Fluorescence Dynamics of Dye Probes in Micelles

Nakul C. Maiti, M. M. G. Krishna, P. J. Britto, and N. Periasamy*

Chemical Physics Group, Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400 005, India
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The fluorescence depolarization dynamics of organic fluorescent dye probes (nile red, cresyl violet, DODCI, rhodamine B, and rhodamine DPPE) were studied in cationic, anionic, and neutral micelles by picosecond time-resolved single-photon-counting technique. The fluorescence anisotropy decay of the dye intercalated inside the micelle is a two-exponential function. The anisotropy decay was interpreted by using a model of rotational (wobbling) and translational diffusion of the dye in the micelle coupled with the rotational motion of the micelle as a whole. The rotational and translational diffusion coefficients of the dye, the order parameter, and the semicone angle for the wobbling diffusion in the micelle were determined. The concept of “microviscosity” in the micelle was critically discussed in the light of the rotational and translational diffusion coefficients and their temperature dependence.

Introduction

The depolarization of fluorescence of organic dye molecules in liquids is one of the powerful techniques for the investigation of the tumbling or rotational motion of the molecule on the picosecond to nanosecond time scale.1 The fluorescence anisotropy decay for a number of organic dye molecules was found to be single exponential in pure solvents,2−11 and the rotational dynamics of the molecule resembles that of an ellipsoid or a sphere. There are also a few reports where the anisotropy decay in liquids was found to be biexponential.12−15 In general, the rotational diffusion coefficient is inversely related to the viscosity of the solvent by the Stokes−Einstein equation for neutral molecules or the Debye−Stokes−Einstein equation for charged molecules. In microheterogeneous media such as micelles and membranes the rotational dynamics of the dye is fundamentally different from that in homogeneous media in two aspects. First, the existence of an aqueous/nonaqueous interface leads to an orientationally nonrandom equilibrium distribution of the molecules, and second, the molecular dynamics is highly restricted. Understanding the fluorescence dynamics in microheterogeneous media such as micelles is helpful for the interpretation of time-resolved fluorescence dynamics in complex but important biological systems.

An organic molecule is readily soluble in an aqueous micellar solution because of the favorable (hydrophobic) sites for solubilization in the micellar aggregate.16−18 It is well established that the site of solubilization is near the interface for a wide variety of organic molecules.19−21 The fluorescence anisotropy decay of the organic molecule is directly related to the reorientation dynamics of the excited molecules and hence best suited for the investigation of local molecular dynamics near the site. A unique feature of the nanometer size micelle is the fluorescence depolarization as a result of reorientation due to translational motion of the molecule along the surface. In homogeneous media and in planar membranes the translational motion of the molecule does not reorient the molecule. Previous studies have considered various models for the reorientation dynamics of the molecule inside the micelle.22−26 All these studies, except that of Que et al.,26 ignore the contribution of translational motion to the anisotropy decay. The fluorescence anisotropy decay of a fluorescent molecule in a spherical micelle is best described by a model of restricted rotational motion of dye (wobbling-in-cone model) coupled with translational motion on the surface and rotation of the whole micelle. This model is used in the present study of fluorescence anisotropy decay of five organic dye probes in cationic, anionic, and neutral micelles.

The fluidity of organized molecular assemblies such as micelles and membranes are frequently estimated by the quantitative parameter called microviscosity.16,17,27,28 The concepts involved in the estimation of microviscosity in micelles are the same as those for the estimation of viscosity in pure liquids, namely, applicability of Stokes−Einstein equations for the translational and rotational diffusion coefficients. The concept of microviscosity has been critically discussed in the light of the diffusion coefficients for the organic probes in micelles.

Experimental Section

Materials. Laser grade dyes, nile red, cresyl violet perchlorate (CV), 3,3′-diethyloxadacarbocyanine iodide (DODCI), and rhodamine B were used as received from Exciton, Inc. Rhodamine labeled with a lipid, rhodamine-DPPE, was purchased from Molecular Probes. Figure 1 shows the chemical structures of the five dyes. The fluorescence decays of these dyes in methanol were single exponential, indicating the purity of the dye. Sodium docetyl sulfate (SDS) (Sigma Chemical Co.), cetyltrimethylammonium bromide (CTAB) (Aldrich Chemicals), and Triton-X 100 (TX) Sigma Chemicals) were checked to be fluorescence-free and used as received. Micellar samples were prepared by stirring the dye in warm solutions of surfactant in deionized water for about 1 h.

Fluorescence decays were measured using a picosecond laser coupled with a time-correlated single-photon-counting (TCSPC) spectrometer described previously.29,30 The fluorescence decays were obtained for three orientations of the emission polarizer: magic angle of 54.7° and parallel and perpendicular orientations with respect to the excitation polarization. Typically, the peak count in the fluorescence decays was (1−2) × 104 for lifetime measurements and (2−3) × 104 for anisotropy decays. The perpendicular component of the fluorescence decay was corrected for the G-factor of the spectrometer, which was determined31 as follows. The G-factor (defined as the ratio of the sensitivities of the spectrometer for parallel and perpendicular

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* Author for correspondence. Fax: 091 22 215 2110/2181. email: peri@tifrvax.tifr.res.in.
polarization of light) was determined using cresyl violet in methanol ($\tau_f = 3.23$ ns, $\tau_r = 130$ ps) for which the fluorescence emission is practically depolarized at times greater than 1 ns after excitation. The $G$-factor is the ratio of the collection times for which the tails of the fluorescence decays of parallel and perpendicular components match exactly. Steady-state anisotropy measurements were done using a Shimadzu RF-540 spectrofluorimeter.

