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How Critical Micelle Temperature Influences Rotational Diffusion of Hydrophobic Probes Solubilized in Aqueous Triblock Copolymer Solutions

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Rotational diffusion of two structurally similar hydrophobic probes, 2,5-dimethyl-1,4-dioxo-3,6-diphenylpyrrolo-[3,4-*c*]pyrrole (DMDPP) and 1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DPP), has been examined in aqueous solutions of poly(ethylene oxide)$_{20}$−poly(propylene oxide)$_{70}$−poly(ethylene oxide)$_{20}$ triblock copolymer as a function of temperature. These studies have been carried out to explore the influence of critical micelle temperature (cmt) on probe dynamics. It has been observed that, below cmt, the anisotropy decays can be adequately described by single-exponential functions with one time constant each for DMDPP and DPP. However, above cmt, biexponential functions with two time constants are needed to satisfactorily fit the anisotropy decays. Another important observation is that both the probes rotate more rapidly below the critical micelle temperature. The dynamics of the probe molecules are akin to that in a homogeneous solution below cmt, whereas above cmt, the rotational diffusion of the probes has been accounted by the two-step model, which is usually employed to explain the results in micelles. A comparison between the microviscosities of these micelles with other nonionic micelles such as Triton X-100 and Brij-35 reveals that the internal environment of the micelles formed with the triblock copolymer is less fluid.

1. Introduction

Of late, numerous studies[1−12] have appeared in the literature dealing with the aggregation and phase behavior of water-soluble triblock copolymers, owing to their widespread industrial applications. The triblock copolymers composed of poly-(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) units have the chemical composition (PEO)$_x$−(PPO)$_y$−(PEO)$_x$, where *x* and *y* represent the number of ethylene oxide and propylene oxide units, respectively. The amphiphilic nature of these copolymers arises from the temperature-dependent solubility of PPO blocks in water. Below 288 K, PPO is soluble in water, but it turns hydrophobic at elevated temperatures because of its diminishing hydrogen bonding with water. In contrast, PEO is predominantly hydrophilic within the temperature range 273−373 K.[4] As a consequence, these triblock copolymers form aggregates above a critical micelle concentration (cmc) and a critical micelle temperature (cmt) with a core consisting of predominantly PPO and a corona made up of hydrated PEO blocks. The cmts and cmcs of a number of aqueous triblock copolymers have been determined in a systematic manner by Alexandridis et al.[5] It has become evident from their study that copolymers with a larger number of PPO units formed micelles at lower concentrations, and for a given copolymer concentration, they have lower cmts. Other important micellar parameters such as aggregation number, hydrodynamic radius, and core radius are also available in the literature for the micelles formed with triblock copolymers in water.[6,10]

In view of their large size and well-defined micellar structure, micelles formed with triblock copolymers possess the potential to be employed as microreactors for carrying out reactions that are not feasible in aqueous or organic solvents. To realize this potential, it is essential to investigate the internal properties of these micelles thoroughly. In other words, issues such as how solutes solubilized in these micelles move and what kind of microenvironment they experience must be systematically explored. Fluorescence depolarization of solutes solubilized in these micelles is one of the convenient means of tackling this problem, and the present report is one such endeavor.

For this purpose, we have selected a triblock copolymer with the chemical formula (PEO)$_{20}$−(PPO)$_{70}$−(PEO)$_{20}$ whose trade name is P123. The copolymer P123 is chosen because its micellar phase is well-characterized and the micellar properties are adequately documented in literature.[5,6,10] The cmt of P123 is concentration-dependent in the sense that solutions with higher concentrations have lower cmts. Typically, the cmt of 1% w/v aqueous solution of P123 is 289 K, which implies that below this temperature only monomer units of P123 are present in solution.[5] In this study, we are interested in finding out how the dynamics of probe molecules solubilized in aqueous solutions of P123 is influenced by the cmt. Our aim is to also investigate the microenvironment of these micelles. To this effect, rotational diffusion of two hydrophobic probes, 2,5-dimethyl-1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DMDPP) and 1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DPP) (see Figure 1 for their molecular structures), has been examined in 1% w/v aqueous solutions of P123 over the temperature range 283−318 K in steps of 5 deg. The probes DMDPP and DPP have been selected because their rotational diffusion is reasonably well-understood as a result of numerous investigations in homogeneous solutions,[13−21] nonionic micelles,[22−24] and nonionic reverse micelles.[25,26] Even though both DMDPP and DPP are structurally similar, their chemical nature is somewhat distinct. DPP, because of the presence of two secondary amino groups, forms strong hydrogen bonds with its surroundings, and as a consequence, its rotational motion is much slower than

