Rotational Diffusion of Hydrophobic Probes in Brij-35 Micelles: Effect of Temperature on Micellar Internal Environment

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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 studied in nonionic Brij-35 micelles as a function of temperature to explore the micellar internal environment. Analysis of the anisotropy data reveals that the probes are located in the interfacial region of the micelle and also undergo slow lateral diffusion and fast wobbling motion that are linked to the rotation of the micelle as a whole. From light scattering studies, it has been well-established that there is no variation in the size and hydration levels of Brij-35 micelles in the temperature range 283−323 K. Hence, it is logical to expect that there is no change in the site of solubilization of the probes in the micelles with temperature. An attempt has been made to determine the microviscosity of these micelles from the average reorientation times of the noninteracting probe DMDPP.

1. Introduction

Light scattering methods are often used to determine the physical properties such as size, shape, and hydration levels of micelles. Fluorescence depolarization method, on the other hand, is complementary to light scattering methods in the sense that it probes the internal environment of the micelles. These experiments are usually carried out by monitoring the fluorescence of a probe that is solubilized in the micellar phase. It is always ensured that the micellar environment is not perturbed by maintaining a low concentration of the probe. The information gleaned from such studies can give insight into many chemical reactions that transpire in organized media. Hence, a number of investigations have been carried out during the last few decades to accomplish this objective.[1−13]

It has been well established that physical properties such as polarity, microviscosity, and hydration levels inside the micelles are not uniform. In view of this, solute molecules solubilized in micelles tend to seek different regions of the micelle depending on their chemical nature. The micellar properties, both external as well as internal, can be altered by changing the temperature and also by introducing additives such as electrolytes. Changes in the micellar internal environment will also bring about a change in the location of the solubilized species. Nonionic micelles such as Triton X-100 (TX-100) swell in size with an increase in temperature and also upon the addition of salt.[14−18] Besides enhancement in size, there is also a marked increase in the degree of hydration.[15,18] We have recently carried out fluorescence depolarization studies 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), in TX-100 micelles, in an attempt to understand how the changes in micellar properties influence the dynamics of probe molecules.[9,10] One of the important findings of our studies is that the probe molecules are pushed inward more toward the stern layer and away from the surface because of the penetration of water molecules inside the micelle with an increase in the degree of hydration.

In the present paper, we wish to extend these studies to another nonionic micelle formed with the surfactant Brij-35 (poly(oxyethylene(23)) dodecyl ether). The hydrophilic part of the surfactant in both TX-100 and Brij-35 micelles is the same except for the length of the oxyethylene chain. The number of oxyethylene groups in TX-100 is 9.5, whereas in Brij-35, this number is 23. Nevertheless, both of these micelles differ in the hydrophobic part of the surfactant; TX-100 has p-(1,1,3,3-tetramethylbutyl)phenyl group while Brij-35 has dodecyl group. Because the majority of the probe molecules tend to get solubilized in the interfacial region of the micelle, which essentially consists of the hydrophilic part of surfactant units, the dynamics of the probe molecules are expected to be comparable in both the micelles. Even though the hydrophilic parts of TX-100 and Brij-35 surfactant units are chemically similar, the micelles formed with TX-100 and Brij-35 surfactant units are significantly different. As mentioned earlier, the size of TX-100 micelle and degree of hydration increase significantly upon increasing the temperature,[15] whereas that of Brij-35 remain more or less the same in the temperature range 283−323 K.[19] Hence, it is expected that the site of solubilization of the probes inside Brij-35 micelles should also remain unchanged with an increase in temperature. Under these circumstances, rotational diffusion studies involving the probes DMDPP and DPP in principle should give information about the internal environment of Brij-35 micelles. Besides probing the internal environment of these micelles, we are also interested in comparing the dynamics of DMDPP and DPP in Brij-35 to that in TX-100 micelles. To obtain the abovementioned information, we have carried out time-resolved fluorescence depolarization experiments with the probes DMDPP and DPP (see Figure 1 for molecular structures of the probes) in Brij-35 micelles in the temperature range 283−323 K. The remainder of the paper is organized in the following manner. Section 2 briefly describes

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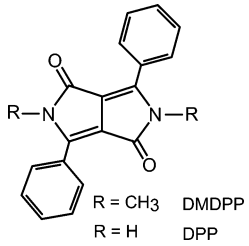

Figure 1. Molecular structures of the probes DMDPP and DPP.

the experimental methods and data analysis that were used to obtain the rotational relaxation of the probes in micelles. Results are presented in section 3 and are discussed in the following section. The conclusions are summarized in the final section.

