock copolymers in the presence of sodium dodecyl sulfate, at 20 and 40 °C. The block copolymers differed in the ethylene oxide blocks, one (L64) containing a total of 26 EO units on the two blocks and the other (F68) 156 units; both had 30 PO units in the hydrophobic middle block. Neither of the EPEs form micelles by themselves at the low temperature but form mixed micelles with SDS, even at SDS concentrations as low as 1 mM. The aggregation numbers obtained from fluorescence quenching studies indicate that about 3 SDS molecules per EPE are needed to "glue" together the PO blocks into a hydrophobic core at the low temperature. The micelles formed at low SDS concentrations are small, with aggregation numbers down to 15 for SDS, associated with 4–5 EPEs. At high SDS concentrations the micelles approach pure SDS micelles. L64 forms micelles at 40 °C. These are large but decrease rapidly in size with the addition of SDS. The ^{13}C chemical shift for the methyl carbons in the PPO block are progressively shifted more upfield in the transformation from the large L64 micelles to the small mixed ones; the shift in neat PPO is even more upfield and is close to the shift for the methyl groups in the PPO block of F68 unimers in aqueous solution. The shifts are probably indicative of a change from an extended conformation in the large micelles to much more coiled conformations in the small and unimer micelles as well as in the neat PPO liquid. The shifts of the methylene carbons in the PEO blocks go downfield on addition of SDS to both of the EPEs in aqueous solution, much in the same way as when SDS is added to PEO solutions. The change of the shifts of the individual carbons in the alkyl chain of SDS on addition of the EPEs to SDS micelles follows a similar pattern for both EPEs. Except for the strong upfield shift for the C1 carbon, which is also obtained when PEO interacts with SDS, they are all in the downfield direction and much stronger than the change given by only PEO. An interesting periodicity is observed with particularly small shifts for carbons 4, 7, and 10, 11.

Introduction

Water-soluble triblock copolymers of the poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) type (EPE, poloxamers) are well-known as commercial preparations, e.g., under the trade names as Pluronics or Synperonics, and have found important applications in various fields. They are available in a broad variety of types, with different average overall size and different average lengths of the hydrophobic middle block, PPO, and the hydrophilic end blocks, PEO. The water solutions of these substances present a number of interesting properties: they aggregate into micelles and have cloud point phenomena similar to solutions of conventional nonionic surfactants;[1-3] some of them display a peculiar gelling behavior, both at temperatures somewhat below the cloud point and at normal temperatures and high concentrations; others present a rheological behavior similar to that of polymer solutions.[4,5]

Poly(ethylene oxide) itself is completely miscible with water at normal temperatures but has a solubility gap with the lower critical solution temperature above 100 °C. Karlström et al.[6] have recently presented a model that explains many of the properties of PEO in solution. It is based on an analysis of the energies of different conformers of the PEO chain and their interaction with a polar solvent. Out of 25 sterically possible conformers of the CH_2–CH_2–O– segment, 2 have the preferred arrangement with trans conformation around the C–O bonds and gauche around the C–C bond. These structures are polar with a large dipole moment and would interact favorably with polar solvents like water, whereas the rest of the conformers are less polar, with small or no dipole moments. At low temperatures the polar conformations dominate, and water is a good solvent for the polymer. With increasing temperature more EO groups take on nonpolar conformations, and the polymer–polymer interactions get gradually more favorable than the polymer–water interactions, leading eventually to phase separation and a solubility gap at the cloud point. The conformation equilibrium for the PO units of the PPO polymer has not been analyzed in the corresponding way, but a similar situation should be at hand. In this case it is known that only short chains are water-soluble, i.e., have the lower consolute temperature above the freezing point, and that for long chains the solubility gap spans most of the composition space.[7] At a polymerization degree of 7 the cloud point is just above 40 °C, and less than 20% water is contained in the polymer-rich phase that separates out. The cloud point is decreased to –7 °C at a polymerization degree of 20.[8,9]

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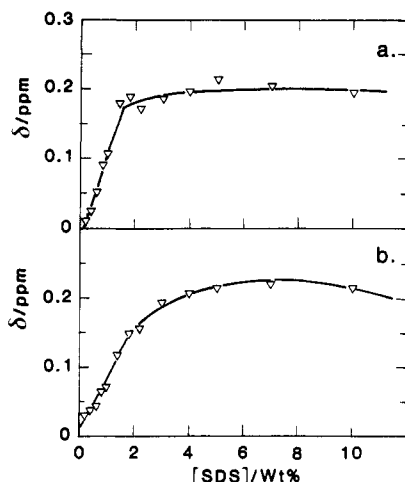(7) Kjellander, R.; Florin, E. *J. Chem. Soc., Faraday Trans 1* **1981,** *77,* 2053.

Figure 1. ^{13}C chemical shifts (in ppm) of the methylene carbons in the PEO blocks relative to the pure 1 wt % EPEs in water, for mixtures of SDS and F68 (a) and L64 (b).

The cloud point of EPEs varies with the size and the fractions of PEO and PPO and is displaced further below that of PEO with increasing size of the PPO block. The EPEs studied in this contribution, L64 (molecular weight 2900, composed of 30 PO and 26 EO units) and F68 (molecular weight 8600, 30 PO and 156 EO units), have the same average length of the PPO block, which by itself would have been insoluble in water. In L64 with the short PEO blocks, the hydrophobicity of the PPO parts is large enough to promote micelle formation at 40 °C in a 1% solution, but not at 20 °C, whereas the long PEO blocks of F68 prohibit micelle formation at low concentrations and temperatures below 50 °C. On interaction with a charged surfactant like SDS the cloud point of both nonionic micelle-forming surfactants and pluronics is known to increase, which is readily understood from electrostatic effects: association of the surfactant with the nonionic polymer or micelle introduces repulsive charges which counteract the attractive forces responsible for the clouding. The micelle formation is also affected. In PEO, SDS starts to form small micellar aggregates at a concentration well below the normal cmc. The polymer interacts with the micelle interface where some of its segments replace water molecules in contact with the core, whereas others form loops. Mixed micelles are formed by SDS and many nonionic surfactants; these micelles resist better than pure nonionic ones growth into large aggregates at high temperatures and concentrations.[10]

For this study of the interaction of SDS with EPEs, we have chosen one substance, L64, that behaves mainly as a nonionic surfactant in aqueous solutions, and one, F68, where the long PEO segments dominate its behavior at ordinary temperatures. ^{13}C NMR chemical shifts were determined for both the PEO methylenes and the PPO methyls and for the carbons in the alkyl chain of the surfactant. These data inform of the conformations in the mantle and in the micelle core. The aggregation numbers were obtained by time-resolved fluorescence quenching studies.