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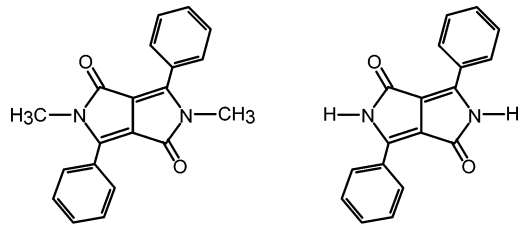

DMDPP DPP

Figure 1. Molecular structures of probes DMDPP and DPP.

DMDPP. In addition, it has been observed that in nonionic reverse micelles both DMDPP and DPP are solubilized in different regions of the core. In this report, we also wish to compare the microenvironment of P123 micelles with other nonionic micelles such as Triton X-100 (TX-100) and Brij-35 by utilizing the data from our earlier work.[22,24] The outline of the remainder of this paper is organized in the following manner: In section 2, sample preparation and the time-resolved fluorescence depolarization method, which was used to measure the rotational diffusion of the probes, are briefly described. The results obtained from these measurements are presented in section 3 and are discussed in section 4. The summary of this work is presented in the final section.

2. Experimental Section

The probes DMDPP and DPP are from Ciba Specialty Chemicals, Inc., and P123 is from Aldrich. All the chemicals are of the highest available purity and were used as such. Deionized water from Millipore was used in the preparation of the samples. An appropriate amount of P123 was weighed in a glass bottle, and to this, a requisite quantity of water was added. The bottle was closed with a cap and refrigerated. A clear solution of P123 in water was obtained after a period of about 12 h. The samples were prepared by dissolving DMDPP and DPP in aqueous solutions of P123 by gentle heating in a water bath. The probes are sparingly soluble because of the low concentration of the polymer, which is 1.7 mM. However, the concentrations of DMDPP and DPP are sufficient to give appreciable counts under laser excitation.

Time-resolved fluorescence measurements were carried out using the time-correlated single-photon counting[27] facility at the Tata Institute of Fundamental Research, Mumbai, and details of the system have been described elsewhere.[14] In brief, the frequency-doubled output of a picosecond Ti:sapphire laser (Tsunami, Spectra Physics) was used as the excitation source, and the probes DMDPP and DPP were excited at 440 nm with a vertically polarized pulse. Fluorescence decays were collected in parallel $I_{||}(t)$, perpendicular $I_{\perp}(t)$, and 54.7° $I(t)$ orientations of the emission polarizer with respect to the polarization of the excitation radiation. The emission in all three cases was monitored at 550 nm. A cutoff filter OG 515 was also placed before the collection lens of the monochromator to eliminate the scattered light. For fluorescence lifetime (τ_f) measurements, 10 000 peak counts were collected, and in the case of anisotropy measurements, 20 000 peak counts were collected for $I_{||}(t)$, and $I_{\perp}(t)$ was corrected for the polarization bias or the G-factor of the spectrometer. The decays were collected in 512 channels with a time increment of 20 ps/ch, 40 ps/ch, or 80 ps/ch. Each measurement was repeated at least 2−3 times, and the average values are reported. The desired sample temperature was attained with the help of a temperature controller, Eurotherm.

