Are the Experimentally Determined Microviscosities of the Micelles Probe Dependent?

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With an intent to address the question posed in the title, rotational diffusion of two dissimilar probes, 2,5-dimethyl-1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DMDPP) and coumarin 6 (C6), has been investigated in small aqueous micelles formed with the surfactants sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), 2-phenyldodecanesulfonate (2-PDS), 3-phenyldodecanesulfonate (3-PDS), 4-phenyldodecanesulfonate (4-PDS), and 6-phenyldodecanesulfonate (6-PDS) using the time-resolved fluorescence depolarization method. The decay of anisotropy for both the probes in all the micelles could be adequately described by a sum of two exponentials with slow and fast time constants. These results have been rationalized on the basis of a two-step model consisting of fast-restricted rotation of the probe and slow lateral diffusion of the probe in the micelle that are coupled to the overall rotation of the micelle. From the order parameter values it has been established that the probes are located in the stern layer of the micelles. Microviscosities of the six micelles have been obtained from the average reorientation times of the probes in micelles and it has been observed that both the probes sense almost identical microviscosity for a given micelle.

1. Introduction

Microviscosity is one of the important internal properties of a micelle and hence considerable effort has been directed toward its "measurement" during the last few decades.[1−24] Despite numerous studies by a large number of research groups, a true mastery in the experimental determination of this quantity has not been attained, necessitating fresh investigations. Fluorescence,[1−20] ESR,[21−23] and NMR[24] are among the prominent spectroscopic methods employed by the researchers to determine the microviscosity of the micelles. Fluorescence spectroscopy utilizes photophysical properties of the fluorescent probe, introduced into the micellar system in micromolar concentrations, which are sensitive to the microenvironment surrounding the probe. The fluorescence methods comprise measuring either the relative intensities of monomer to excimer emission of the probe or the depolarization of the fluorescence, and probes have been chosen according to the property that is being monitored.

Pownall and Smith[2] have used intermolecular excimer formation of pyrene to determine the microviscosities of micelles formed with the surfactants, alkyltrimethylammonium bromides of varying alkyl chain lengths and found that the measured microviscosities of these micelles are an order of magnitude higher than those determined by Shinitzky et al.[1] who employed the fluorescence depolarization method. The excimer formation method relies on the translational diffusion of the pyrene molecules to form the excited dimer, which is sensitive to the viscosity of the surrounding medium. Rodgers and Wheller[6] have mentioned that viscosity, which characterizes translational motion, is much higher than the viscosity that describes the rotational diffusion and as a consequence the intermolecular excimer formation method senses higher microviscosities compared to the fluorescence depolarization method. In a latter study, Emert et al.[9] have used intramolecular excimer forming probes and obtained microviscosities that are comparable to those reported by Shinitzky et al.[1] According to them, in the case of the intermolecular excimer formation method, the probe molecules may or may not distribute themselves among the available micelles in a manner that is accurately described by the statistical methods. Hence this method presents difficulties of explicitly including the distribution of the probe molecules in the determination of micelle parameters from the experimental quantities. A subsequent study by Turro et al.[10] employed a similar probe, which also facilitates the formation of intramolecular excimer and substantiated the results of Emert et al.[9] Even though there seemed to be an agreement between the order of the microviscosities obtained using both intramolecular excimer formation and fluorescence depolarization methods, an exact match between microviscosities determined with two different probes using the same technique has proved to be elusive. To illustrate this fact, Zachariase[8] obtained microviscosity values for sodium dodecyl sulfate (SDS) micelles at 293 K with the probes diphenylpropane and dipyrenylpropane, respectively, as 4 and 19 mPa s. The differences in the values obtained are rationalized on the basis of nonisotropic microviscosity of the SDS micelle. The smaller molecule, diphenylpropane can move in a more fluid part of the micelle interior, whereas the movements of the larger dipyrenylpropane are determined by the less fluid parts of the SDS micelle. The data obtained with the fluorescence depolarization method are also not exempt from such discrepancies. The microviscosity values of cetyltrimethylammonium bromide (CTAB) micelles reported by Shinitzky et al.[1] with the probes 2-methylanthracene (2MA) and perylene differ by a factor of 1.5. The smaller values of microviscosity recovered in the case of perylene compared to 2MA have been ascribed to the longer fluorescence lifetime of perylene, and hence the measured steady-state anisotropy with perylene has a contribution from the rotation of the micelle as well. The two instances mentioned here merely exemplify the inconsistencies present in the reported microviscosity values and