Experimental Section

All *NMR chemical shift* measurements at 40.0 °C were performed on a Bruker AM 400 spectrometer. The shift measurements at different temperatures were performed on a Varian XL-300 spectrometer. Complete proton decoupling was achieved by using WALTZ decoupling to avoid heating the sample. No susceptibility corrections were deemed necessary since the solutions were dilute (about 1% in water), so sample and reference solutions were quite similar. The observed shift effects (up to 1 ppm) are much larger than any possible susceptibility artifacts. Solutions were made by dilution of a stock solution in 5-mm-o.d. NMR
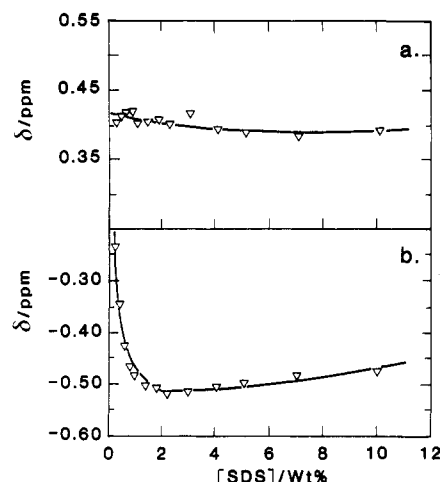
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Figure 2. ^{13}C chemical shifts (in ppm) of the methyl carbon in the PPO block relative to the pure 1.0 wt % EPE in water for mixtures of SDS with F68 (a) and L64 (b). A shift difference of 0.88 ppm was obtained between the PPO methyl carbons of L64 (which is in micellar form) and F68 (as unimer) in 1% aqueous solution.
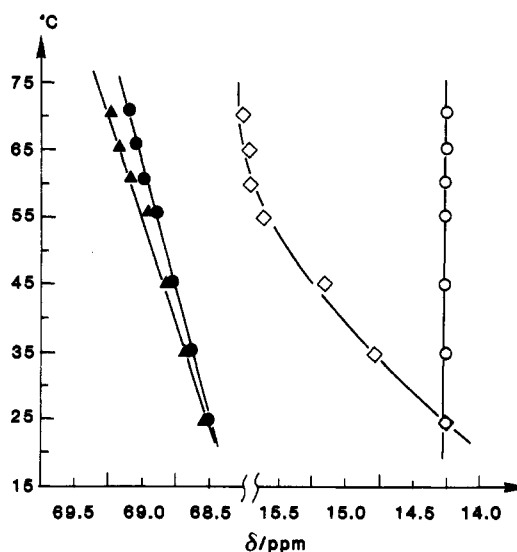

Figure 3. ^{13}C chemical shifts (in ppm) as a function of temperature for (O) methyl carbons in net PPO, ($\Diamond$) methyl carbons of the PPO block of L64 in water, ($\bullet$) methylene carbons in the PEO polymer in water, and ($\blacklozenge$) methylene carbons in the PEO blocks of L64 in water.

tubes. D$_2$O was used as solvent to provide a lock signal. Tetramethylsilane was used as external reference.

Fluorescence decay data were collected with the time-correlated single-photon counting technique, using an apparatus described earlier.[11] The setup uses a mode-locked Nd:YAG laser (Spectra Physics Model 3800) to synchronously pump a cavity-dumped dye laser (Spectra Physics, Models 375 and 344S) for the excitation at 323 nm, using the dye DCM, and frequency doubling in a KDP crystal. The pyrene monomer emission was measured at 393 nm and the excimer emission at 530 nm.

Materials. The Synperonics L64 and F68 from Serva, Germany, sodium dodecyl sulfate from BDH, special grade, and dimethylbenzophenone from Aldrich were all used as supplied. Pyrene (Aldrich) was recrystallized twice from ethanol.

Results and Discussion

^{13}C *Chemical shifts* were determined at 40 °C for the methylene carbons in the PEO segments (Figure 1) and for the methyl carbons of the PPO segments (Figure 2) in 1 wt % solutions of the EPEs with varying SDS concentrations. The temperature dependence of the chemical shifts of the PPO and PEO carbons

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Figure 4. ^{13}C chemical shifts (in ppm) of carbons C2–C12 in the dodecyl chain of SDS relative to pure 2 wt % SDS in water, for mixtures of 2 wt % SDS with L64.

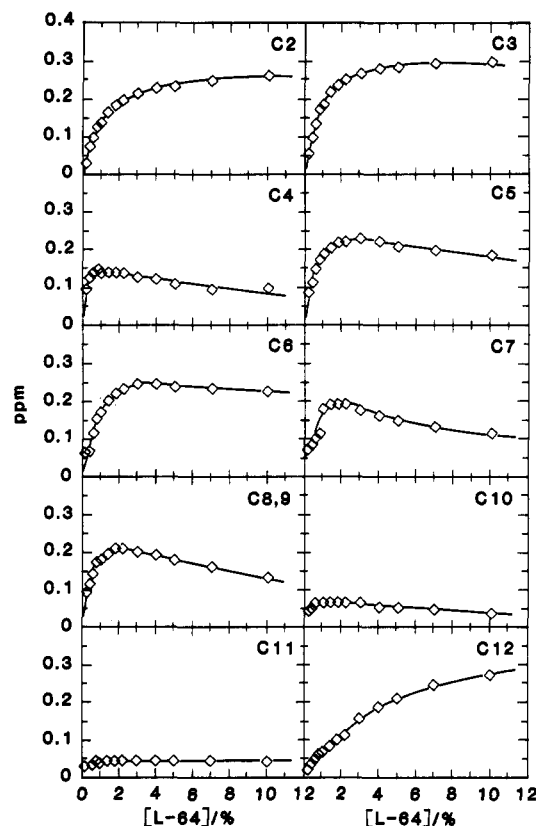
Figure 5. ^{13}C chemical shifts (in ppm) of carbons C2–C12 in the dodecyl chain of SDS relative to pure 2 wt % SDS in water, for mixtures of 2 wt % SDS with F68.

Figure 6. ^{13}C chemical shifts (in ppm) of carbon C1 in SDS relative to pure 2 wt % SDS in water, for mixtures of 2 wt % SDS with F68 (a) and L64 (b).

is reported in Figure 3. The change of the shifts for each of the individual carbons in the alkyl chain of micellar SDS on addition of EPE is reported in Figures 4–6.