The decays measured in this manner are convoluted with the instrument response function (IRF), which was measured by replacing the sample with a solution that scatters light. The full width at half-maximum (fwhm) of the IRF is about 50 ps. Lifetimes of the probes DMDPP and DPP in aqueous solutions of P123 were obtained from the measured fluorescence decays and the instrument response function, by the iterative reconvolution method using the Marquardt algorithm as described by Bevington.[28] Likewise, the anisotropy decay parameters were obtained by simultaneous fit[29,30] of parallel $I_{||}(t)$ and perpendicular $I_{\perp}(t)$ components. The criteria for a good fit was judged by statistical parameters such as the reduced χ^2 being close to unity and the random distribution of the weighted residuals. Details concerning the analysis of the fluorescence and anisotropy decays have been mentioned in our earlier publication.[22]

TABLE 1: Fluorescence Lifetimes and Anisotropy Decay Parameters of DMDPP in 1% Aqueous Solutions of P123 as a Function of Temperature

T/K	τ_f/ns	β	τ_1/ns	τ_2/ns	$\langle\tau_r\rangle^a$/ns
283	7.97	1.0	0.32 ± 0.03		0.32 ± 0.03
288	7.96	1.0	0.29 ± 0.01		0.29 ± 0.01
293	8.38	0.63 ± 0.03	5.9 ± 0.2	1.2 ± 0.1	4.2 ± 0.3
298	8.60	0.70 ± 0.02	4.7 ± 0.3	1.0 ± 0.1	3.6 ± 0.3
303	8.59	0.69 ± 0.03	3.5 ± 0.2	0.9 ± 0.1	2.7 ± 0.2
308	8.58	0.54 ± 0.04	2.9 ± 0.2	0.9 ± 0.1	2.0 ± 0.2
313	8.56	0.50 ± 0.05	2.5 ± 0.2	0.8 ± 0.1	1.7 ± 0.2
318	8.54	0.42 ± 0.01	2.2 ± 0.2	0.7 ± 0.1	1.3 ± 0.2

[a] Calculated using eq 2.

TABLE 2: Fluorescence Lifetimes and Anisotropy Decay Parameters of DPP in 1% Aqueous Solutions of P123 as a Function of Temperature

T/K	τ_f/ns	β	τ_1/ns	τ_2/ns	$\langle\tau_r\rangle^a$/ns
283	6.80	1.0	1.4 ± 0.1		1.4 ± 0.1
288	6.70	1.0	1.2 ± 0.1		1.2 ± 0.1
293	7.16	0.76 ± 0.04	11.6 ± 0.7	2.4 ± 0.3	9.4 ± 1.0
298	7.21	0.67 ± 0.02	9.5 ± 0.7	3.3 ± 0.3	7.5 ± 0.7
303	7.15	0.68 ± 0.05	8.4 ± 0.9	2.0 ± 0.6	6.4 ± 1.2
308	7.14	0.71 ± 0.02	6.1 ± 0.2	1.3 ± 0.1	4.7 ± 0.3
313	7.12	0.70 ± 0.01	5.1 ± 0.2	1.2 ± 0.1	3.9 ± 0.2
318	7.09	0.65 ± 0.01	4.1 ± 0.1	0.8 ± 0.1	2.9 ± 0.2

[a] Calculated using eq 2.

3. Results

The fluorescence decays of DMDPP and DPP in aqueous solutions of P123 can be adequately described by single-exponential functions. The lifetimes of DMDPP and DPP are tabulated in Tables 1 and 2, respectively. It is evident from these tables that the lifetimes of both probes are marginally lower below cmt compared to the ones measured above cmt, which is due to the different environments experienced by the probe molecules. Above cmt, the τ_f values of both DMDPP and DPP decrease marginally with an increase in temperature. The sole exceptions are the values at 293 K, which are somewhat lower. The probable reason for such an observation is the existence of both monomer and micelle forms of P123 in solution at this temperature,[31] and in such a scenario, the recovered τ_f represents some kind of intermediate value.