2. Experimental Section

The probes DMDPP and DPP are from Ciba Specialty Chemicals Inc., Switzerland, and the surfactant Brij-35 is from Pierce Chemical Company, U.S.A. All of the chemicals are of the highest available purity and were used as such. Deionized water from Millipore was used in the preparation of the micelle samples. The concentration of the surfactant was 20 mM and that of the probes were in the range of $10^{-5}-10^{-6}$ M.

Time-resolved fluorescence measurements were carried out using time-correlated single-photon counting[20] facility at the Tata Institute of Fundamental Research, Mumbai, and details of the system have been described elsewhere.[21] In brief, the frequency-doubled output of a picosecond Ti:saphire laser (Tsunami, Spectra Physics) was used as the excitation source and the probes DMDPP and DPP were excited at 455 nm with a vertically polarized pulse. Fluorescence depolarization was monitored by measuring the fluorescence decays parallel and perpendicular with respect to the polarization of the excitation source. Lifetimes were measured by collecting the fluorescence decays at the magic angle (54.7°) orientation of the emission polarizer. The emission in all the three cases was monitored at 550 nm. For lifetime measurements, 10 000 peak counts were collected. However, in case of anisotropy measurements, for the parallel component of the decay, 20 000 peak counts were collected and the perpendicular component of the decay was corrected for the *G* factor of the spectrometer. The decays were collected in 512 channels with a time increment of 38.5 ps/ch. Each measurement was repeated at least 2−3 times, and the average values are reported. The experiments were performed in the temperature range 283−323 K, and the desired sample temperature was achieved with the help of a temperature controller, Eurotherm.

The decays measured in this manner are convoluted with the instrument response function, which was measured by replacing the sample with a solution that scatters light. Lifetimes of the probes DMDPP and DPP in Brij-35 micelles were obtained from the fluorescence decays measured at magic angle polarization $I(t)$ and the instrument response function, by iterative reconvolution method using Marquardt algorithm as described by Bevington.[22] Likewise, the anisotropy decay parameters were obtained by simultaneous fit[23,24] of parallel $I_{\parallel}(t)$ 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. Because the details of the analysis have been mentioned in our earlier publications,[9,10] we refrain from further discussion.

3. Results

Fluorescence decays of both DMDPP and DPP in Brij-35 micelles are adequately described by exponential functions with single lifetimes in the temperature range 283−323 K. The lifetimes of DMDPP decrease marginally from 8.29 to 8.15 ns with an increase in temperature, and for DPP, this decrease is from 6.95 to 6.82 ns. Figure 2 gives the measured and fitted (to single exponential functions) fluorescence decays of DMDPP and DPP at 298 K together with the residual distributions. The residual distributions for both DMDPP and DPP are random indicating that the fitted functions satisfactorily describe the measured decays.

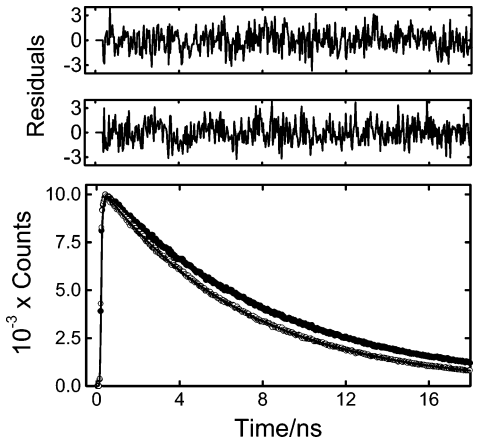

Figure 2. Fluorescence decays of DMDPP (●) and DPP (○) in Brij-35 micelles at 298 K. The solid lines were obtained by fitting the data to single-exponential functions, and the lifetimes are 8.26 and 6.89 ns, respectively, for DMDPP and DPP. The upper and lower panels of the figure represent the residual distributions for DMDPP and DPP, respectively. The instrument response function whose full-width at half-maximum is about 40 ps is not shown in the figure for the sake of clarity.