The ^{13}C chemical shifts of the carbons in alkyl chains have been shown to depend mainly on the trans/gauche conformation ratio[12-14] and less on the environment. It has been argued[15] that also in ethylene oxide segments the trans/gauche ratio of the C–C bond is most important. The energy difference between the C–O trans/gauche conformations is much larger (about 12 kJ/mol) than that of the C–C isomers (about 2 kJ/mol with the gauche conformation at lowest energy in polar solvents).[6a] Solvent effects are likely to influence the shifts not only by changing the trans/gauche ratio but also directly; the direct effect was considered less important, however, at least in interactions with water.[15] Figure 3 shows the methylene carbon shifts in aqueous solutions of PEO and L64 to be very similar and change downfield in the same way with temperature. The downfield shift would thus be indicative of an increase in the high-temperature C–C trans conformer population. The shifts go downfield on addition of SDS as well (at concentrations where micelles are formed) for both L64 and F68 (Figure 1) and also for PEO according to the results of Cabane.[16] In the interaction with SDS micelles, the high-temperature, nonpolar conformers of the PEO chain seems to favored.

The effect of SDS levels off at high concentrations. In PEO this occurs at a concentration where the chains are saturated with SDS (in the form of polymer-bound micelles somewhat smaller than free micelles[17,18]) and formation of free SDS micelles com-
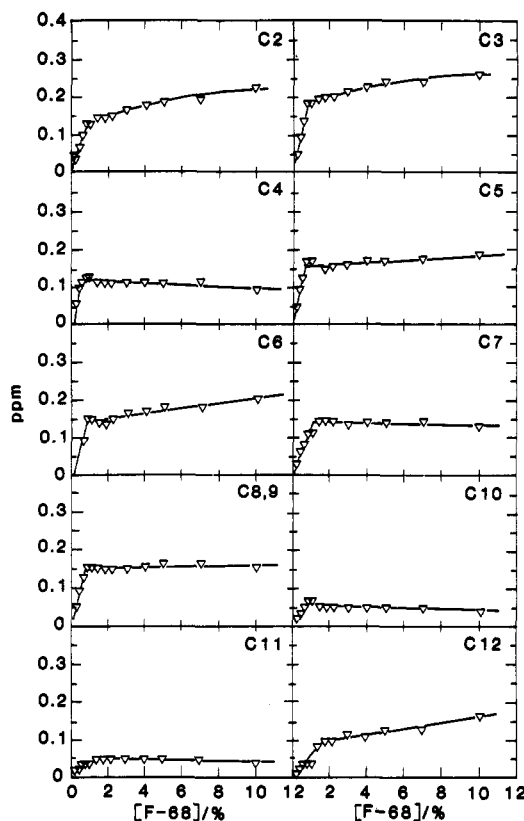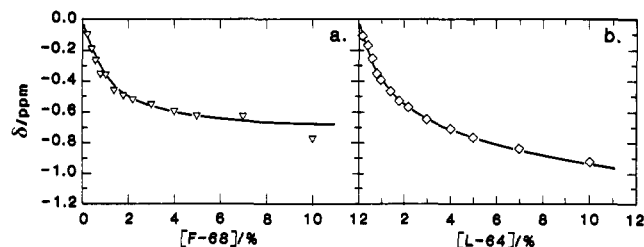
mences. In the EPE solutions the saturation sets in when there are about 60 surfactants for each polymer molecule, indicating that SDS micelles containing on average one EPE molecule are present. The shifts at saturation were 0.28 ppm downfield for PEO and somewhat less, 0.20 ppm for the EPEs. The number of EO groups interacting with the micelle interface is much smaller in L64, 0.4 EO/SDS, than in F68, 2.6, or 2.4 in the case of PEO (based on an aggregation number of 60 for the micelles). The similar saturation level in these rather different situations suggests that the effect is not due to a direct interaction between ethylene oxide segments and the SDS headgroups, but rather to a stabilization of the nonpolar conformations of the segments by interaction with the exposed parts of the micellar core. The composition of the core is the same in mixed micelles containing one F68 or one L64, comprising in both cases 30 PO groups and some 60 dodecyl chains. The micelles formed in PEO solutions have pure hydrocarbon cores and give a somewhat larger shift at saturation.

The PEO chains at the micelle interface can then be envisioned to replace water molecules and interact in nonpolar sequences with the hydrocarbon core at exposed patches between the headgroups. Remaining loops may contain dipolar segments and interact with water, headgroups, and counterions.

The methylene carbon shift observed for the PEO blocks in aqueous solutions without SDS is very similar for L64, F68, and

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PEO. Also the change with temperature is the same. The shift is evidently not affected by the micelle formation which occurs in L64 from about 30 °C. It appears therefore that the nonpolar conformations of the PEO segments are not stabilized by a PPO core in the same way as by a hydrocarbon core.

^{13}C *shifts of the PPO methyl groups* are presented in Figure 2. It is important to notice that the quantity shown is the change of the shift from its value in aqueous solutions of F68 and L64 at 40 °C, where L64 is in micellar form and F68 in unimer form. The shift difference between these states was about 0.88 ppm. On addition of as little as 0.2% (6.9 mM) SDS, the ^{13}C shift of the PPO methyls of F68 goes downfield by 0.40 ppm and stays almost constant on further increase of the surfactant concentration. For L64 the methyl carbons in the core of the micelles are shifted downfield by 0.88 ppm compared to those of the F68 unimers in water, and from Figure 3, by about the same amount, or 0.75 ppm, from neat PPO in the same direction. Addition of SDS gives a rapid upfield shift to a maximum of 0.5 ppm at 2% SDS. At 10% SDS the shifts for F68 and L64 are the same, as expected, since now the PPO blocks are in both cases solubilized by almost normal SDS micelles.

The reason for the shift changes when PPO interacts with the surfactant micelles is not clear. Medium effects cannot be very important since neat PPO and the PPO block of F68 unimers in water show similar shifts. At 25 °C aqueous L64 and neat PPO give similar shifts; at this temperature and concentration L64 is also present mainly as unimers or small oligomers, which would be expected to be in good contact with water. The strong downfield shift for PPO in pure L64 micelles as compared to the shifts in neat PPO, in L64 micelles, and in L64/SDS mixed micelles seems to reflect a difference in packing and chain conformation and probably indicates the presence of large extended structures in the L64 micelles.