The anisotropy decays of both probes in P123, on the other hand, are more sensitive to cmt. At temperatures of 283 and 288 K, which are below cmt, the anisotropy decays can be fit by single-exponential functions. Above cmt, however, they follow a biexponential function of the form given by eq 1.

$$r(t) = r_0[\beta \exp(-t/\tau_1) + (1 - \beta) \exp(-t/\tau_2)] \qquad (1)$$

In eq 1, τ_1 and τ_2 are the two time constants associated with

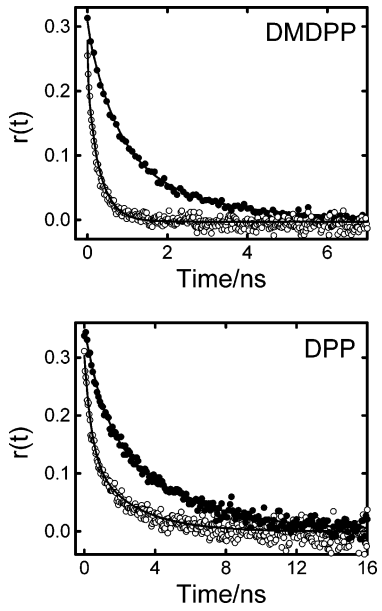

Figure 2. Anisotropy decays of DMDPP and DPP in aqueous solutions of P123 at 283 K (○) and 318 K (●). Notice that faster anisotropy decays have been observed for DMDPP as well as DPP at lower temperatures. These decays were measured below and above the critical micellar temperatures. In other words, the decay at 283 K is in a monomer solution of P123, whereas the one at 318 K is in a micellar solution. The smooth lines passing through them are the fitted curves. In a monomer solution, the anisotropy decays of DMDPP and DPP follow single-exponential functions with time constants of 0.32 ± 0.03 ns and 1.4 ± 0.1 ns, respectively, at 283 K. In a micellar solution, however, the anisotropy decays of both the probes can be described by biexponential functions, and the average reorientation times are 1.3 ± 0.2 ns and 2.9 ± 0.2 ns, respectively, for DMDPP and DPP at 318 K.

thedecay of the anisotropy and β is the percentage contribution of τ_1 to the decay of the anisotropy. r_0 is the inherent depolarization, which is the characteristic feature of a given molecule. To compare the anisotropy decays measured under different conditions, the quantity average reorientation time $\langle\tau_r\rangle$ is defined in the following manner:

$$\langle\tau_r\rangle = \beta\tau_1 + (1-\beta)\tau_2 \qquad (2)$$

The anisotropy decay parameters together with the average reorientation times obtained from eq 2 are also given in Tables 1 and 2 for DMDPP and DPP, respectively. A quick glance at these tables reveals that the anisotropy decays, besides following single-exponential functions below cmt, are significantly faster than the ones measured above cmt for both probes, and this facet has been depicted in Figure 2.

4. Discussion

The intriguing results presented in the preceding section can be comprehended in terms of the temperature-dependent aggregation behavior of P123 in water. As briefly mentioned in the Introduction, a 1% w/v solution of P123 in water forms micelles above 289 K, and the aggregation number N_{agg}, hydrodynamic radius r_h, and core radius r_c of such micelles as a function of temperature, which were obtained from the literature,[5,10] are given in Table 3. It is evident from the table that with an increase in temperature the aggregation number of these micelles goes up. However, the hydrodynamic radius remains more or less the same, especially from 303 to 318 K. This observation has been rationalized on the basis of dehydration of PEO blocks at higher temperatures resulting in almost identical coronal volume.[10]

TABLE 3: Properties of P123 Micelles as a Function of Temperature

T/K	N_{agg}[a]	r_c[a]/nm	r_h[b]/nm	τ_M[d]/ns
298	86	5.2	5.77	174.2
303		7.1[c]	7.96[c]	402.9
308	244	7.3	8.18	388.1
313	287	7.7	8.63	407.0
318	297	7.8	7.73	378.5

[a] N_{agg} and r_c values were taken from ref 10. [b] r_h values were taken from ref 5. [c] Values obtained by interpolation of the data. [d] τ_M values were calculated using eq 6.

Apart from the temperature-dependent aggregation behavior of P123 in water, it is also essential to have knowledge pertinent to the location of the probes in this system in order to understand the observed results. In view of these criteria, further discussion is segregated into three parts: location of the probes and rotational diffusion of the probes below and above cmt.