Biexponential functions with two time constants are needed to fit the anisotropy decays of DMDPP and DPP in Brij-35 micelles at all the temperatures studied. The functional form of the anisotropy decay $r(t)$ is given by the following equation

$$r(t) = r_0[\beta \exp(-t/\tau_{slow}) + (1-\beta)\exp(-t/\tau_{fast})] \quad (1)$$

where r_0 is the limiting anisotropy, which describes the inherent depolarization for a given molecule.[25] The r_0 values obtained from the analysis are in the range of 0.312−0.358. However, r_0 values obtained from the steady-state fluorescence depolarization measurements in glucose glass are 0.364 ± 0.006 and 0.362 ± 0.004 for DMDPP and DPP, respectively.[26] The lower r_0 values obtained from the time-resolved experiments are probably due to rapid depolarization of the fluorescence, which the single-photon counting setup could not resolve. τ_{slow} and τ_{fast} are the two reorientation times of the probe in the micelle and β is the preexponent that gives the relative fractions of slow and fast components. Fluorescence lifetimes, together with the anisotropy decay parameters for DMDPP and DPP in Brij-35 micelles in the temperature range 283−323 K are given in Tables 1 and 2, respectively. The average reorientation time $\langle\tau_r\rangle$ was calculated using the following relation and the values of $\langle\tau_r\rangle$ are also given in the tables

$$\langle\tau_r\rangle = \beta\tau_{slow} + (1-\beta)\tau_{fast} \quad (2)$$

A quick glance at the tables reveals that the average reorientation times of both DMDPP and DPP in Brij-35 micelles decrease by nearly a factor of 4 upon raising the temperature from 283 to 323 K. Also $\langle\tau_r\rangle$ values of DMDPP are about two times faster than that of DPP over the entire temperature range studied. This

TABLE 1: Fluorescence Lifetimes and Anisotropy Decay Parameters of DMDPP in Brij-35 Micelles as a Function of Temperature Together with the Microviscosities of the Micelles

temp/ K	τ_f/ ns	β	τ_{slow}/ ns	τ_{fast}/ ns	$\langle\tau_r\rangle^a$/ ns	η^b/ mPa s
283	8.29	0.58 ± 0.01	2.15 ± 0.07	0.57 ± 0.05	1.49	30.6
288	8.28	0.58 ± 0.01	1.75 ± 0.05	0.48 ± 0.04	1.22	25.5
293	8.27	0.58 ± 0.02	1.43 ± 0.06	0.41 ± 0.05	1.00	21.3
298	8.26	0.41 ± 0.02	1.34 ± 0.05	0.41 ± 0.03	0.79	17.1
303	8.23	0.43 ± 0.02	1.20 ± 0.04	0.35 ± 0.03	0.72	15.8
313	8.19	0.45 ± 0.02	0.85 ± 0.03	0.23 ± 0.03	0.51	11.6
323	8.15	0.37 ± 0.01	0.72 ± 0.02	0.21 ± 0.02	0.40	9.4

[a] Calculated using eq 2. [b] Obtained from $\langle\tau_r\rangle$ values using eq 5 (see text for details).

TABLE 2: Fluorescence Lifetimes and Anisotropy Decay Parameters of DPP in Brij-35 Micelles as a Function of Temperature

temp/ K	τ_f/ ns	β	τ_{slow}/ ns	τ_{fast}/ ns	$\langle\tau_r\rangle^a$/ ns
283	6.95	0.69 ± 0.01	3.85 ± 0.06	0.90 ± 0.05	2.94
288	6.93	0.64 ± 0.02	3.53 ± 0.04	0.81 ± 0.06	2.55
293	6.92	0.65 ± 0.01	2.98 ± 0.05	0.70 ± 0.10	2.18
298	6.89	0.63 ± 0.01	2.52 ± 0.05	0.63 ± 0.05	1.82
303	6.87	0.54 ± 0.01	2.47 ± 0.04	0.64 ± 0.04	1.63
313	6.84	0.46 ± 0.02	2.08 ± 0.06	0.59 ± 0.05	1.28
323	6.82	0.48 ± 0.04	1.38 ± 0.07	0.38 ± 0.03	0.86

[a] Calculated using eq 2.