Fluorescence Decay Data Analysis. The fluorescence decays were fitted to the appropriate mathematical functions by the standard iterative method of convolution with instrument response function and comparison with raw data until the good fit criteria (lowest value for reduced $\chi^2$ and random distribution of weighted residuals) were attained.\textsuperscript{32} The parameter values were adjusted in successive iterations based on the Levenberg-Marquardt method.\textsuperscript{33,34}

The fluorescence decay at magic angle polarization was fitted to a single exponential to get the lifetime. In a few cases (CV and rhodamine B) or two forms of the dye in the micelle (DODCI) and $\alpha$ is the fractional intensity associated with $\tau_f$.

Parallel and perpendicular components of fluorescence decays were fitted simultaneously\textsuperscript{35,36} to eqs 2 and 3 in all cases except those cases where the dye is distributed in two phases.

\begin{equation}
I_\parallel(t) = \frac{1}{3}I(t)[1 + 2r(t)]
\end{equation}

\begin{equation}
I_\perp(t) = \frac{1}{3}I(t)[1 - r(t)]
\end{equation}

where $r(t)$ is the anisotropy decay. The basic approach to the fitting strategy has been discussed in detail before.\textsuperscript{7} An additional criterion used in the present work is to seek agreement between the values of steady-state anisotropy measured in an independent experiment and the value calculated from the anisotropy decay parameters using eq 5, 7, or 10. In pure solvents (water and $n$-butanol) $I(t)$ is a single exponential and $r(t)$ is also a single exponential (eq 4):

\begin{equation}
r(t) = r_0 \exp(-t/\tau_r)
\end{equation}

Figure 1. Molecular structure of dyes.
\[ r_{ss} = r_0 \tau_s (r_1 + \tau_f) \]  

In cases where the dye is present only in the micelle, \( f(t) \) is a single exponential and \( r(t) \) is biexponential (eq 6).

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

Data analysis using eqs 2 and 3 and eq 6 for \( r(t) \) requires optimization of nine parameters (\( \tau_s, r_0, \tau_{slow}, \tau_{fast}, \beta, \) two scale factors, and two shift parameters). Of these \( \tau_s \) is known from the analysis of decay at magic angle polarization, and this value was fixed in the analysis. Fixing \( \tau_s \) helps to recover reproducible values for the anisotropy decay parameters. \( r_{ss} \) is calculated using eq 7.

\[ r_{ss} = r_0 [\beta \tau_{slow} (r_1 + \tau_{slow}) + (1 - \beta) \tau_{fast} (r_1 + \tau_{fast})] \]  

In the case of CV in CTAB or TX and rhodamine B, the dye is distributed in two phases. Equations 8 and 9 are used to fit the polarized fluorescence decays.

\[ I_{\parallel}(t) = \alpha (1/3) I_1(t) [1 + 2 r_1(t)] + (1 - \alpha) (1/3) I_2(t) [1 + 2 r_2(t)] \]  
\[ I_{\perp}(t) = \alpha (1/3) I_1(t) [1 - r_1(t)] + (1 - \alpha) (1/3) I_2(t) [1 + r_2(t)] \]  

\( \alpha \) is the fractional intensity in water, \( I_1(t) \) and \( I_2(t) \) are the intensity decays, and \( r_1(t) \) and \( r_2(t) \) are the anisotropy decays in water and micelle. In these cases the fluorescence decay (at magic angle polarization) is biexponential (eq 1), and thus, \( I_{\parallel}(t), I_{\perp}(t), \) and \( \alpha \) in eqs 8 and 9 are known. Further, the anisotropy decay function of \( r(t) \) for the aqueous phase can be determined independently. Fixing all these parameters (\( \alpha, \tau_1, \tau_2, r_0, \) and \( \tau_{ss} \)) with known values reduces the number of parameters to be optimized to those of \( r_2(t) \), which describes the anisotropy decay in the micellar phase. It was found that a biexponential function, eq 6, gave a satisfactory fit. In these cases \( r_{ss} \) is calculated by eq 10.

\[ r_{ss} = \frac{r_0 [\alpha \tau_1^0 (r_1) + (1 - \alpha) \tau_2^0 (r_2)]}{\alpha \tau_1^0 (r_1) + (1 - \alpha) \tau_2^0 (r_2)} \left[ \frac{\beta \tau_{slow} (r_1 + \tau_{slow}) + (1 - \beta) \tau_{fast} (r_1 + \tau_{fast})}{\tau_{slow} + \tau_{fast} + r_1 + r_2 + \tau_{slow} + \tau_{fast} + r_1 + r_2} \right] \]  

Criteria for Good Fit. A good fit of the raw data is indicated by a random distribution of the weighted residuals, defined as,

\[ r_i = \frac{(F_i^c - F_i^s)}{(F_i^c)^{1/2}} \]  

where \( F_i^s \) and \( F_i^c \) are experimental and calculated intensities. There are several tests to examine the randomness of the weighted residuals. The standard practice is to examine the distribution of residuals in the following order: (1) check visually the plot of residuals vs channel number for randomness, (2) calculate the value of \( \chi^2 \) (eq 12) and check if the value is in the range 0.8–1.2.

\[ \chi^2 = \frac{1}{N_{data}} \sum_{i=1}^{N_{data}} r_i^2 \]  

In addition, an autocorrelation plot of residuals and the value of the Durbin–Watson parameter are also used in this work, wherever necessary.