Location of the Probes. Any probe dissolved in micellar media can be solubilized either in the micellar phase or the aqueous phase or can be partitioned between the two phases, depending on its chemical nature. Because the probes used in the present study, DMDPP and DPP, are hydrophobic, it is logical to expect that they will be located in the micellar phase. Even though these probes are neutral and non-dipolar (without a permanent dipole moment), they possess polar functional groups and thus may be sparingly soluble in the aqueous phase. To verify this hypothesis, minute quantities of DMDPP and DPP were added to water, and the samples were sonicated and heated to 353 K. The solutions were then allowed to equilibrate for more than 12 h. Fluorescence spectra of the sample containing DPP could not be recorded as the sample did not emit, and also, no counts were observed even under laser excitation. This result is not surprising considering the fact that DPP forms different types of aggregates in the solid state because of intermolecular hydrogen bonding through the two NH groups.[32] As a consequence, DPP is sparingly soluble only in select organic solvents with which it can form hydrogen bonds at the two NH sites so that the intermolecular hydrogen bonds between the aggregates are broken. In other words, DPP is soluble in solvents such as alcohols, dimethyl sulfoxide, acetone, ether, and also molecules that have PEO and PPO units such as the ones used in the present study. On the other hand, steady-state fluorescence spectra could be recorded for the sample with DMDPP even though emission intensity was very feeble. These observations indicate that DPP is not soluble in the aqueous phase of the micellar solution, whereas there is a finite probability for the presence of DMDPP in the aqueous phase.

To find out whether in the presence of P123 the probe DMDPP gets distributed between the two phases, the fluorescence lifetime of DMDPP was measured in water at 298 K and has been found to be 7.79 ns. This value is much less than the one measured in the solution containing P123 at the same temperature, which is 8.60 ns (see Table 1). If DMDPP were to be solubilized in micellar as well as aqueous phases, the fluorescence decay at 298 K would have contained two decay components, one corresponding to the micellar phase and the other to the aqueous one, and the preexponential factors would have given the percentage distribution of the probe in both these phases. On the contrary, as already mentioned, the fluorescence decays of DMDPP in aqueous solutions of P123 at all the temperatures could be adequately fit with one lifetime. This exercise confirms that, even though DMDPP is soluble enough

in water to record emission spectra and measure lifetime, in the presence of P123, it is completely solubilized in the micellar phase. To substantiate this point further, anisotropy decays of DMDPP in water were measured at 298 K, and the reorientation time has been found to be 92 ± 6 ps. In contrast, τ_1 and τ_2 values of DMDPP in P123 at 298 K are 4.7 ± 0.3 ns and 1.0 ± 0.1 ns, respectively (see Table 1), which are much higher than the value obtained in water. The controlled experiments carried out in this manner and also the arguments presented here clearly rule out the possibility that DMDPP is partitioned between micellar and aqueous phases in the presence of P123.

Having established that both DMDPP and DPP reside in the micellar phase, now it needs to be ascertained whether they are solubilized in the palisade layer or the core of these micelles. From our earlier work[22−24] involving the rotational diffusion of these probes in nonionic micelles such as TX-100 and Brij-35, it has been proven that they are located in the palisade layer of the micelles, which is essentially made up of PEO units. We arrived at this conclusion on the basis of the fluorescence lifetime data for DMDPP and the solubility criteria for DPP. The fluorescence lifetimes of DMDPP in nonpolar solvents such as *n*-hexane, cyclohexane, hexadecane, benzene, and squalane are 5.58, 6.04, 6.59, 6.12, and 6.71 ns, respectively, at 298 K, whereas the τ_f values of DMDPP in TX-100 and Brij-35 micelles are in the range 8.3−8.70 ns. These data clearly indicate that, even though DMDPP is soluble in alkane-like solvents, it is not solubilized in the cores of TX-100 and Brij-35 micelles, which consist of nonpolar alkyl chains. In the case of DPP, the evidence is much simpler to deduce, as it is not soluble in alkane-like solvents because of the reasons mentioned before. Moreover, extensive investigations carried out in the literature[33−36] pertinent to the sites of solubilization of organic molecules in micelles also indicate that they are indeed solubilized at or near the micelle−water interface. On the basis of the conclusions available in the literature and also from our earlier experience with the probes DMDPP and DPP in TX-100 and Brij-35 micelles, it is only reasonable to conclude that both probes are solubilized in the palisade layer of the P123 micelles.