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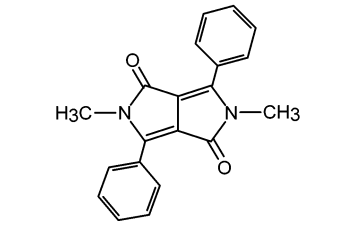
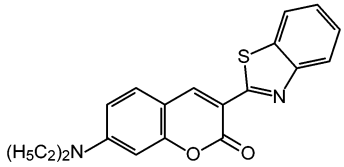


DMDPP



Coumarin 6

Figure 1. Molecular structures of the probes.

are by no means exhaustive. For detailed information, the reader is advised to go through the literature provided.[1−20]

The large variations present in the values of microviscosities reported in the literature has led to the criticism of the concept itself.[13,25,26] Such a censure stems from the fact that different probes are preferentially located in varied environments in a micelle and therefore sense different values of the microviscosity. Another objection to the concept of microviscosity concerns the presence of a probe, which perturbs the surroundings of the micelle and hence reports the microviscosity that is far from being ideal. Despite these pitfalls and criticisms, microviscosity is a very useful concept to get a better appreciation of many chemical reactions that transpire in organized media and consequently needs to be reexamined with the aid of novel probes and improvised methodologies. The present investigation is an endeavor in that direction.

One of the central issues this report is going to focus on is to quell the misconceptions concerning the concept of microviscosity and we hope to accomplish this objective by adopting the following strategy. In this work, rotational diffusion of a nondipolar probe, 2,5-dimethyl-1,4-dioxo-3,6-diphenylpyrrolo-[3,4-*c*]pyrrole (DMDPP) and a dipolar probe, coumarin 6 (C6) (see Figure 1 for molecular structures of the probes) will be studied in small aqueous micelles using the time-resolved fluorescence depolarization method. These two probes have been chosen because they are similar in size but distinct in shape and their rotational dynamics has been comprehensively investigated in homogeneous solvents[27−36] and in the isotropic phase of a liquid crystal.[37] Moreover, rotational relaxation of DMDPP together with its hydrogen bonding counterpart, 1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DPP) has also been studied in nonionic micelles[20,38,39] and reverse micelles.[40] One of the observations from these extensive sets of investigations[20,27−40] is that the probes DMDPP and C6 do not experience specific interactions with the surrounding medium in such a way that their rotational motion is impeded. In view of their noninteracting and hydrophobic nature, the probes are expected to be located in the same region of the micelle and hence report identical microviscosity. The studies will be carried out in two of the most commonly employed micelles; SDS and CTAB and also in micelles formed with the surfactant phenyldodecanesulfonate (PDS). Depending on the position of the phenyl group, PDS can have surfactants with differing alkyl chain lengths. In the present study, the surfactants 2-phenyldodecanesulfonate (2-PDS), 3-phenyldodecanesulfonate (3-PDS), 4-phenyldodecanesulfonate (4-PDS), and 6-phenyldodecanesulfonate (6-PDS) are being used and it must be noted that the sizes of the PDS micelles vary with the position of the phenyl group. Besides trying to ascertain whether a unique value of microviscosity can be obtained for a given micelle by employing two different probes, we are also curious to find out how the internal environment of a micelle is influenced by the marginal increase in the radii of the micelles. It will be interesting to find out whether the microviscosities sensed by the probes DMDPP and C6 for a given micelle would be identical. The remainder of the paper is organized in the following manner. Section 2 describes the experimental methods used to measure the rotational diffusion of the probes in the micelles. Results are presented in section 3 and are discussed in section 4. The conclusions of this work are summarized in the final section.

2. Experimental Section

The probes DMDPP and C6 are from Ciba Specialty Chemicals Inc., and Aldrich, respectively, whereas the surfactants SDS and CTAB are from Gibco Life Technologies and Hopkin & Williams, respectively. The PDS surfactants are a gift from Prof. G. J. T. Tiddy of the University of Manchester Institute of Science and Technology, England, routed through my friend the late Dr. V. J. P. Srivatsavoy. The counterions of the PDS surfactants are made up of sodium ions and the only exception is 2-PDS, which has K^+ as the counterion. 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 micelle samples. The concentrations of the surfactants were 50 mM for SDS, 3-PDS, 4-PDS, and 6-PDS, and for CTAB and 2-PDS it was 15 mM. The probe molecules were dissolved in the micelle solutions by gentle heating in a water bath and it was ensured that the concentrations of the probes were in the range $10^{-5}-10^{-6}$ M.