^{13}C *Chemical Shifts of the SDS Dodecyl Chain Carbons.* The dependence of the shifts on the EPE concentration (Figures 4–6) follows a similar pattern for all carbons in both cases: there is an initial phase with a rapid change of the shift and a final phase with constant shifts, or with a slow change, for some carbons in a direction opposite to the initial one. At the lowest additions, less than one EPE molecule is present per micelle—assuming an aggregation number of 60 as in pure SDS solutions, this ratio is obtained with 0.3% L-64 or 0.8% F-68 in a 2 wt % SDS solution. At lower EPE concentrations there must be micelles both with and without EPE, but since the exchange times of the SDS molecules[19]—and perhaps also of the EPEs—for the micelle–water–micelle processes are short on the NMR time scale, only the average environment should be important. The break point at low additions of the EPEs probably indicates a change of size and packing of the micelles.

The shifts from the pure SDS micelles observed at the different carbons are similar with both EPEs but, with the exception for C1 (Figure 6), differ considerably from those found on addition of PEO.[16] The strong upfield shift for C1 amounts to almost 0.5 ppm after an addition of 1% of either of the EPEs or PEO and increases further, at a slower rate, when more is added. This shift is most probably an polarization effect, due to the replacement of water molecules by EO segments at the micelle interface.[16] For the other carbons the shifts are all in the downfield direction and much larger than those observed by Cabane[16] on addition of PEO—this polymer is not expected to enter the micelle core. Most remarkable in the pattern displayed in Figure 7 is a periodicity of three: the shifts are low at carbons 4, 7, and 10. This is apparent for both EPEs but not at all in the corresponding plots for addition of alcohols to zwitterionic surfactant micelles.[20] The pattern is evident already at 2% EPE and becomes more marked at higher concentrations. The origin of this effect is probably to be found in the influence from the poly(propylene oxide) chain with its repeat unit of three atoms and can be due to either a
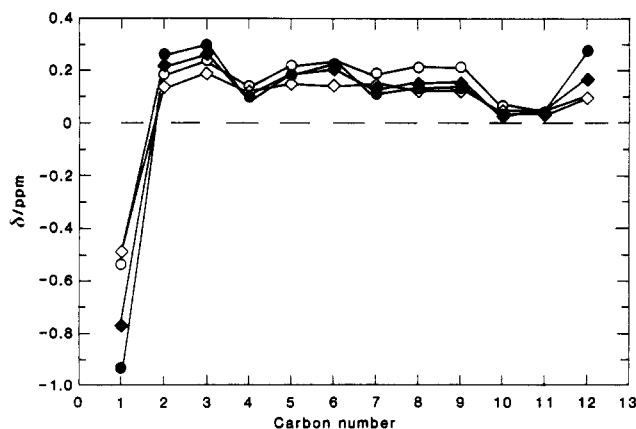

Figure 7. ^{13}C chemical shifts (in ppm) of carbons C1–C12 in the dodecyl chain of SDS relative to pure 2 wt % SDS in water, for mixtures of 2 wt % SDS with L64 and F68: (○) 1.8% L64, (◇) 10% L64, (●) 1.8% F68, (◆) 10% F68. The carbons are numbered from the polar end.
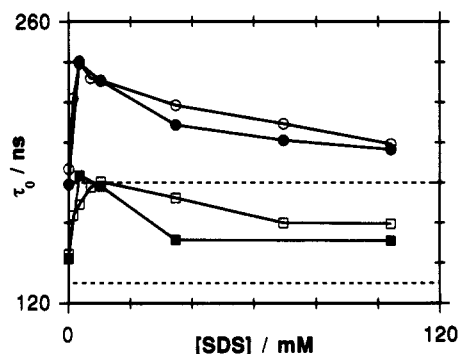

Figure 8. Fluorescence lifetime of pyrene in mixed micelles of EPE and SDS: filled symbols, F68; open, L 64; circles, 20 °C; squares, 40 °C. The dashed lines represent the lifetimes in pure SDS micelles at the two temperatures.

polarization effect exerted by the oxygen atom in the PO unit or conformational effects from steric interaction between the methyl group of the PO unit and the alkyl chain of SDS.

Carbon C12 shows an unexpectedly large downfield shift. Similar downfield shifts were reported for the ending methyl carbon in a zwitterionic surfactant micelle upon the inclusion of long-chain alcohols.[20] Downfield shifts were observed when the alcohol chain was longer than that of the surfactant and upfield when it was shorter. It was also found that in mixed micelles of tetradecyl- and hexadecyltrimethylammonium bromide the terminal methyls had different chemical shifts. This was explained in terms of an increased chain folding, i.e., increased gauche population, in the longer chain.[20] In the present case it seems plausible that the downfield shift of the terminal carbon is due simply to the fact that the SDS chain is shorter than the PPO block.

Fluorescence Spectra and Lifetime of Pyrene. The fluorescence lifetime of pyrene varies with SDS concentration in solutions of L64 and F68 as shown in Figure 8. In solutions without SDS the lifetime is similar to that obtained in SDS micelles at the same temperature. Small additions of SDS increase the lifetime in all cases up to a maximum between 4 and 10 mM SDS; at higher concentrations the lifetimes return slowly toward the values for pure SDS micelles. These measurements refer to aerated solutions. Addition of PEO to SDS micelles increases the fluorescence lifetime in aerated, but not in deoxygenated, solutions to similar values as obtained by addition of SDS to the EPEs.[18] The ethylene oxide mantle of the mixed micelles evidently shields the pyrene from oxygen quenching somewhat, whereas pyrene associated with EPE in the absence of SDS is exposed to about the same extent as it is in SDS micelles. The protection starts to build up already at very low additions of SDS.

The intensities of the vibronic peaks in the fluorescence spectrum are sensitive to the environment of pyrene; the ratio of the in-

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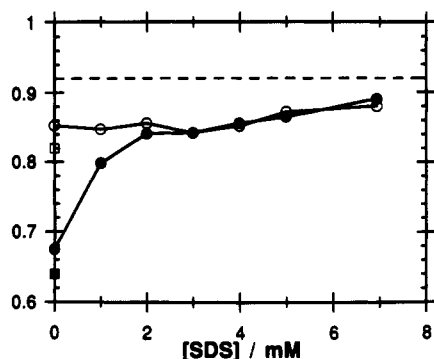
Figure 9. The III/I ratio for pyrene in L64 at low additions of SDS: open symbols, 40 °C; filled symbols, 20 °C. The squares represent F68, and the dashed line represents pure SDS micelles.