In the case of simultaneous fit of parallel and perpendicular components of fluorescence decay data the above criteria were adequate for the simple cases where \( I(t) \) and \( r(t) \) were single-exponential functions as in pure solvents. However, in cases of micellar systems where \( I(t) \) or \( r(t) \) or both are biexponential the following additional criteria were found to be useful in deciding the goodness of fit: (1) a visually acceptable fit of the raw data of \( r(t) \) (see Figure 5) and (2) a good agreement between the value of \( r_{ss} \) calculated from the optimized values of anisotropy parameters and \( r_{ss} \) measured experimentally by steady-state fluorescence.

The error associated with the value of the optimized parameters depends upon the number of parameters simultaneously optimized. Occasionally, the value of a parameter may not be properly estimated at all. That is, the criteria for goodness of fit can be satisfied for a wide range of values of a less sensitive parameter. An example of this type is the optimization of the value of \( \tau_1 \) using a fluorophore for which \( \tau_1 << \tau_s \). It is necessary therefore to estimate the error in anisotropy decay times, especially for \( \tau_{slow} \) in micellar systems. This was done using the plot of \( \chi^2 \) vs \( \tau_{slow} \). To obtain these plots \( \tau_{slow} \) was varied as a fixed parameter in the data analysis. The efficiency of this method was tested with simulated fluorescence decay data (see below).

Fluorescence decay data (parallel and perpendicular components) were simulated (40 ps/ch) using an instrumental response function of width 4 ps. The values of the Durbin–Watson parameter were found to be useful as described above. In the case of micellar systems, where \( I(t) \) or \( r(t) \) or both are biexponential the following additional criteria were found to be useful in deciding the goodness of fit: (1) a visually acceptable fit of the raw data of the parallel component of the simulated decay (eq 12) and (2) a good agreement between the value of \( r_{ss} \) obtained from the analysis of simulated decay data and the value of \( r_{ss} \) calculated from the optimized values of anisotropy parameters and \( r_{ss} \) measured experimentally by steady-state fluorescence.
function (experimentally determined) for the following values for fluorescence (single exponential) and anisotropy (biexponential) decay parameters: $	au_f = 2$ ns, $	au_{fast} = 0.5$ ns, $	au_{slow} = 5$ ns, $\beta = 0.5$, and $\rho_0 = 0.3$. The peak counts in the simulated data for the parallel component were 2000, 10 000, and 20 000 before the addition of Poisson noise. Each of these simulated data sets were analyzed to extract best-fit parameters for the anisotropy decay. Figure 2A shows plots of $\chi^2$ vs $\tau_{slow}$ obtained in the analysis of simulated fluorescence decay data. It is observed that $\chi^2$ is insensitive to $\tau_{slow}$ if the peak count is only 2000. It will be impossible to determine $\tau_{slow}$ in this case. When the peak count is 20 000, $\chi^2$ is sufficiently sensitive to $\tau_{slow}$ to indicate a good minimum at $\tau_{slow} = 5$ ns, and therefore one can rule out $\tau_{slow}$ values outside the range of $5 \pm 0.5$ ns as unacceptable. It is clear from the analysis of simulated data that a peak count of $2 \times 10^4$ or above is desirable in the experimental data in order to obtain an accurate estimate of $\tau_{slow}$.

**Figure 3.** Plot of steady-state anisotropy ($r_{ss}$) vs $X ([\text{surfactant}]/\text{cmc})$. (A) Cresyl violet in different micelles: SDS (▲), TX-100 (●), and CTAB (■). (B) Nile red in different micelles: SDS (▲), TX-100 (●), and CTAB (■) (nile red being insoluble in water, there is no data for $X = 0$). (C) DODCI in different micelles: SDS (▲), TX (●), and CTAB (■).

**Figure 4.** Fluorescence decay profile of 5 µM nile red (5 µM) in SDS (30 mM) recorded at magic angle polarization, $\lambda_{ex} = 580$ nm, $\lambda_{em} = 640$ nm. $\tau_1 = 2.43$ ns, $\chi^2 = 1.05$. (A) Instrument response function and the fluorescence decay. The solid line through the fluorescence decay is the best fit for a single-exponential function. (B) Distribution of the weighted residuals for the best fit of fluorescence decay.