Time-resolved fluorescence depolarization measurements were carried out using the time-correlated single-photon counting[41] facility at the Tata Institute of Fundamental Research, Mumbai, and details of the system have been described elsewhere.[28] 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 C6 were excited at 460 nm with a vertically polarized pulse. The decay of the anisotropy was monitored by measuring the fluorescence decays parallel $I_{||}(t)$ and perpendicular $I_{\perp}(t)$ with respect to the polarization of the excitation source. Fluorescence decays $I(t)$ at the magic angle (54.7°) orientation of the emission polarizer were also collected for the determination of lifetimes. The emission in all three cases was monitored at 550 nm. 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 either 20 or 40 ps/ch. Each measurement was repeated at least two to three times with the same sample and the average values are reported. All the measurements were performed at 298 K and the sample temperature was maintained 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 C6 in micelles were obtained from the measured fluorescence decays and the instrument response function, by the iterative reconvolution method using Marquardt algorithm, as described by Bevington.[42] Likewise, the anisotropy decay parameters were obtained by simultaneous fit[43,44] of parallel $I_{||}(t)$ and perpendicular $I_{\perp}(t)$ components. The criteria

TABLE 1: Anisotropy Decay Parameters of DMDPP and C6 in Micelles

	β		τ_{slow}/ns		τ_{fast}/ns		$\langle\tau_r\rangle$/ns[a]	
micelle	DMDPP	C6	DMDPP	C6	DMDPP	C6	DMDPP	C6
SDS	0.24 ± 0.01	0.22 ± 0.01	1.14 ± 0.04	2.89 ± 0.01	0.28 ± 0.02	0.68 ± 0.01	0.49 ± 0.03	1.17 ± 0.04
CTAB	0.52 ± 0.02	0.68 ± 0.01	1.07 ± 0.05	2.25 ± 0.03	0.33 ± 0.03	0.72 ± 0.02	0.71 ± 0.06	1.76 ± 0.04
2-PDS	0.38 ± 0.02	0.63 ± 0.04	1.29 ± 0.02	2.05 ± 0.15	0.36 ± 0.02	0.62 ± 0.18	0.71 ± 0.04	1.52 ± 0.22
3-PDS	0.46 ± 0.03	0.63 ± 0.02	1.22 ± 0.10	2.11 ± 0.10	0.36 ± 0.02	0.70 ± 0.07	0.76 ± 0.08	1.59 ± 0.12
4-PDS	0.48 ± 0.02	0.70 ± 0.04	1.25 ± 0.02	1.87 ± 0.07	0.29 ± 0.01	0.49 ± 0.07	0.75 ± 0.04	1.46 ± 0.13
6-PDS	0.47 ± 0.03	0.64 ± 0.01	1.29 ± 0.01	1.95 ± 0.01	0.32 ± 0.03	0.62 ± 0.04	0.78 ± 0.05	1.47 ± 0.04

[a] Calculated using eq 2.

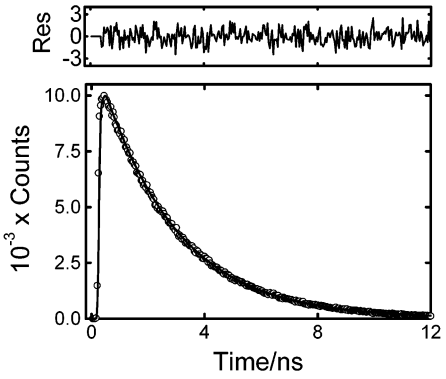


Figure 2. Fluorescence decay of C6 (○) in SDS micelles at 298 K. The smooth line through the data points is the fitted one to the single-exponential function, and the lifetime is 2.61 ns. The instrument response function whose full width at half-maximum is about 40 ps is not shown in the figure for the sake of clarity. The upper panel represents the residual distribution for the single-exponential fit.