Rotational Diffusion Below cmt. Because P123 exists as individual monomer units in water below cmt, the rotational diffusion of the probes under these conditions should, in principle, be similar to that observed in a number of homogeneous solvents.[13−21] The rotation of DPP is slower than that of DMDPP by over a factor of 4 at 283 K as well as at 288 K. One of the reasons for such behavior is the presence of strong hydrogen-bonding interactions of the probe through its secondary amino groups with the oxygen atoms of the PEO and PPO units. Now, we are interested in comparing the reorientation times of DMDPP with the ones calculated using the Stoke−Einstein−Debye (SED) hydrodynamic theory.[37] Because DMDPP is a medium-sized solute molecule that does not strongly interact with most solvents,[13−21] its rotational diffusion has adequately been described by the SED theory with the slip boundary condition.[38] The calculated reorientation times with slip and stick boundary conditions at unit viscosity (η) and temperature (T) that have been taken from our earlier work[13] are 13.18 × η/T and 41.41 × η/T ns K (mPa s)$^{-1}$, respectively. A comparison between the experimentally measured reorientation times and the theoretically calculated numbers with stick boundary condition indicates that the rotation of DMDPP is slower by a factor of 1.7−1.8, which is very slow compared to its rotation in a number of solvents.[13−21] What is the reason for such slow rotation of DMDPP in aqueous solutions of P123? The rationale is the hydrophobic nature of the probe, which prevents it from experiencing the bulk viscosity of the medium, and as a consequence, the probe molecule is engulfed by the copolymer. In other words, the microenvironment offered by the copolymer surroundings is much less fluid than the macroscopic viscosity of water, even in the absence of specific interactions. If DMDPP were to experience aqueous surroundings, its reorientation times would have been 142 and 123 ps at 283 and 288 K, respectively, on the basis of its measured value in water at 298 K. A similar explanation is valid even in the case of DPP, because it is also a hydrophobic probe. However, the presence of specific interactions between the probe and its surroundings impedes its rotation significantly compared to DMDPP. It has been demonstrated in our earlier work[19,20] that the degree of slowness of the rotation of DPP compared to that of DMDPP depends on the strength of the interaction between the solute and the solvent, which is in the range 1.5−3.0 in numerous solvents.[13−21] Nonetheless, in the present system this factor exceeds 4, which is an indication that DPP not only experiences specific interactions but also resides in a different location of the copolymer with respect to DMDPP, a result similar to that observed in reverse micelles of TX-100.[25,26]

Rotational Diffusion Above cmt. The copolymer, P123, associates and forms micelles above cmt, and hence, the rotational diffusion of the probes is quite different compared to what has been observed below cmt. As already mentioned in the previous section, the anisotropy decays are described by biexponential functions with two time constants, which is due to the probe molecule experiencing two different kinds of motions in the micellar environment. It is a well-known fact that aromatic probes usually reside at or near the interface and undergo a slow lateral diffusion on or inside the curved surface of the micelle and also a fast wobbling motion in an imaginary cone. These two motions are coupled to the overall rotation of the micelle, which is known as the two-step model.[39−42] This model has been applied successfully to explain the rotational relaxation of organic solutes in confined systems such as micelles,[22−24,43−46] reverse micelles,[25,26,47] thermosensitive core−shell latex particles,[48] and polymer−surfactant aggregates.[49] The experimentally measured quantities, τ_1, τ_2, and β, are related to the model parameters by the following equations:[43]

$$\frac{1}{\tau_1} = \frac{1}{\tau_L} + \frac{1}{\tau_M} \tag{3}$$

$$\frac{1}{\tau_2} = \frac{1}{\tau_W} + \frac{1}{\tau_1} \tag{4}$$

$$\beta = S^2 \tag{5}$$

In eqs 3−5, τ_L, τ_W, and τ_M are the time constants for lateral diffusion, wobbling motion, and overall rotation of the micelle, respectively. β is the square of the order parameter S, which follows the inequality $0 \le S^2 \le 1$.[43] The time constant for the rotation of the micelle as a whole, τ_M, has been calculated using the SED relation with stick boundary condition.[37]

$$\tau_M = \frac{4\pi r_h^3 \eta}{3kT} \tag{6}$$

where k is the Boltzmann constant. The τ_M values calculated using eq 6 are also given in Table 3. Because the micelles formed with P123 are large, the time constants for the overall rotation of the micelles are in the range of a few hundreds of nanoseconds. As a result, τ_1 essentially represents the time constant for lateral diffusion. From the order parameter, half-