**Results**

Steady-state anisotropy ($r_{ss}$) is an excellent indicator of the efficiency of solubilization of the dye in the three micelles. The dye molecule bound to the micelle tumbles slowly compared to the free dye in water, and hence $r_{ss}$ increases when the surfactant concentration is increased. $r_{ss}$ attains a maximum value when all the dye molecules are micellized. The plots of $r_{ss}$ vs $X ([\text{surfactant}]/\text{cmc}$, where cmc is the critical micelle concentration) for three dyes (nile red, cresyl violet, and...
DODCI) in the three micelles (SDS, CTAB, and TX) are shown in Figure 3. For \( x = 0 \), the steady-state anisotropy is that of the dye in water, if the dye is soluble. For \( 0 < x \leq 1 \), a region in which the surfactant concentration is below the cmc, the micelles are not fully formed. However, the steady-state anisotropy increases in this region also because the dye may be associated with incompletely aggregated micellar structures and hence the fluorescence depolarization is less. If the dye has a greater affinity for the micelle, then the increase in the anisotropy will be sharp in the region \( 0 < x < 1 \) and the value becomes constant for \( x \geq 1 \). As seen in the plots in Figure 3B, the dye nile red, which is insoluble in water, has a greater affinity for micellization in all three micelles. A similar behavior (Figure 3C) is also observed for the cationic dye DODCI in all three micelles. For these two dyes the solubilization of the dye may be considered complete for \( 5 < x < 10 \), and the fraction of the dye remaining in water is negligible. In the case of cresyl violet the anisotropy plots (Figure 3A) indicate that a constant value is attained for \( x > 1 \) in SDS, but the plateau value is not attained in CTAB and TX even for \( x \approx 30 \). It is presumed that the cationic dye CV has a greater affinity for water than the micellar environment of positively charged CTAB or neutral TX. The preferential micellization in SDS is attributable to the Coulombic attraction between the negatively charged SDS and the positively charged dye.

The fluorescence decay of the dyes in micelles and in pure solvents (water and \( n \)-butanol) were investigated. The dye concentration was below 10 \( \mu \)M in all the cases. The fluorescence decay in water and \( n \)-butanol were single exponential, and the lifetimes are given in Table 1. For fluorescence decay measurements in the micelles, the surfactant concentration used were well above the cmc: typically, 60 mM (SDS), 28 mM (CTAB), 10 mM (TX). The concentration of micelle ([micelle] = ([surfactant] − cmc)/aggregation number) was 0.07 mM for TX, 0.85 mM for SDS, and 0.44 mM for CTAB. The corresponding \( x \) values are 6.8 for SDS, 30.4 for CTAB, and 38.5 for TX (calculated using known values (Table 2) for cmc and aggregation number at 25 °C: \( 8.8 \times 10^{-3} \) M and 62 (SDS), \( 9.2 \times 10^{-4} \) M and 60 (CTAB), \( 2.6 \times 10^{-4} \) M and 143 (TX)).

The ratio of the micelle to dye (typically 1−5 \( \mu \)M) concentration is >100 for all cases in SDS and CTAB and >50 in TX. For this ratio, the dye is distributed as one per micelle (Poisson distribution). The fluorescence decays were single exponential for all dyes in SDS except rhodamine B. The values of lifetimes and amplitudes are given in Table 1. The observation of a biexponential decay for CV in CTAB and TX and rhodamine B in all micelles is due to the distribution of the dye in aqueous and micellar phases. It was observed that one of the two lifetimes was close to the lifetime (2.04 ns) for CV in water. Figure 4 shows a plot of the fluorescence decay of CV in SDS and the results of fitting the decay data to a single-exponential function.

The fluorescence anisotropy decay of the dye in a pure solvent (water or \( n \)-butanol) is single exponential. The values of \( r_0 \) and \( \tau \) (\( \tau = \tau_{\text{slow}} \)) are given in Table 1. In the case of micellar systems where the fluorescence decay is a single exponential, the fluorescence depolarization is solely due to the rotational dynamics of a single fluorophore species encapsulated in the micelle. The polarized fluorescence decays (parallel and

### Table 1: Fluorescence Intensity and Anisotropy Decay Parameters for the Fluorescence Dye Probes in Water, Butanol, and Micelles