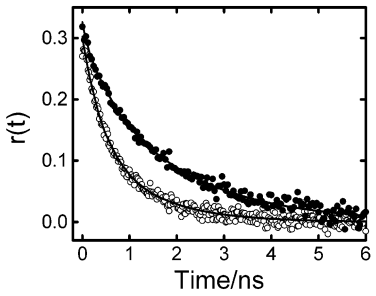


Figure 3. Anisotropy decays of DMDPP (○) and C6 (●) in CTAB micelles at 298 K. The smooth lines passing through the points are the fitted ones. Notice that the average reorientation times of C6 are about 2.5 times longer than that of DMDPP, which is not because of any specific interaction between the probe and the micelle but due to larger hydrodynamic volume experienced by C6 owing to its shape factor and boundary condition parameters.

for a good fit were 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[38] and hence we refrain from further discussion.

3. Results

The fluorescence decays of both DMDPP and C6 in all the micelles studied could be adequately described by single exponential functions. Figure 2 gives the fluorescence decay of C6 in SDS micelles together with the residual distribution, which is random, indicating that, the decay can indeed be described by a single exponential function with one lifetime. The lifetimes of DMDPP and C6 are around 8.30 and 2.60 ns, respectively, and are almost independent of the nature of the micelle.

In contrast, a sum of two exponentials are needed to describe the anisotropy decays whose functional form is given by[45]

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

where τ_{slow} and τ_{fast} are the two reorientation times of the probe in the micelle and β is a preexponent, which gives the relative contributions of the slow and fast components. r_0 is zero-time anisotropy and is a measure of the inherent depolarization of the probe molecule. It has been observed that the limiting anisotropy values obtained from the time-resolved experiments for both the probes in micelles were found to be 5−25% smaller than the true r_0 values obtained from the steady-state anisotropy measurements in highly viscous media[27,31] due to some rapid depolarization of the fluorescence, which is beyond the time resolution of our single-photon counting setup. The anisotropy decay parameters of both the probes in all the micelles are given in Table 1. Inspection of the table reveals that the ratio of τ_{slow} to τ_{fast} for both DMDPP and C6 are in the range 3−4. The average reorientation times $\langle\tau_r\rangle$, which were obtained using the following expression, are also given in the table. $\langle\tau_r\rangle$ is often used to compare the anisotropy decays, as it is a model independent parameter.

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

Although both the probes are of comparable size, the average reorientation times of C6 are about a factor of 2.0 or more, longer than those of DMDPP in all the micelles. This fact has been illustrated in Figure 3, which gives the anisotropy decays of DMDPP and C6 in CTAB micelles. The longer $\langle\tau_r\rangle$ values observed in the case of C6 compared to DMDPP are not because of any specific interactions between C6 and the micelles but due to larger hydrodynamic volume experienced by C6 owing to its shape factor and boundary condition parameters. This aspect will be explained in detail later during the course of the discussions.

4. Discussion

The fact that two time constants have been recovered from anisotropy decays of the probes in micelles indicates the necessity to consider the following options. It is possible that the probe molecules are experiencing anisotropic rotational diffusion along different symmetry axes. Another reason could be that they are located in two distinct regions of the micelle, the core and the stern layer. Because the probes are hydrophobic, they cannot be solubilized in the aqueous phase of the micelle. We can rule out the possibility of anisotropic rotational diffusion of the probes on the basis of our earlier work in isotropic solvents[28,31,36] where time-resolved measurements have been performed. In these studies, it has been observed that decay of anisotropy of the probes could be satisfactorily described by single exponential functions. For the probes to be located in

TABLE 2: Hydrodynamic Radii and Reorientation Times of the Micelles Used in the Study

micelle	r_M/Å[a]	τ_M/ns[b]
SDS	19.4	6.6
CTAB	25.7	15.4
2-PDS	24.2	12.8
3-PDS	22.9	10.9
4-PDS	21.6	9.1
6-PDS	19.1	6.3

[a] r_M value for SDS and CTAB are from refs 61 and 26, respectively. For the PDS series, the core radius was obtained using eq 2 of ref 62 and the shell thickness was taken to be 10 Å as determined in ref 63. [b] τ_M values were calculated using eq 5.