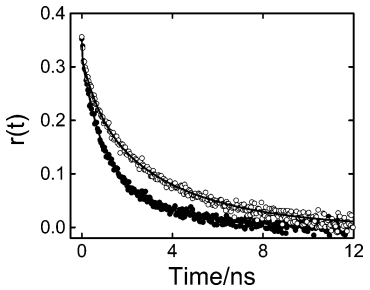

Figure 3. Anisotropy decays of DMDPP (●) and DPP (○) in Brij-35 micelles at 283 K. The smooth lines passing through them are the fitted ones. The average reorientation times defined by eq 2 are 1.49 and 2.94 ns, respectively, for DMDPP and DPP.

fact has been illustrated in Figure 3 where anisotropy decays of DMDPP and DPP at 283 K are displayed together.

4. Discussion

To understand the dynamics of probe molecules in micelles and subsequently explore their internal environment, it is essential to have knowledge of the probe location in the micelle and also the structure of the micelle itself. Recently, Phillies et al.[19] have carried out a detailed study of Brij-35 micelles in the temperature range 283−343 K using light scattering methods. According to their findings, the micelle interior is divided into three zones; a central anhydrous region, an inner hydrated region containing concentrated surfactant chains and entrapped solvent, and an outer corona containing at least a few surfactant chains through which water is free to move. The chains in this region are sufficiently concentrated as to present an effective entropic barrier preventing other micelles from entering the region but are sufficiently dilute so that solvent flows through the region. Hydrodynamic radius r_M of the micelle encloses the first two regions of the micelle. The radius that encloses all the three regions of the micelles is known as the radius of closest approach and for estimation of parameters such as degree of

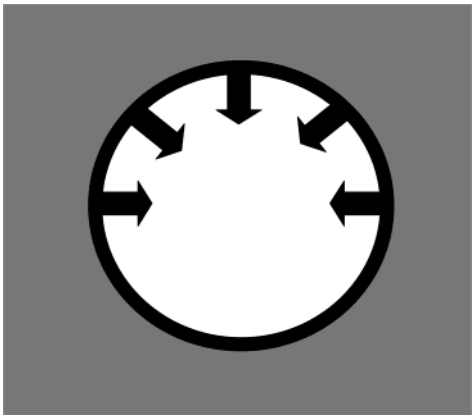

Figure 4. Pictorial depiction of lateral diffusion of the probe molecule inside the micellar surface. The bold arrow represents the probe molecule and the shaded area represents the aqueous phase. The figure, however, does not show the inner region (core) and outer coronal region, which contains at least a few surfactant chains, explicitly.

hydration; water in the outer corona is not included.[19] The aggregation number of Brij-35 micelles is 37 at 283 K and goes up to 44 at 318 K, only at 343 K it increases to 63. The degree of hydration is around 3.7 at 283 K and remains almost the same till 318 K, but decreases to 1.4 at 343 K. The hydrodynamic radius is approximately 44 Å in the temperature range 283−323 K.

Having obtained the physical properties of Brij-35 micelles from literature,[19] now our aim is to establish the location of the probes DMDPP and DPP in these micelles. Observation of single-exponential fluorescence decays at all of the temperatures studied indicates that the probes are located at only one site in the micelles. Nevertheless, such an argument cannot be considered authentic because exceptions to this rule do exist in the literature. Cang et al.[27] have observed that the probe 2-ethylnaphthalene is dynamically partitioned between core and interfacial region of a number of cationic micelles, and despite such partitioning, fluorescence decays were adequately fit to single-exponential functions. However, one of the probes used in the present study DPP is not soluble in hydrocarbon like solvents due to strong intermolecular hydrogen bonding.[28] Hence, it has to be solubilized in the interfacial region of the micelle where it can form hydrogen bonds with the oxyethylene units. Moreover, it was shown in our recent studies involving these probes in TX-100 micelles that the site of solubilization is the interfacial region from the analysis of anisotropy decays. A similar approach will be adopted in case of Brij-35 micelles as well.