<table>
<thead>
<tr>
<th>dye/solvent/micelle</th>
<th>( \tau_1 ) (ns)</th>
<th>( \tau_2 ) (ns)</th>
<th>( \alpha_1 )</th>
<th>( r_0 )</th>
<th>( \tau_{\text{slow}} ) (ns)</th>
<th>( \tau_{\text{fast}} ) (ns)</th>
<th>( \beta )</th>
<th>( r_m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>2.04</td>
<td>1</td>
<td>0.330</td>
<td>0.15</td>
<td>1</td>
<td>0.22</td>
<td>1.0</td>
<td>0.020</td>
</tr>
<tr>
<td>butanol</td>
<td>3.18</td>
<td>0.99</td>
<td>0.320</td>
<td>3.83</td>
<td>0.59</td>
<td>0.77</td>
<td>0.094</td>
<td>0.120</td>
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<tr>
<td>SDS</td>
<td>2.94</td>
<td>0.75</td>
<td>0.322</td>
<td>2.05</td>
<td>1</td>
<td>0.43</td>
<td>0.106</td>
<td>0.070</td>
</tr>
<tr>
<td>CTAB</td>
<td>2.04</td>
<td>0.64</td>
<td>0.320</td>
<td>3.83</td>
<td>0.99</td>
<td>0.43</td>
<td>0.45</td>
<td>0.120</td>
</tr>
<tr>
<td>TX-100</td>
<td>2.06</td>
<td>0.77</td>
<td>0.310</td>
<td>5.39</td>
<td>0.81</td>
<td>0.63</td>
<td>0.180</td>
<td>0.100</td>
</tr>
<tr>
<td>DODCI</td>
<td>0.64</td>
<td>0.19</td>
<td>0.314</td>
<td>0.22</td>
<td>1</td>
<td>0.63</td>
<td>0.180</td>
<td>0.100</td>
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<tr>
<td>water</td>
<td>1.61</td>
<td>1</td>
<td>0.385</td>
<td>0.18</td>
<td>1</td>
<td>0.040</td>
<td>0.094</td>
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<tr>
<td>butanol</td>
<td>3.12</td>
<td>0.85</td>
<td>0.352</td>
<td>0.54</td>
<td>1</td>
<td>0.77</td>
<td>0.150</td>
<td>0.094</td>
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<tr>
<td>SDS</td>
<td>2.88</td>
<td>0.79</td>
<td>0.383</td>
<td>2.33</td>
<td>0.51</td>
<td>0.57</td>
<td>0.205</td>
<td>0.094</td>
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<td>CTAB</td>
<td>2.10</td>
<td>0.77</td>
<td>0.358</td>
<td>4.22</td>
<td>1.16</td>
<td>0.31</td>
<td>0.150</td>
<td>0.094</td>
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<tr>
<td>TX-100</td>
<td>2.89</td>
<td>0.77</td>
<td>0.368</td>
<td>7.78</td>
<td>1.60</td>
<td>0.56</td>
<td>0.190</td>
<td>0.094</td>
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<tr>
<td>rhod-DPPE</td>
<td>3.10</td>
<td>0.79</td>
<td>0.250</td>
<td>3.62</td>
<td>1.88</td>
<td>0.38</td>
<td>0.100</td>
<td>0.094</td>
</tr>
<tr>
<td>CTAB</td>
<td>2.07</td>
<td>0.77</td>
<td>0.342</td>
<td>7.09</td>
<td>0.87</td>
<td>0.71</td>
<td>0.218</td>
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<tr>
<td>TX-100</td>
<td>2.67</td>
<td>1</td>
<td>0.334</td>
<td>21.30</td>
<td>2.50</td>
<td>0.48</td>
<td>0.220</td>
<td>0.094</td>
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### Table 2: Radii and Other Physical Parameters of Different Micelles and \( r_m \) at 25 °C

<table>
<thead>
<tr>
<th>micelle</th>
<th>charge (surface) ( N_{\text{surf}} )</th>
<th>cmc (mM)</th>
<th>core radius ( r_c ) (Å)</th>
<th>hydrodynamic radius ( r_h ) (Å)</th>
<th>( r_m ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS</td>
<td>(−)</td>
<td>62</td>
<td>8.0</td>
<td>16.7</td>
<td>20.7, 21.0</td>
</tr>
<tr>
<td>CTAB</td>
<td>(+)</td>
<td>60</td>
<td>0.92</td>
<td>21.7</td>
<td>25.7, 25.7</td>
</tr>
<tr>
<td>TX-100</td>
<td>(neutral)</td>
<td>143</td>
<td>0.26</td>
<td>43</td>
<td>43</td>
</tr>
</tbody>
</table>

\( r_m = 4\pi n^2 \rho/(3kT); r_c \) is the hydrodynamic radius, \( \eta \) is the viscosity of water, \( k \) is the Boltzman constant. \( \text{Equation 2 in ref 47.} \) \( \text{Core radius + head group radius (2 Å)+} \) two layers of water (2 Å) associated with the charged micelles (SDS and CTAB). \( \text{Optimum value from light scattering experiments, ref 42.} \) \( \text{Reference 49.} \) \( \text{Reference 28.} \)
aggregate to form spherical micelles. The fluorescence used in this study have been well characterized. In dilute remains nearly constant with temperature.

In the cases of CV in CTAB and TX or rhodamine B in all the micelles, the fluorescence originates from the dye distributed in aqueous and the micellar phases. The fluorescence decays at magic angle, parallel, and perpendicular polarization components are given by eqs 1, 8, and 9, respectively. \( I(t) \) and \( r_1(t) \) are the fluorescence and anisotropy decay functions in water, \( I_S(t) \) and \( r_2(t) \) are the corresponding functions in the micelle, and \( \alpha \) is the fractional intensity in water. It was found that the polarized components of fluorescence decays were fitted poorly if \( r_2(t) \) was assumed to be a single exponential. However, a biexponential equation for \( r_2(t) \) (eq 6) was adequate to fit the data. The values for the anisotropy decay parameters of \( r_2(t) \) for these cases are given in Table 1.