tensities of the third and first peaks is usually taken as an indication of the polarity of the environment[21] although interactions of other kinds may be equally important. Figure 9 shows that the III/I ratio in L64 at 40 °C is slightly less than in SDS micelles (a more polar environment with the conventional interpretation) and increases slowly toward the SDS value with increasing SDS concentration. At 20 °C, however, the initial value indicates a much more polar environment which rapidly changes with the SDS concentration to join the high-temperature values at [SDS] ≈ 2 mM and beyond. These observations agree with the notion that micelles of L64 are present already in water at the higher temperature and form rapidly on addition of SDS at the lower temperature. The III/I ratio is always lower in the micelles with PPO in the core than in the pure SDS micelles, whereas the III/I ratio increases when PEO is added to pure SDS micelles.[18]

Time-Resolved Fluorescence Quenching. Representative examples of decay curves are presented in Figure 10. Measurements were performed at 20 and 40 °C for both EPEs (1 wt %) at several concentrations of SDS and usually four quencher concentrations. Reliable determinations of the aggregation number require that the family of decay curves with different quencher concentrations should develop linear tails (in the logarithmic intensity scale) which are parallel to the decay without quencher. This condition was fulfilled for most of the samples with SDS, as exemplified in Figure 9, columns 2–4. Only the samples without SDS, and for L64 at 20 °C and also those with [SDS] below 1.5 mM, gave a systematically different behavior. The well-behaved decay curves were analyzed with simple Infelta model[22]

$$\ln \{F(t)/F(0)\} = -t/\tau_0 + n\{\exp(-k_q t) - 1\} \qquad (1)$$

where $F(t)$ is the fluorescence intensity at time t, τ_0 the natural lifetime, $n = [Q]/[\text{mic}]$ the mean number of quenchers per micelle (assumed randomly distributed among the micelles according to a Poisson distribution), and k_q the first-order quenching rate constant in a micelle with one quencher.

Deviations from this model, as occur at the lowest concentrations of SDS, may have many possible sources.[23] Migration of probes and quenchers is not expected to occur selectively at low SDS concentrations; polydispersity effects combined with the appearance of large micelles probably contribute, and simultaneous solubilization in different environments (diblock micelles, unimer and oligomer micelles, and SDS–EPE mixed micelles) is a complication that prevents an unambiguous interpretation. The results from the well-behaved curves will be discussed first.

The primary results from fittings to the simple model are values of n and k_q, which both give information about the size of the micelles. k_q is expected to decrease with increasing volume of the hydrophobic core and is often assumed to be inversely pro-

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TABLE I: Parameters Derived from Fluorescence Quenching Results for L64–SDS Micelles: Aggregation Numbers for Both Components, Polydispersity Index σ/⟨a⟩, First- and Second-Order Quenching Rate Constants, and Micellar Core Radius

[SDS], mM	τ, ns	⟨a⟩_w[a] SDS	⟨a⟩_w[a] F68	σ/⟨a⟩_w	k_q, 10^7 s⁻¹	k_2, 10^9 M⁻¹ s⁻¹	r,[b] nm
			20 °C				
0.5	199	16.2	112	0.47	3.7	7.3	
1.0	218	18.3	63.3	0.55	3.4	3.8	
1.5	222	18.7	42.9	0.63	3.6	2.8	
2.0	223	17.8	30.8	0.71	3.7	2.1	
2.4	226	19.1	26.4	0.74	3.9	1.9	
2.9	225	17.6	20.2	0.80	3.9	1.5	
3.4	232	17.0	16.7	0.83	4.0	1.3	
3.5	240	14.7	14.6	0.67	5.8	1.7	
3.9	230	17.0	14.6	0.88	4.1	1.2	
4.3	229	17.1	13.1	0.92	4.2	1.1	
7.1	232	14.7	7.2	0.77	5.3	0.8	
10.4	231	18.7	6.2	0.60	6.1	0.9	
34.6	219	34.0	3.4	0.60	4.3	0.6	1.7
104.1	199	62.3	2.1	0.30	3.2	0.5	1.9
			40 °C				
0.0	144		145.0[c]	0.30[c]			4.7
0.5	153	12.8	88.5	0.27	0.4	0.7	4.0
1.0	158	21.2	73.3	0.30	0.6	0.7	3.7
1.5	164	26.8	61.4	0.32	0.6	0.7	3.6
2.0	162	31.8	54.8	0.42	0.8	0.8	3.4
2.4	166	31.3	43.2	0.45	1.0	0.8	3.2
2.9	167	30.4	35.0	0.47	1.1	0.8	3.0
3.4	167	34.0	33.6	0.56	1.3	0.9	3.0
3.5	169	33.0	33.2	0.48	1.6	1.0	3.0
3.9	168	32.6	28.1	0.62	1.6	0.9	2.8
4.3	173	33.7	25.8	0.66	1.7	0.9	2.8
7.1	178	22.2	10.8	0.65	3.6	0.8	2.1
10.4	180	24.4	8.1	0.55	5.5	1.1	2.0
34.6	172	31.7	3.1	0.55	8.3	1.0	1.7
104.0	159	60.1	2.0	0.40	7.0	1.1	1.9

[a] Calculated under the assumption of complete micellization. [b] A value of the core radius is given only if the k_2 value is consistent with the assumption of complete micellization. See text. [c] Values obtained from fits to a two-exponential Infelta-type equation as described in text.

TABLE II: Parameters Derived from Fluorescence Quenching Results for F68-SDS Micelles: Aggregation Numbers for Both Components, Polydispersity Index σ/⟨a⟩, First- and Second-Order Quenching Rate Constants, and Micellar Core Radius

[SDS], mM	τ, ns	⟨a⟩_w[a] SDS	⟨a⟩_w[a] F68	σ/⟨a⟩_w	k_q, 10^7 s⁻¹	k_2, 10^9 M⁻¹ s⁻¹	r,[b] nm
			20 °C				
3.5	239.4	14.3	5.0	0.65	6.0	0.70	1.7
10.4	230.7	20.1	2.3	0.42	4.9	0.40	1.5
34.6	208.7	43.4	1.5	0.69	3.7	0.44	1.7
69.4	201.1	55.4	1.0	0.62	3.0	0.40	1.8
104.1	196.5	72.8	0.8	0.48	2.8	0.47	1.9
			40 °C				
3.5	183.5	15.6	5.4	0.76	7.5	0.95	1.7
10.4	178.1	18.5	2.1	0.65	9.1	0.70	1.5
34.6	151.4	36.1	1.3	0.78	7.7	0.74	1.6
69.4	157.1	55.7	1.0	0.78	6.8	0.92	1.8
104.0	150.9	62.3	0.7	0.49	6.2	0.89	1.8

[a] Calculated under the assumption of complete micellization. [b] A value of the core radius is given only if the k_2 value is consistent with the assumption of complete micellization. See text.

portional to it,[24] as if it were a quasi-first-order rate constant, given by the product of a second-order quenching constant k_2 and the concentration corresponding to one molecule in the core volume. Although this assumption is an oversimplification,[23] we have used it to test the consistency between the experimental k_q values and the sizes deduced from the n values.