two distinct regions of the micelle, a two-exponential fluorescence decay with two lifetimes should have been observed. But on the contrary only one lifetime is observed for each probe, which rules out the possibility that the probes are solubilized in two separate locations of the micelle. Yet, such an argument cannot be considered indisputable, as exceptions to this rule do exist. A recent study by Cang et al.[46] indicates that the probe 2-ethylnaphthalene is dynamically partitioned between two regions of a number of cationic micelles. Despite such partitioning, fluorescence decays were adequately described by single-exponential functions, the reason being the exchange of the probe between the two regions of the micelle is faster than its lifetime. However, for the systems investigated in the present work, concrete evidence for the location of the probes will be provided from the analysis of the anisotropy decays using the two-step model.[47−50]

By now, it has been firmly established from numerous studies[20,26,38−40,51−56] that the observed biexponential anisotropy decay of the probes in micelles is not a consequence of the probe molecule residing at two different sites inside a micelle but due to different kinds of motion experienced by it. According to the two-step model, the probe molecule depending on its position, undergoes slow lateral diffusion at or near the interface of the micelle and also fast wobbling motion in an imaginary cone described by semiangle θ. These two motions are coupled to the rotation of the micelle as a whole. On the basis of the assumption that the fast and slow motions are separable, the experimentally obtained slow and fast reorientation times are related to the time constants for lateral diffusion τ_L, wobbling motion τ_W, and rotation of the micelle as a whole τ_M by the following relations.

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

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

The time constant for the overall rotation of the micelle has been obtained by using Stokes−Einstein−Debye (SED) hydrodynamic theory with the stick boundary condition.[57]

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

where η is the viscosity of the medium in which the rotation of the micelle is taking place and V_h is the hydrodynamic volume of the micelle obtained from the hydrodynamic radius of the micelle r_M. k and T are the Boltzmann constant and absolute temperature, respectively. The hydrodynamic radii of the six micelles employed in this study together with the τ_M values calculated using eq 5 are given in Table 2. In these calculations, η was taken as the viscosity of water. Because the calculated reorientation times of the micelles are sensitive to their radii, there is a significant difference in the τ_M values obtained for 2-PDS and 6-PDS micelles.

τ_L and τ_W values obtained for the two probes in different micelles are given in Table 3. In addition to the dynamical information of the probe in the micelle, the average micelle structure in the vicinity of the probe can be obtained from the order parameter S, which is related to β by the following relation.

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

Table 3 also lists the order parameters obtained for both the probes in all the micelles studied and it can be inferred from the table that the order parameters are in the range 0.5−0.8. Such high values obtained for the order parameters are an indication that the probes are located closer to the interface rather than the interior of the micelles because there is a higher degree of order near the interface. This argument can be further substantiated due to the fact that aromatic probes are preferentially solubilized in the stern layer of a micelle.[58] The order parameters obtained for DMDPP and C6 in a given micelle are almost similar, which suggests that both of them are located in the same region of a micelle. The following relation has been used to obtain the semi cone angle θ from the order parameters.[47]

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

From these parameters, diffusion coefficients for lateral diffusion D_L and wobbling motion D_W have been obtained with the help of the following relations[26,50]

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

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

where $x = \cos\theta$. Lateral diffusion coefficients and wobbling diffusion coefficients thus obtained are also given in Table 3.

TABLE 3: Parameters for the Two-Step Model in Conjunction with the Wobbling-in-Cone Model Obtained for Different Micelles from the Analysis of the Anisotropy Decays for DMDPP and C6

	τ_L/ns		τ_W/ns		S		θ (deg)		$10^{10}D_L$/m^2 s^{-1}		$10^{-8}D_W$/s^{-1}	
micelle	DMDPP	C6	DMDPP	C6	DMDPP	C6	DMDPP	C6	DMDPP	C6	DMDPP	C6
SDS	1.38	5.14	0.37	0.89	0.49	0.47	52.5	53.8	4.5	1.2	4.92	2.11
CTAB	1.15	2.63	0.48	1.06	0.72	0.82	36.9	29.0	9.6	4.2	2.19	0.65
2-PDS	1.43	2.44	0.50	0.89	0.62	0.79	43.9	31.5	6.8	4.0	2.80	0.90
3-PDS	1.37	2.62	0.51	1.05	0.68	0.79	39.7	31.5	6.4	3.3	2.34	0.76
4-PDS	1.45	2.35	0.38	0.66	0.69	0.84	39.0	27.2	5.4	3.3	3.05	0.93
6-PDS	1.62	2.82	0.43	0.91	0.69	0.80	39.0	30.7	3.8	2.2	2.70	0.84

TABLE 4: van der Waals Volumes and Hydrodynamic Volumes of DMDPP and C6 Calculated with Slip Boundary Condition Together with the Ones Obtained from the Measured Reorientation Times in Different Solvents

volume	DMDPP[a]	C6[b]
V/Å^3	281	303
V_h(slip)/Å^3	183	436
V_h(dodecane)/Å^3	–	429
V_h(hexadecane)/Å^3	197	451
V_h(decanol)/Å^3	199	–

[a] From ref 27. [b] From ref 31.