The anisotropy decay of DODCI in CTAB and TX is biexponential. However, Figure 3 shows that \( r_\alpha \) attains a constant value for \( x > 2 \), indicating that the dye is micellized for the experimental condition of \( x = 30.4 \) (CTAB) and \( x = 38.5 \) (TX). The two lifetimes are therefore associated with the dye in the micelle. In this case the parallel and perpendicular components of fluorescence were fitted to eqs 2 and 3, where \( I(t) \) is biexponential. In these cases also, a biexponential function for \( r(t) \) gave a good fit to the experimental data. The values of the anisotropy parameters are given in Table 1.

The effect of varying the temperature on the fluorescence intensity and anisotropy of nile red in SDS was studied in the temperature range 15–50 °C. Table 3 summarizes the variation of all the fluorescence and anisotropy parameters with temperature. Increasing temperature decreases the fluorescence lifetime, the steady-state anisotropy, and the anisotropy decay parameters, \( r_{\text{slow}}, r_{\text{fast}}, \) and \( \beta \). \( r_0 \) is the only parameter that remains nearly constant with temperature.

**Discussion**

The structures of the micelles formed by the three surfactants used in this study have been well characterized. In dilute aqueous solutions, but above cmc, the surfactant molecules aggregate to form spherical micelles. The fluorescence anisotropy decay of the dye molecule bound to the micelle is a consequence of the reorientation dynamics of the excited state of the molecule as well as that of the micelle. Several models for the reorientation dynamics of a molecule in the micelle are possible. There are at least two models (mode 1 and 2 in Figure 6) that predict the anisotropy decay to be single exponential. In the first model (model 1) the dye molecule is rigidly attached to the micelle, and the reorientation dynamics for the molecule is identical with that of the spherical micelle which is single exponential with \( r_M \) as the decay constant. In the second model (model 2) the dye molecule is in the core of the micelle (which may be considered as a homogeneous medium having physical properties resembling that of an oil drop), and the reorientation dynamics is single exponential with a time constant \( r_M^{-1} + r_\tau^{-1} \), where \( r_\tau \) is the anisotropy decay constant in the "oil drop". None of the anisotropy decays for the five dyes in the three micelles are single exponential, and hence the above two models are ruled out.

Models of reorientation dynamics predicting bi- and triexponential anisotropy decays have been considered before. For example, Klein and Haar considered a model where the dye molecule is preferentially situated near the surface and the rotation of the fluorophore about a molecular axis is sufficient to account for the anisotropy decay. Chou and Wirth also considered a similar model for acridine orange bound to the micelle. Visser et al. have considered the model where the local dynamics of the dye is approximated to the wobbling-in-cone model for the dye solubilized in the interfacial region of the micelle. All the above models take into account the rotation of the micelle, but the possibility of reorientation of the dye as a result of the translational diffusion of the molecule in the micelle was not considered. In homogeneous media and in planar membranes, the translational diffusion of the molecule does not reorient the molecule. In a spherical micelle, the dye molecule is preferentially situated near the interface and the molecule is oriented with respect to the interface (nonzero order parameter). For such a case translational diffusion on the two-dimensional spherical surface of the micelle is possible. The transport of the molecule along the spherical surface inevitably reorients the molecule with respect to its initial orientation. The fluorescence anisotropy decay function due to the surface transport depends upon the orientation of the molecule-fixed emission dipole with respect to the normal to the spherical surface. In the simplest case where the molecular dipole is parallel to the surface normal the reorientation dynamics due to transport of the molecule on the spherical surface is identical with the isotropic rotational diffusion of the molecule which is situated at the center of the sphere, and the following equality holds: \( D_1 = D_0/r_M^2 \), where \( D_0 \) is the isotropic rotational diffusion constant, \( D_1 \) is the translational diffusion coefficient, and \( r_M \) is the radius of the micelle. For the case of isotropic rotational diffusion of a spherical rotor the correlation decay is single exponential and the time constant is \( r_\tau = (1 + 1/D_1 r_M)^{-1} \). For fluorescence depolarization experiments \( l = 2 \) and \( r_\tau = (6D_1)^{-1} \). Thus, for the fluorescence depolarization due to surface transport the time constant is \( r_D = r_M^2/6D_0 \). Quitevis et al. have included the translational diffusion of the dye together with the wobbling-in-cone dynamics model for the analysis of fluorescence anisotropy decays. (It may be noted however that the equation \( r_D = r_M^2/6D_0 \) given in ref 26 is incorrect.) In this model (model 4 in Figure 6), the contribution to the anisotropy decay comes from three independent motions: wobbling of the dye molecule in a restricted region (assumed for simplicity as a cone), translational diffusion of the dye along the spherical surface, and rotation of the micelle as a whole. For this model \( r(t) \) is given by eq 13:

\[
r(t) = r_0 S^2 + (1 - S^2) \exp(-t/r_\tau) \exp\{-r(1/r_D + 1/r_M)\}
\] (13)

\( r_0 \) is the initial anisotropy at \( t = 0 \), \( S^2 \) is the square of order parameter (which is a measure of the equilibrium orientational distribution of the dye) for the intercalation of dye in the micelle, \( r_\tau \) is the time constant for the wobbling motion of the dye, \( r_D \) is the reorientation time constant due to the translational diffusion of dye along the spherical micellar surface, and \( r_M \) is the reorientation time constant for the spherical micelle. Comparison of eq 13 with biexponential eq 6, which was used to fit the experimental data, gives the following relations between the experimental and model parameters.