TABLE 4: Order Parameters, Cone Angles, Lateral Diffusion Coefficients, and Wobbling Diffusion Coefficients for DMDPP and DPP in P123 Micelles as a Function of Temperature Obtained from the Analysis of the Anisotropy Decays

	S		θ/deg		$D_L \times 10^{10}$/m^2 s^{-1}		$D_W \times 10^{-8}$/s^{-1}	
T/K	DMDPP	DPP	DMDPP	DPP	DMDPP	DPP	DMDPP	DPP
298	0.84	0.82	27.2	29.0	9.3	4.5	0.48	0.14
303	0.83	0.82	28.1	29.0	23.7	9.8	0.54	0.26
308	0.73	0.84	36.1	27.2	30.4	14.3	0.78	0.37
313	0.71	0.84	37.6	27.2	39.2	19.2	0.93	0.39
318	0.65	0.81	41.8	29.8	45.9	24.5	1.26	0.73

angle θ of the cone of the wobbling motion has been calculated using eq 7.[40,43]

$$S = \frac{1}{2}\cos\theta(1 + \cos\theta) \tag{7}$$

The parameters τ_L, τ_W, and θ, which were obtained from the eqs 3, 4, and 7, have been used to calculate the diffusion coefficients for lateral diffusion D_L and wobbling motion D_W with the aid of the following relations:[40,41,44]

$$D_L = \frac{r_c^2}{6\tau_L} \tag{8}$$

$$D_W = \frac{1}{[(1 - S^2)\tau_W]}\left[\frac{\cos^2\theta(1 + \cos\theta)^2}{2(\cos\theta - 1)}\left\{\ln\left(\frac{(1 + \cos\theta)}{2}\right) + \frac{(1 - \cos\theta)}{2}\right\} + \frac{(1 - \cos\theta)}{24}(6 + 8\cos\theta - \cos^2\theta - 12\cos^3\theta - 7\cos^4\theta)\right] \tag{9}$$

For calculating D_L, r_c instead of r_h was used because the probes DMDPP and DPP are hydrophobic and are unlikely to be in the vicinity of the hydrated part of the corona consisting of PEO units. However, with an increase in temperature, the PEO units are dehydrated, but the extent of which is not known. In view of this situation, the radius of the micellar surface on which the probes are undergoing lateral diffusion is some kind of intermediate value between r_c and r_h. The calculated values of S, θ, D_L, and D_W for DMDPP and DPP in the temperature range 298−318 K are given in Table 4. There appears to be no significant change in the order parameters of both probes. In contrast, the respective diffusion coefficients (D_L as well as D_W) increase with an increase in temperature, as expected.

Comparison of the Microenvironment of P123 with Other Nonionic Micelles. At this juncture, it is interesting to compare the microenvironment of P123 micelles with other nonionic micelles such as TX-100 and Brij-35, because the outer shell of all three micelles comprises PEO units and the only difference is the number of PEO units. P123, TX-100, and Brij-35 have 20, 9−10, and 23 PEO units, respectively. Moreover, the probes are solubilized in the region containing PEO units in all three micellar systems. For a comparison of the microenvironments, the average reorientation times of DMDPP in P123 from this work and that of TX-100 as well as Brij-35 from our earlier work[22,24] have been employed. This is due to the fact that DMDPP does not strongly interact with the surroundings; as a consequence, its hydrodynamic volume remains the same from system to system, and this aspect has been thoroughly discussed in our earlier papers.[24,46] It has been found that a hydrodynamic volume (V_h) of 183 Å^3 for DMDPP,[13] which is calculated with the slip boundary condition by treating the probe as an asymmetric ellipsoid, adequately accounts for its rotation in a number of solvent systems.[13−21] The same value has been used to calculate the microviscosities (η_m) of micelles[24,46] with the aid of the SED equation:

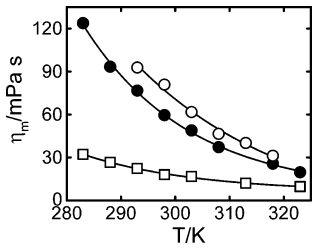

Figure 3. Plots of microviscosities of the micelles P123 (○), TX-100 (●), and Brij-35 (□) obtained from the average reorientation times of the probe DMDPP. The smooth lines through the data points were obtained by fitting them to exponential functions. The data for TX-100 and Brij-35 were taken from our earlier work (refs 22 and 24).

$$\eta_m = \frac{\langle\tau_r\rangle_p kT}{V_h} \tag{10}$$

In eq 10, $\langle\tau_r\rangle_p$ is the average reorientation time of the probe without the contribution from the overall rotation of the micelle. However, in the case of large nonionic micelles such as P123, TX-100, and Brij-35, $\langle\tau_r\rangle_p$ and $\langle\tau_r\rangle$ are more or less the same, because $\tau_M >> \langle\tau_r\rangle$. The microviscosities obtained in this manner for the three micelles as a function of temperature are presented in Figure 3. It is evident from the figure that η_m values of P123 micelles are higher by factors of 1.2−1.3 and 3.3−4.5 compared to TX-100 and Brij-35 micelles, respectively. This result clearly indicates that the magnitude of η_m not only depends on the number of PEO units but also on the hydration levels. Because DMDPP is a hydrophobic probe, it resides in an environment that is devoid of water and accordingly senses the microviscosity of the micelle. However, it is difficult to fathom exactly how the interplay of the three factors, namely, the number of PEO units, the hydration levels, and the exact location of the probe determines the microviscosity of these micelles.

Conclusions

It is a well-established fact that surfactant molecules possess distinct hydrophilic and hydrophobic groups, and as a consequence, they form aggregates in water known as micelles above a certain concentration, the cmc. Triblock copolymers, on the other hand, acquire the amphiphilic character because of preferential solubility of one block over the other above a certain temperature, the cmt. In view of this situation, the cmt, as well as the cmc, plays an important role in the formation of micelles in the case of triblock copolymer solutions. With an intent to understand how this cmt influences the dynamics of the species solubilized in triblock copolymer solutions, the present study has been undertaken, and the important conclusions are as follows: In this work, the rotational diffusion of two structurally similar hydrophobic probes DMDPP and DPP has been investigated in aqueous solutions of P123 as a function of temperature. It has been observed that there is a drastic variation in rotational diffusion of the probes below and above cmt. Below cmt, single-exponential functions are sufficient to describe the anisotropy decays of the both probes, which is similar to what has been observed in numerous solvents. However, the reorientation times of both probes are significantly slower than

predicted by the SED theory with the stick boundary condition. This is due to the hydrophobic nature of the probes, which causes them to reside in an environment that is surrounded by the monomer units of P123. In contrast, above cmt, biexponential functions with two time constants are needed to fit the anisotropy decays of the probes. The rotational diffusion of the probes is explained by the two-step model, which is often invoked to rationalize the dynamics in micelles. Another important observation is that the anisotropy decays of the probes below cmt are significantly faster than the ones measured above cmt, indicating that the micellar environment is less fluid for probe rotation even at higher temperatures. The microviscosities of P123 micelles have been compared with other nonionic micelles such as TX-100 and Brij-35, because all of them are composed of ethylene oxide headgroups, and it has been found that the η_m values of P123 are higher than those of TX-100 and Brij-35 micelles by factors of 1.2−1.3 and 3.3−4.5, respectively, in the temperature range studied.

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Note Added after ASAP Publication

A production error occurred during original ASAP posting of this article on February 23, 2005, resulting in an error in the title. The correct version was published ASAP on February 25, 2005.

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