The D_L values are in the range $(1.2-9.6) \times 10^{-10}$ m^2 s^{-1} and the D_W values $(0.65-4.92) \times 10^8$ s^{-1} and their ranges are in agreement with the ones obtained for noninteracting probes of similar size in small micelles.[26,51]

Having accounted for the location and dynamics of the probe molecules in micelles using the two-step model, we now turn our attention to the central theme of this work, which is to estimate the microviscosity of the micelles. Microviscosity can be obtained from the average reorientation time under the assumption that $\langle\tau_r\rangle$ follows SED relation. However, two issues need to be circumvented to achieve this objective. First, experimentally obtained $\langle\tau_r\rangle$ has two contributions, one due to the rotation of the probe in the micelle and the other due to the rotation of the micelle itself. The contribution of τ_M becomes important especially when the size of the micelle is small and the rotation of the probe is comparable to its time scale. The average reorientation time due to the rotation of the probe in the micelle $\langle\tau_r\rangle_P$ has been obtained using the following relation.

$$\frac{1}{\langle\tau_r\rangle} = \frac{1}{\langle\tau_r\rangle_P} + \frac{1}{\tau_M} \tag{10}$$

In view of the fact that the rotation of the micelle also contributes to the depolarization of the fluorescence of the probe, it must be emphasized that $\langle\tau_r\rangle_P$, rather than $\langle\tau_r\rangle$, should be used in the estimation of the microviscosities.

Another issue that needs due attention is the determination of hydrodynamic volume of the probes because the probes used in the study are not spherical. As a first step in that direction, van der Waals volumes of both DMDPP and C6 were obtained using Edward's increment method[59] and are found to be 281 Å^3 and 303 Å^3, respectively. The axial radii of both DMDPP and C6 were estimated with the aid of Corey−Pauling−Koltum (CPK) scaled atomic models and the reorientation times with stick and slip[60] hydrodynamic boundary conditions were calculated by treating them as asymmetric ellipsoids. Details of the calculations have been presented elsewhere.[27,31] The hydrodynamic volumes obtained for both the probes with slip boundary condition are given in Table 4. It is obvious from the table that even though the van der Waals volumes of the two probes do not vary by more than 8%, the hydrodynamic volume of C6 calculated with slip boundary condition is a factor of 2.4 larger than that of DMDPP. The reason for such a large differences in the V_h values of the two probes is due to their distinct shapes, which in turn determine the shape factors and boundary condition parameters. Hydrodynamic volume is a product of van der Waals volume V, shape factor f, and the boundary condition parameter C_{slip} and is given by the relation, $V_h = VfC_{slip}$.

Now the important question that needs to be answered is how real are these theoretically calculated numbers. To answer this question, hydrodynamic volumes obtained from the experimentally measured reorientation times in noninteracting solvents such as hexadecane and 1-decanol for DMDPP and deodecane and hexadecane for C6 are also given in Table 4. It is evident from the table that the hydrodynamic volumes experienced by the probes in large noninteracting solvents are in good agreement with the ones obtained using the slip boundary condition for both the probes. This exercise confirms that the hydrodynamic volumes calculated using the SED theory match with the "true" hydrodynamic volumes experienced by DMDPP and C6 in these solvents. However, it must be noted that the boundary condition parameter and hence the hydrodynamic volume for these probes are sensitive to the size of the solvent.[29,30,35] In such a scenario, whether the hydrodynamic volumes experienced by the probes DMDPP and C6 in micelles would be similar to the ones obtained in large noninteracting solvents and the calculated hydrodynamic volumes with slip boundary condition can be employed to obtain the microviscosities. The answer to this question is affirmative because the probe molecules are undergoing somewhat restricted rotation in the micelles and under such circumstances, the fragment of the surfactant unit with which the probe molecule is in contact cannot be larger than the solvents such as 1-decanol or hexadecane. A similar justification has been used by us to obtain the microviscosities of Brij 35 micelles with the probe DMDPP recently.[20] In view of the arguments presented, we have employed the hydrodynamic volumes calculated with slip boundary condition, average reorientation times of the probes in micelles and obtained the microviscosities (η_m) of the micelles with the aid of the following SED relation.