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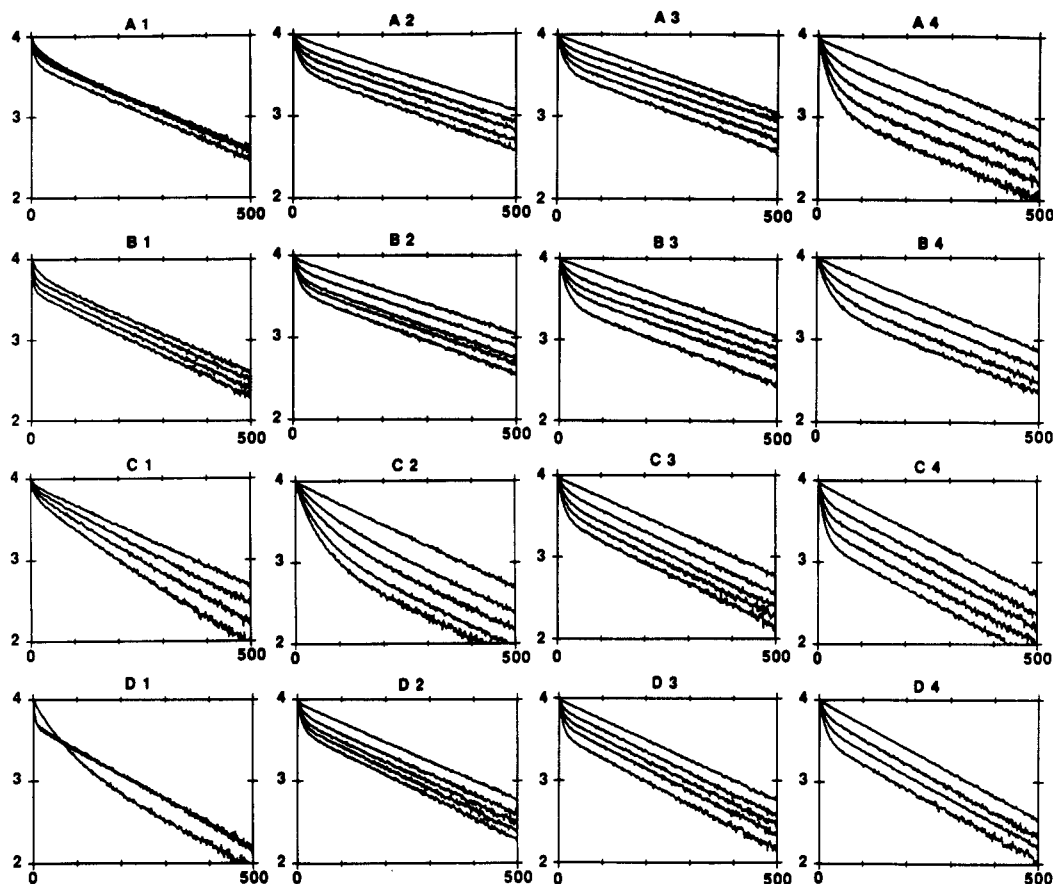
Figure 10. Fluorescence decay curves for pyrene in solutions of EPEs and SDS, with dimethylbenzophenone as quencher at several concentrations. Sequences A and C are for L64, at 20 and 40 °C, respectively; B and D refer to F68 at the same temperatures. Column 1 is for solutions without SDS, and the SDS concentration is 0.1%, 0.3%, and 3.0% w/v in columns 2–4. The vertical scale gives the logarithm of the number of counts, and the horizontal scale the time in nanoseconds.

With the quencher concentration known, the micelle concentration is directly obtained from n, but in order to calculate the aggregation numbers of SDS and EPE in the mixed micelles, it is also necessary to know to what extent these components are present in micellar form. The results given in Tables I and II are based on the assumption that SDS and EPEs are completely aggregated in the mixed micelles. Evidence from surface tension and dye solubilization shows a critical concentration for the onset of micelle formation at a concentration of 1.7–2 mM SDS in F-68, whereas no such critical point was apparent in L-64.[25] Reducing, in the calculations, the concentration of bound SDS by 1.7 mM leads to a significant reduction of the SDS aggregation number in F-68 at 0.1% and 0.3% SDS to values of 7 and 17, respectively, at 20 °C and to 7.7 and 15.5 at 40 °C.

At each SDS concentration measurements were performed usually at four quencher concentrations. The resulting q-average aggregation number, $\langle a \rangle_q$, decreased with the quencher concentration, indicating a polydispersity of the micelle size.[26,27] By linear regression the weight-average aggregation number, $\langle a \rangle_w$, and the width of the distribution, σ, were obtained according to the relation[11,27]

$$\langle a \rangle_q = \langle a \rangle_w - \tfrac{1}{2}\sigma^2 [Q]/[SDS] + ... \tag{2}$$

$\langle a \rangle_w$ and $\sigma/\langle a \rangle_w$ are presented in the tables. The polydispersity values are uncertain in each individual case, but the overall impression of rather broad distributions should be correct.

The second-order rate constant in Tables I and II was calculated by using core volumes obtained by assigning a contribution of 0.357 nm³ from each SDS molecule and 2.9 nm³ from each EPE[28]

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to the hydrophobic volume. (The hydrophobic radius reported in the tables is obtained by assuming the core be spherical.) The resulting k_2 values are reasonably constant at each temperature, at least at high SDS concentrations, indicating a consistent interpretation. A closer examination of the long series of values obtained for L64 at 40 °C shows that the k_q values are proportional to $V^{-1.16}$ rather than to $1/V$. A similar dependence, with an exponent of −1.2, has been noted earlier for quenching in SDS and CTAC micelles in the prescence of salt.[23]

For L64 at 20 °C, however, the assumption that all L64 are associated in the micelles at SDS concentrations up to 10 mM is not compatible with the high and almost constant values obtained for k_q, which are similar to the value determined for pure SDS micelles with an aggregation number of 65, at this temperature. The aggregation number for SDS varies little in this range of compositions. It seems as if the mixed micelles that form at the low temperature are saturated with L64 and have a constant composition. If the k_q values are used for calculating the core volume, assuming that $k_2 = 0.6 \times 10^9$ M⁻¹ s⁻¹—a little more than in pure SDS micelles (0.53 × 10⁹ M⁻¹ s⁻¹)—the result is that 4–5 L64 would be associated with 17–19 SDS in the mixed micelles.