\[
\beta = S^2
\] (14)

\[
1/r_{\text{slow}} = 1/r_D + 1/r_M
\] (15)

\[
1/r_{\text{fast}} = 1/r_R + 1/r_D + 1/r_M
\] (16)
It is worth noting here that model 3 (Figure 6), which does not include lateral diffusion ($D_l = 0$ or $r_D = \infty$), predicts the anisotropy decay to be biexponential, which is also consistent with the experimental observation. However, model 3 predicts that the slow component, $\tau_{\text{slow}}$, must be equal to the rotational correlation time of the micelle, $\tau_M$. Comparison of the experimental values of $\tau_{\text{slow}}$ (Table 1) for the five dyes in the three micelles with the value of $\tau_M$ (Table 2) shows that $\tau_{\text{slow}} \ll \tau_M$, and therefore model 3 is not applicable. Hence, lateral diffusion is an important mechanism of fluorescence depolarization.

The translational diffusion coefficient ($D_t$) is related to $\tau_D$ by eq 17.

$$D_t = r_M^2/6\tau_D$$

$r_M$ is the radius of the spherical surface in which the dye diffuses. The wobbling rotational diffusion coefficient ($D_w$) is calculated using the anisotropic parameters $\tau_r$ and $S$. According to the wobbling-in-cone model, $^{40}$

$$D_w = \{\tau_r(1 - S^2)^{-1} - x^2(1 + x)^2\{1n[(1 + x)/2] + (1 - x)/2\}(2(1 - x))^{-2} + (1 - x)(6 + 8x - x^2 - 12x^3 - 7x^4)/24\}$$

where $x = \cos \theta_0$. $\theta_0$ is the semicone angle in the wobbling-in-cone model, which is determined from the value of the order parameter and eq 19. $^{40}$

$$S = 0.5 \cos \theta_0(1 + \cos \theta_0)$$

From the above discussion and equations, it is clear that the micellar parameters $\tau_{\text{ss}}$ and $\tau_M$ must be known in order to calculate the structural ($S$ and $\theta_0$) and dynamical parameters ($D_t$ and $D_w$) for the dye bound to the micelle. In this study, we have chosen the most extensively studied micellar systems whose structural and physical properties are well-known from the previous studies. $^{16,17,28}$ $r_M$ is taken to be the core radius of the micelle. The lipophilic-labeled rhodamine DPPE was chosen in this study with an expectation that lateral diffusion would be negligible and thereby determine $\tau_M$ experimentally. However, even for this molecule lateral diffusion was appreciable and $\tau_{\text{slow}}$ was far less than the value of $\tau_M$ for the three micelles. The most important consideration for $\tau_M$ is the shape of the micelle, which is approximately spherical for all the cases (Table 2). For a spherical particle (micelle) $\tau_M$ is related to the volume, viscosity ($\eta$), and temperature by Stokes–Einstein relation (eq 20):

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

$r_h$ is the hydrodynamic radius of the micelle. The calculated values for $\tau_M$ are given in Table 2 together with the radii and other data for the micelles.

### Table 3: Temperature Dependence of Rotational Dynamic Parameters

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$\tau_{\text{ns}}$</th>
<th>$\tau_{\text{slow}}$</th>
<th>$\tau_{\text{fast}}$</th>
<th>$\beta$</th>
<th>$\tau_M$ (ns)</th>
<th>$S$</th>
<th>$\theta_0$ (deg)</th>
<th>$D_{\text{t}} \times 10^{-8}$ (s$^{-1}$)</th>
<th>$D_{\text{w}} \times 10^{10}$ (m$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>2.57</td>
<td>0.33</td>
<td>2.38</td>
<td>0.75</td>
<td>0.438</td>
<td>0.103</td>
<td>11.00</td>
<td>0.66</td>
<td>41.0</td>
</tr>
<tr>
<td>25</td>
<td>2.43</td>
<td>0.33</td>
<td>1.99</td>
<td>0.57</td>
<td>0.357</td>
<td>0.090</td>
<td>8.30</td>
<td>0.60</td>
<td>45.4</td>
</tr>
<tr>
<td>30</td>
<td>2.33</td>
<td>0.35</td>
<td>1.75</td>
<td>0.47</td>
<td>0.295</td>
<td>0.083</td>
<td>7.39</td>
<td>0.54</td>
<td>49.0</td>
</tr>
<tr>
<td>40</td>
<td>2.12</td>
<td>0.33</td>
<td>1.35</td>
<td>0.40</td>
<td>0.192</td>
<td>0.070</td>
<td>5.86</td>
<td>0.44</td>
<td>55.9</td>
</tr>
<tr>
<td>50</td>
<td>1.92</td>
<td>0.33</td>
<td>1.18</td>
<td>0.29</td>
<td>0.182</td>
<td>0.060</td>
<td>4.75</td>
<td>0.43</td>
<td>56.7</td>
</tr>
</tbody>
</table>