$$\eta_m = \frac{\langle\tau_r\rangle_P kT}{V_h} \tag{11}$$

TABLE 5: Microviscosities of the Micelles Obtained from the Average Reorientation Times of the Probes in Micelles

	η_m/mPa s	
micelle	DMDPP	C6
SDS	11.9	13.4
CTAB	16.6	18.8
2-PDS	16.9	16.2
3-PDS	18.4	17.5
4-PDS	18.4	16.4
6-PDS	20.0	18.1

The microviscosities obtained in this manner with two different probes in six micelles are given in Table 5. The η_m values determined using DMDPP and C6 for a given micelle are almost identical within the limits of experimental error. In other words, the microviscosity of a micelle is independent of the probe that is employed. The η_m values reported here, however, correspond to that of the stern layer of the micelles, as both the probe molecules are solubilized in that region and not in the core of the micelles. This is the reason there is almost no change in the microviscosity of the PDS micelles irrespective of their size. At this juncture, it is tempting to compare the microviscosities of SDS and CTAB micelles determined by us to those available in the literature, but we refrain from doing so because most of the data available in the literature have either been obtained with a single probe or mostly probe dependent when more than one probe has been employed.

In light of these results, it is pertinent to discuss why the microviscosities obtained until now were found to be probe dependent. Because we have employed the fluorescence depolarization method to obtain the microviscosities, it is more logical to compare the results determined with this method rather than with intermolecular or intramolecular excimer formation

methods. From the survey of the literature, it has been noticed that in a majority of the studies the steady-state fluorescence depolarization method and Perrin's[45] equation have been used to obtain η_m. However, Perrin's equation is valid only when the anisotropy of the probe decays with one time constant and it has been observed in numerous time-resolved studies that anisotropy decays of a number of probes in micelles follow two-exponential functions. Another reason for the observed probe dependency of the microviscosity of the micelles is that some of the studies employed chemically dissimilar probes that not only solubilized in different regions of a micelle but were also found to be strongly interacting with the surrounding environment. In such a scenario, hydrodynamic volume of the probe cannot be obtained from the calibration curves in solvents of comparable viscosities, as its magnitude depends on the strength of the interaction between the solute and the solvent.[36] On the basis of the outcome of this study, we can suggest that the probes chosen for the determination of microviscosity of the micelles should not strongly interact with the surroundings. Moreover, their rotational dynamics should be thoroughly investigated in isotropic media so that their hydrodynamic volumes and also their ability to interact with the surroundings can be properly assessed. In addition to these two precautions, the location of the probes in the micelles should be properly ascertained. By following these guidelines, we believe that microviscosities of the micelles can be determined that are independent of the probe.

4. Conclusions

In the case of Newtonian liquids, the perception of viscosity is clearly conceptualized and experimental methods for its measurement are readily available. However, for microheterogeneous systems such as micelles, the concept of fluidity or microviscosity is not clearly understood and methods to determine this property are still in infancy. Even though fluorescence methods have often been employed to measure the microviscosity of the micelles, the η_m values thus obtained are found to be probe dependent. In an attempt to find out whether one can circumvent this predicament involving the probe dependency of the measured microviscosity of micelles, the present study has been undertaken and the important conclusions are as follows. In this study rotational diffusion of two dissimilar probes, a nondipolar probe DMDPP and a dipolar probe C6, has been investigated in six different micelles using the time-resolved fluorescence depolarization method. The observed biexponential anisotropy decays of the probes in micelles have been explained with the aid of the two-step model consisting of fast-restricted rotation of the probe and slow lateral diffusion of the probe in the micelle. The location of the probes is ascertained from the order parameters, which is the stern layer of the micelles for both the probes employed in this study. The microviscosities of the micelles have been estimated with the help of the SED hydrodynamic theory from the average reorientation times and also using realistic values for the hydrodynamic volumes of the probes. The microviscosities determined in this manner were found to be independent of the probe for a given micelle and to the best of our knowledge such a result has not been obtained previously.

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