From numerous studies available in the literature,[3−10] it has been well established that the biexponential anisotropy decay of the probes observed in micellar systems is not due to the fact that the probe is solubilized in two distinct regions of the micelle nor due to anisotropic rotations of the probe. On the other hand, the observed biexponential decay is due to the probe experiencing different kinds of rotation in micellar media, such a behavior is often explained using the two step model.[29−32] According this model, the probe molecules undergo slow lateral diffusion on the spherical surface of the micelle and also fast wobbling motion in the micelle that are coupled to the rotation of the micelle as a whole. Because the probes used in the present study are hydrophobic by nature, the lateral diffusion does not occur on the surface of the micelle instead it takes place inside the micelle as depicted in Figure 4. The probes move by exchanging positions or by migrating through interstitial sites. The experimentally measured τ_{slow} and τ_{fast} are related to the

TABLE 3: r_M and τ_M Values of Brij-35 Micelles as a Function of Temperature

temp/K	[a] r_M/Å	[b] τ_M/ns	temp/K	[a] r_M/Å	[b] τ_M/ns
283	44	119	303	44	68
288	44	102	313	44	54
293	44	88	323	44	44
298	44	77			

[a] r_M values were taken from ref 19. [b] τ_M values were calculated using eq 5.

TABLE 4: Parameters for the Two-Step Model in Conjunction with Wobbling-in-Cone Model Obtained from Experimental Results for DMDPP

temp/ K	τ_L/ ns	τ_W/ ns	S	θ^o	$D_L \times 10^{10}$/ $m^2\ s^{-1}$	$D_W \times 10^{-8}$/ s^{-1}
283	2.19	0.78	0.76	33.9	14.7	1.17
288	1.78	0.66	0.76	33.9	18.1	1.38
293	1.45	0.57	0.76	33.9	22.3	1.60
298	1.36	0.59	0.64	42.5	23.7	2.26
303	1.22	0.49	0.66	41.1	26.4	2.57
313	0.86	0.32	0.67	40.5	37.5	3.86
323	0.73	0.30	0.61	44.6	44.2	4.79

time constants for lateral diffusion τ_L, wobbling motion τ_W, and the overall rotation of the micelle τ_M by the following equations:

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

$$\frac{1}{\tau_{fast}} = \frac{1}{\tau_W} + \frac{1}{\tau_{slow}} \tag{4}$$

τ_M can be obtained using the Stokes−Einstein-Debye relation[33] with stick boundary condition

$$\tau_M = \frac{\eta V_h}{kT} \tag{5}$$

where V_h is the hydrodynamic volume of the micelle that can be obtained from its hydrodynamic radius, η is the viscosity of water, and k and T are the Boltzmann constant and absolute temperature, respectively. Table 3 gives τ_M values of Brij-35 micelles in the temperature range 283−323 K. The τ_M values decrease from 119 to 44 ns as the temperature is raised from 283 to 323 K. The decrease in τ_M values is solely due to the decrease in the viscosity of water as the hydrodynamic radius of Brij-35 micelle remains the same in this temperature range. These time constants give dynamical information regarding the motion of the probe in the micelle and also that of the micelle itself. However, important information regarding the location of the probe and the structure of the micelle around it can be obtained from the preexponential factor β, which is related to the generalized order parameter S by the following equation:

$$\beta = S^2 \tag{6}$$

The order parameter is a measure of the equilibrium orientational distribution of the probe and satisfies the inequalities $0 \le S^2 \le 1$. If the fast motion is isotropic,[3] $S = 0$, and if it is completely restricted, $|S| = 1$.