A consequence of this interpretation would be that L64 is distributed between two states in these solutions: mixed micelles and unimers. The change of the III/I values of low SDS concentration (Figure 9) would then indicate that the pyrene molecules greatly favor the mixed micelles with a significant fraction associated with the unimers only below 2 mM SDS. In this composition range, however, the decay curves for pyrene without quencher could not be decomposed unambiguously into two independent components. The reason is probably that the lifetimes are rather similar and that only little pyrene remains associated with unimers. From the decay of pyrene in pure L64 at 20 °C we can estimate that already without SDS more than 90% of the pyrene molecules are associated with micelles formed from diblock molecules, present as impurities at a level of 3% in the L64

sample.[29] Addition of SDS strongly increases the volume fraction of the hydrophobic domains and reduces the fraction of unmicellized pyrene.

To get consistency in the interpretation of the fluorescence quenching results, we are thus forced to assume that the first mixed micelles that form at low SDS concentrations are composed of 4–5 L64 polymers and 17–19 surfactants; the rest of the EPEs remain as unimers and are fully micellized first well above 10 mM (0.3%) SDS in a 1% L64 solution. The much more hydrophilic F68, which does not form micelles by itself even at 40 °C, becomes fully associated with the micelles already at 0.3% SDS, due to the larger molecular weight of F68: a 1% solution is 3.4 mM in L64 but only 1.2 mM in F68. At 0.1% SDS the k_q value and the aggregation number calculated after correction for the amount of free SDS indicate that mixed micelles with about 3 SDS per F-68 are formed.

The fluorescence decay curves from the solutions without SDS reported in the first column of Figure 10 are anomalous. The decay families for F68 at both temperatures and L64 at the low temperature show rapid initial quenching of pyrene in solutions with no added quencher. This quenching is due to excimer formation, and excimer fluorescence was also registered. The added quencher changes the fraction of quenched pyrene only slightly. This behavior, undoubtedly due to the fact that the hydrophobic probe and quencher become concentrated in hydrophobic domains formed by a small fraction of the EPEs, was discussed in detail recently.[29] Its origin is the presence of a small fraction (about 3% in L64) of diblock material, which is more hydrophobic and forms micelles earlier than the triblock material.

For L64 at 40 °C with small or no addition of SDS the decay curves indicate that large micelles are formed. The exponential tails are not well developed which makes the fitting to the Infelta equation (1) uncertain. Large aggregation numbers were indicated, however, and correspondingly low values for the first-order quenching constant. Even larger aggregation numbers and a smaller polydispersity were obtained by using a two-exponential Infelta-type equation in the fittings,[11] a method that in effect consists of a back-extrapolation of the decay tail to time zero, using the unquenched decay constant, to give the fraction of micelles without quencher and hence the aggregation number. These values, which are reported in Table I, should be more reliable.

Micelle Core Radius and Area. The radius of the assumed spherical hydrophobic core of the micelle reported in Tables I and II is rather small with the exception of the L64 micelles with low SDS content at 40 °C. The diameter of the hydrophobic core of the pure L64 micelle is close to 9 nm, which should be compared with the length of the stretched PPO chain of 11 nm. The PPO chains are thus much more extended in the micelles than in the polymer bulk. (The end-to-end distance of the PPO chain as a random coil would be about 2.4 nm.) This finding explains the large downfield shifts observed in the NMR measurements for the methyl carbons in the L64 micelles as compared to the bulk (Figure 3) and the upfield shifts when the size of the micelles decreases with the SDS concentration (Figure 2). The shifts at SDS concentrations of 1% and more are similar to those for F-68 and are thus characteristic for small mixed micelles.

For comparison with the hydrodynamic radius, as obtained from dynamic light scattering (DLS) measurements, a total micelle radius can be estimated by adding to the hydrodynamic radius an estimate of the thickness of the PEO shell. Assuming that five water molecules are associated with each EO in the shell, and using the values suggested by Nagarajan[28] for the volumes of the water molecule and the EO group, 30 and 64.6 Å^3, respectively, the shell thickness should be about 2.0 nm for pure L64 micelles at 40 °C, giving a total radius of 6.65 nm. This is in satisfactory agreement with the DLS studies[25] which give even larger values for the hydrodynamic radius, by 1–2 nm, and show also that the size distribution at 1% and 40 °C is broad, which complicates the comparison with the fluorescence quenching results. For the L64-SDS micelle with 34.6 mM SDS, the EO groups without
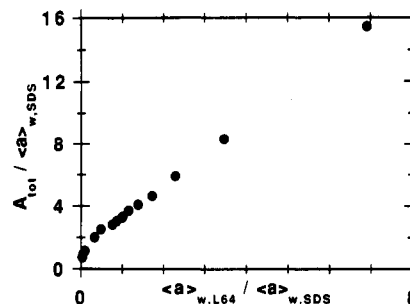

Figure 11. The hydrophobic core area per SDS monomer in SDS–L64 micelles vs the ratio of the aggregation numbers at 40 °C. The slope and ordinate at the origin of the tangent gives the partial interfacial areas at each point.

water could provide a shell thickness of only 1.2 Å, i.e., less than monolayer coverage.

The total interfacial area of the core can be divided into contributions from SDS, A_s, and the EPE, A_p, by splitting $A/\langle a \rangle_s$ vs $\langle a \rangle_p / \langle a \rangle_s$.[30]

$$A/\langle a \rangle_s = A_s + A_p \langle a \rangle_p / \langle a \rangle_s \quad (3)$$

where $\langle a \rangle_{p,s}$ are the aggregation numbers with respect to EPE and SDS, respectively. The data for L64 at 40 °C are shown in Figure 11. The relationship is not linear, which means that the area contributions from the two components depend on the composition (not unexpectedly). The initial linear part starts at $A_s \approx 0.6$ nm^2, which is the area of SDS at the interface of the pure micelle, and has a slope which gives $A_p \approx 4$ nm^2, whereas the long linear portion at low SDS concentrations indicates $A_s \approx 1.2$ nm^2 and $A_p \approx 2$ nm^2. The latter value is in good agreement with the area per L64 for the pure L64 micelle from the data in Table I, 1.94 nm^2. For the nonionic surfactant $C_{12}E_8$ the aggregation number of the pure micelle[31] gives an area of 0.5 nm^2 per headgroup, whereas the effective area is 0.7 nm^2 on first additions to a SDS micelle.[30] The large initial values of the effective areas of the nonionic surfactant and the polymer indicate that their inclusion in the SDS micelle either increases the electrostatic repulsion between the charged headgroups or decreases the tension of the water–core interface.