The time constants for lateral diffusion, wobbling motion, and the order parameters that were obtained from eqs 3, 4, and 6 are given in Tables 4 and 5 for DMDPP and DPP, respectively. Because the time constants for the overall rotation of the micelle are significantly larger than the τ_{slow} values, τ_{slow} and τ_L are almost identical. τ_L and τ_W values of DPP are significantly longer than that of DMDPP because of the specific interactions between DPP and the oxyethylene groups of the surfactant units. However, these interactions are not strong enough so as to observe the overall rotation of the Brij-35 micelles experimentally. The order parameters for DMDPP are in the range of 0.76 to 0.61 and for DPP this range is 0.83−0.69. The high values of the order parameters reveal that the probes are solubilized in the interfacial region of the micelle, as there is a high degree of order compared to the interior of the micelle. Another observation is that the order parameters of DPP are marginally higher than that of DMDPP, but it is not clear whether any significance can be attached to these minor differences. The order parameters, however, for both the probes decrease upon increasing the temperature indicating that the probes become more mobile at higher temperatures.

TABLE 5: Parameters for the Two-Step Model in Conjunction with Wobbling-in-Cone Model Obtained from Experimental Results for DPP

temp/ K	τ_L/ ns	τ_W/ ns	S	θ^o	$D_L \times 10^{10}$/ $m^2\ s^{-1}$	$D_W \times 10^{-8}$/ s^{-1}
283	3.98	1.17	0.83	28.1	8.1	0.55
288	3.66	1.05	0.80	30.7	8.8	0.73
293	3.08	0.91	0.81	29.8	10.5	0.79
298	2.61	0.84	0.79	31.5	12.4	0.95
303	2.56	0.86	0.73	36.1	12.6	1.18
313	2.16	0.82	0.68	39.7	14.9	1.45
323	1.42	0.52	0.69	39.0	22.7	2.22

The lateral diffusion coefficients[6,7] and the wobbling diffusion coefficients[31] were obtained from the following relations

$$D_L = \frac{r_M^2}{6\tau_L} \tag{7}$$

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

where $x = \cos\theta$ and θ is the semicone angle in the wobbling-in-cone model, which was obtained using the following relation:[3]

$$\theta = \cos^{-1}\left[\frac{1}{2}\{(1+8|S|)^{1/2} - 1\}\right] \tag{9}$$

The values of D_L, D_W, and θ that were calculated using eqs 7, 8, and 9 are also given in Tables 4 and 5, respectively, for DMDPP and DPP. The D_L values increase by a factor of 3 and D_W by a factor of 4 for both the probes as the temperature is raised from 283 to 323 K. It has already been mentioned that there is no change in the size and hydration levels of Brij-35 micelles with an increase in temperature, and hence, the location of the probes inside the micelles remains unchanged. As a consequence, the observed changes in the diffusion coefficients with temperature are only due to variation in the microviscosity of the micelles.

The outcome of this analysis has prompted us to proceed one step further and determine the microviscosity of Brij-35 micelles from the experimentally obtained average reorientation times. The main assumption involved in such an exercise is that the average reorientation time follows Stokes−Einstein−Debye[33] relation as given by eq 5 and η in such a scenario represents the microviscosity of the micelle instead of bulk viscosity of the solvent. But the task of obtaining the hydrodynamic volume of the probes is nontrivial. Hydrodynamic volume for a given

probe is a product of van der Waals volume V, shape factor f, and boundary condition parameter C ($V_h = VfC$). The values of V and f for these probes can be calculated with a reasonable degree of accuracy. However, numerous rotational dynamics studies[21,26,34−39] involving DMDPP and DPP in a variety of solvent systems indicate that the boundary condition parameter is sensitive to the choice of the solvent. For DMDPP, which does not strongly interact with the solvents, the boundary condition parameter in a large solvent like 1-decanol follows slip. It must also be noted that even subslip behavior has been observed in the solvent squalane[38] that is much larger than 1-decanol. Because the rotational motion of these probes in micelles is somewhat restricted, it is not unreasonable to assume that the fragment of the surfactant unit with which the probe molecule is in contact is similar in size to 1-decanol. Hence, the slip boundary condition can be used for the rotation of DMDPP in Brij-35 micelles. In other words, the same hydrodynamic volume that has been obtained for DMDPP in 1-decanol can be used for Brij-35 micelles as well. From the temperature-dependent rotational relaxation studies of DMDPP in 1-decanol,[34] the value of the hydrodynamic volume obtained is 190 Å^3. Using this value for the hydrodynamic volume and from the $\langle\tau_r\rangle$ values at each temperature, microviscosities of Brij-35 were obtained using eq 5 and are given in Table 1. It can be inferred from the table that microviscosity of Brij-35 micelles decreases by over a factor of 3 as the temperature is raised from 283 to 323 K.

There have been reports in the literature that microviscosity determined in this manner is sensitive to the choice of the probe. The plausible reasons for the probe dependency of microviscosity is due to the fact that different probes are located in varied environments of the micelle and also the manner in which the probes interact with their surroundings. For example, in the present study, the average reorientation times of DPP are about a factor of 2 longer than that of DMDPP (compare columns 6 of Tables 1 and 2) because of specific interactions between the surfactant units and the probe even though both these probes are located in the same region of the micelles as evident from the order parameters. It has been demonstrated in a number of our recent publications[21,26,34−37] that the specific interactions between the two secondary amino groups of DPP and hydroxyl and sulfoxide groups of the solvents are responsible for the observed slow rotation times of DPP compared to DMDPP. Experimentally measured reorientation times of DPP in 1-decanol were found to be a factor of 3 longer compared to DMDPP.[26,34] The magnitude of this factor depends on the strength of the interaction between the solute and the solvent, which has been confirmed by our very recent study carried out with DMDPP and DPP in ethanol and 2,2,2-trifluoroethanol.[39] In view of these shortcomings, the hydrodynamic volumes obtained from the rotational relaxation studies of DPP in 1-decanol or any other solvent for that matter cannot be employed to obtain the microviscosities of Brij-35 micelles as has been done in case of DMDPP. In other words, the hydrodynamic volume of a hydrogen bonding probe like DPP obtained from the measured reorientation time varies from solvent to solvent, and its exact value depends on the strength of the interaction between the solute and the solvent. Hence, the probe DPP is not the right choice for determining microviscosities of the micelles. In a nutshell, the probes selected for determining microviscosities should be noninteracting and also their rotational dynamics should be extensively studied in homogeneous solvents in order to have an accurate estimate of the hydrodynamic volume.

Recently, we have studied the rotational diffusion of DMDPP and DPP in TX-100 micelles in the temperature range 283−323 K.[9] However, unlike Brij-35 micelles, the size and degree of hydration of TX-100 micelles increases considerably with an increase in temperature. Despite the differences in the physical properties of these two micelles, a comparison of the dynamics of the probe molecules can be made as both the micelles are nonionic and possess similar hydrophilic groups. The average reorientation times of both DMDPP and DPP are about a factor of 3 longer in TX-100 compared to that in Brij-35 at 283 K and this ratio is about 2 at 323 K. Because in both TX-100 and Brij-35 micelles, the probes are solubilized in the interfacial region, this kind of comparison reveals that the microviscosity of TX-100 is about 2−3 times higher than that of Brij-35.

Conclusions

From the temperature dependent rotational relaxation studies of two structurally similar hydrophobic probes in Brij-35 micelles, the following conclusions can be drawn. The anisotropy decays of both the probes are described by biexponential functions with two time constants. This has been rationalized in terms of slow lateral diffusion and fast wobbling motion of the probes that are coupled to the overall rotation of the micelle. From the high values of the order parameters, it is evident that the probes are located in the interfacial region of the micelles as there is a high degree of order near the interface than in the interior of the micelle. Because the size and degree of hydration of Brij-35 micelles does not change in the temperature range studied, it expected that the location of the probes also remains the same. In view of this, the microviscosity of the micelles has been estimated from the average reorientation times of the noninteracting probe DMDPP, which decreases by a factor of 3 as the temperature increases from 283 to 323 K.

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References and Notes

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