The 2 × 13 EO units of L64 require relatively large areas compared to the 8 EO units in $C_{12}E_8$. This is probably a consequence of a weaker hydrophobic effect with PPO in the core than with hydrocarbon chains, so that a larger water-exposed interfacial area is allowed. The data for F68 with 2 × 78 EO units are too scarce for definite statements but indicate that the effective area on first additions to SDS micelles is about twice as large as for L64.

Conclusions

1. The hydrophobic PPO middle block of the EPE block copolymer strengthens the interaction with SDS far beyond that in PEO. The critical aggregation concentration where a cooperative aggregation starts is observed at 5.5 mM SDS in PEO,[18,32] at 1.7 mM in F68, and is unobservably low in L64, even at 20 °C where the polymer should be mainly in unimer form.

2. In solutions of L64 at 40 °C, where large micelles are present originally, the effect of SDS is to decrease their size until eventually the average number of L64 molecules per micelle is less than one; these micelles are similar in size to normal SDS micelles. No micelles are present originally in solutions of F68 at either temperature, nor in L64 solutions at 20 °C. The first micelles formed in these solutions are rather small and contain 4–5 EPE molecules and less than 20 surfactants. The micelles remain at approximately this composition until all polymers are micellized. They then grow slowly to the size of normal SDS micelles, containing one or no

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EPE molecule. For comparison, the micelles first formed in PEO are small with an aggregation number around 20 and increase in size to an aggregation number around 50 at saturation, i.e., at the concentration where free micelles with an aggregation number of about 60 begin to appear.[18]

3. The ^{13}C chemical shift measurements report on the states of the PPO and PEO blocks and the surfactant tails. The methyl carbons in PPO show similar shifts in F68 aqueous solution as in neat PPO and also in nonmicellar L64 at 25 °C. They are shifted strongly downfield in the large micelles of L64 at 40 °C and about half as much downfield in the mixed micelles. We take this as an conformational effect, ranging from compact curls in the neat state and in the unimer micelles in water to a highly extended state in the large L64 micelle.

4. The methylene carbons of the PEO blocks show similar shifts in aqueous solutions of PEO and EPEs and also in micellar L64.

They are shifted downfield in the presence of micellar SDS. It is the high-temperature, nonpolar conformers of the PEO blocks that are stabilized by the micelle surface. The nonpolar segments are envisioned to replace water in contact with the hydrophobic core between the charged headgroups, with loops of more polar segments interacting with water and the charges. The observed shielding of excited pyrene from quenching by oxygen is also explained in this way.

5. For the shifts of the alkyl chain carbons of SDS, the most notable effect from interactions with the EPEs is a periodicity of three, reflecting the period of the PPO chain.

Stochastic Model for Fluorescence Quenching in Monodisperse Micelles with Probe Migration

M. H. Gehlen,*,† M. Van der Auweraer,† S. Reekmans,† M. G. Neumann,‡ and F. C. De Schryver*,†

Chemistry Department, Katholieke Universiteit Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium, and Instituto de Física e Química de São Carlos, Universidade de São Paulo, Brazil (Received: August 27, 1990; In Final Form: February 15, 1991)

Fluorescence quenching in monodisperse micelles with probe migration and Poisson-distributed quencher molecules is analyzed theoretically and by numerical simulation. An exact solution for the fluorescence decay is derived and expressed as a series of generalized self-convolution products of an Infelta–Tachiya type equation. Based on Almgren's approach and data analysis of synthetic sample decays, an approximated solution to the fluorescence decay is also derived.

I. Introduction

Fluorescence quenching in micellar solution has been one of the most useful methods in the determination of structural and kinetic parameters such as the mean aggregation number and the rate constants of a micelle–probe–quencher system. The expression for the observed fluorescence decay (eq 1) after a delta pulse

$$f(t) = A_1 \exp(-A_2 t + A_3(\exp(-A_4 t) - 1)) \qquad (1)$$

excitation in the case of an "immobile" probe (probe with a small probability to undergo migration between micelles during its excited-state lifetime) and a mobile quencher, was derived by Infelta[1] and Tachiya.[2] In eq 1 the A parameters are expressed explicitly as

$$A_1 = f(0) \qquad (2)$$

$$A_2 = k_o + k_q k_- \bar{n}(k_q + k_-)^{-1} \qquad (3)$$

$$A_3 = \bar{n}k_q^2(k_q + k_-)^{-2} \qquad (4)$$

$$A_4 = k_q + k_- \qquad (5)$$

with k_o the deactivation rate constant of the fluorescent probe in the absence of quenchers, k_q the first-order rate constant of the intramicellar quenching, k_- the exit rate constant for a quencher from a micelle, and $\bar{n}$ the average number of quenchers per micelle.

Equation 1 describes the quenching dynamics in the micelles if the quencher molecules exchange via the aqueous phase, as described by

$$M_n + Q \xrightleftharpoons[(n+1)k_-]{k_+} M_{n+1} \qquad n = 0, 1, 2, ... \qquad (6)$$
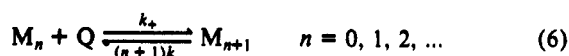
which leads to a Poisson distribution of the quencher molecules over the micelles.

$$P_n = \frac{\bar{n}^n}{n!} \exp(-\bar{n}) \qquad n = 0, 1, 2, ... \qquad (7)$$

When the exchange rate constant of the quencher (k_-) is much smaller than the fluorescence decay constant (k_o), the quencher can be considered as an immobile species and in this case, eq 1 reduces to a more simple form.[3]

$$f(t) = f(0) \exp\{-k_o t + \bar{n}[\exp(-k_q t) - 1]\} \qquad (8)$$

Some extensions of the above treatment have been worked out to take into account static quenching[4] and polydispersity,[5,6] still retaining the initial condition that the probe can be considered as an immobile species.

However, compartmentalized reactions at high micelle concentration or in the presence of additives,[7] in reversed micelles, microemulsions,[8] and in certain polyelectrolyte solutions, may have to take into account probe migration or exchange of both species during the lifetime of the excited probe. Mechanisms such as hopping[9] of the probe or the so-called fusion–fission process[10,11]

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† Katholieke Universiteit Leuven.
‡ Universidade de São Paulo.