### Table 4: Values of the Parameters for the Model (Wobbling-in-Cone + Translational Diffusion) Derived from the Experimental Results (Dyes in Micelles)

<table>
<thead>
<tr>
<th>dye/solvent/micelle</th>
<th>$S$</th>
<th>$\theta_0$ (deg)</th>
<th>$D_{\text{w}} \times 10^{-8}$ (s$^{-1}$)</th>
<th>$D_{\text{w}} \times 10^{10}$ (m$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nile red SDS</td>
<td>0.00</td>
<td>90</td>
<td>3.88</td>
<td>5.00</td>
</tr>
<tr>
<td>butanol</td>
<td>0.60</td>
<td>45.4</td>
<td>1.86</td>
<td>1.77</td>
</tr>
<tr>
<td>CTAB</td>
<td>0.71</td>
<td>37.5</td>
<td>1.36</td>
<td>1.95</td>
</tr>
<tr>
<td>TX-100</td>
<td>0.79</td>
<td>31.5</td>
<td>0.34</td>
<td>3.31</td>
</tr>
<tr>
<td>cresyl violet</td>
<td>0.00</td>
<td>90</td>
<td>2.22</td>
<td>2.03</td>
</tr>
<tr>
<td>butanol</td>
<td>0.59</td>
<td>45.6</td>
<td>2.71</td>
<td>1.71</td>
</tr>
<tr>
<td>CTAB</td>
<td>0.67</td>
<td>40.2</td>
<td>0.92</td>
<td>1.47</td>
</tr>
<tr>
<td>TX-100</td>
<td>0.79</td>
<td>31.0</td>
<td>0.81</td>
<td>5.00</td>
</tr>
<tr>
<td>DODC</td>
<td>0.00</td>
<td>90</td>
<td>4.11</td>
<td>2.03</td>
</tr>
<tr>
<td>butanol</td>
<td>0.76</td>
<td>34.1</td>
<td>1.21</td>
<td>1.75</td>
</tr>
<tr>
<td>CTAB</td>
<td>0.77</td>
<td>33.2</td>
<td>1.02</td>
<td>1.47</td>
</tr>
<tr>
<td>TX-100</td>
<td>0.88</td>
<td>23.4</td>
<td>0.73</td>
<td>5.00</td>
</tr>
<tr>
<td>rhodamine B</td>
<td>0.00</td>
<td>90</td>
<td>3.08</td>
<td>2.03</td>
</tr>
<tr>
<td>butanol</td>
<td>0.75</td>
<td>34.6</td>
<td>2.39</td>
<td>1.43</td>
</tr>
<tr>
<td>CTAB</td>
<td>0.55</td>
<td>48.6</td>
<td>1.03</td>
<td>1.35</td>
</tr>
<tr>
<td>TX-100</td>
<td>0.75</td>
<td>34.6</td>
<td>0.70</td>
<td>3.53</td>
</tr>
<tr>
<td>rhodamine-DPPE</td>
<td>0.62</td>
<td>54.2</td>
<td>0.61</td>
<td>0.73</td>
</tr>
<tr>
<td>butanol</td>
<td>0.84</td>
<td>27.2</td>
<td>0.63</td>
<td>0.53</td>
</tr>
<tr>
<td>TX-100</td>
<td>0.69</td>
<td>39.0</td>
<td>0.41</td>
<td>0.73</td>
</tr>
</tbody>
</table>

The values for $S$, $\tau_r$, $\tau_M$, $D_t$, $D_w$, and $\theta_0$ were calculated for nile red, CV, DODC, rhodamine B, and rhodamine-DPPE in SDS, CTAB, and TX micelles and are given in Table 4. The values for these dyes in water and butanol are also given for comparison. The value of $D_w$ in butanol was obtained using $D_w = (6r_c)^{-1}$. The values of $D_w$ in the micelle were calculated using eq 18.

**Order Parameter and $\theta_0$** The order parameter for the dye molecules in butanol is zero because the dye molecule tumbles freely and the equilibrium orientational distribution is completely random. The order parameter for all the dye probes in the micelles is in the range 0.55–0.88 ($\theta_0$ varying from 45° to 27°), indicating that the equilibrium orientational distribution is highly constrained because of the aqueous/nonaqueous interface in the micelle. That is, the dye molecules do have a preferential orientation with respect to the interface. As will be discussed in a later section (temperature study) the order parameter decreases with increasing mobility (diffusion) of the dye in the micelle.

**Wobbling Diffusion Coefficient** According to the wobbling-in-cone model, the molecule wobbles freely inside a cone of semiangle $\theta_0$. The values for $\theta_0$ and wobbling diffusion coefficient, $D_w$, are the quantitative parameters for this model. The results shown in Table 4 indicate that the wobbling diffusion coefficients of all the dye molecules, excluding rhodamine DPPE, are in the range (0.34–2.7) $\times 10^8$ s$^{-1}$. These values are a factor 2–6 less than the rotational diffusion coefficient for the same dye in n-butanol, where the wobbling is free. The rotational diffusion coefficient is the least for the rhodamine-DPPE even though the cone angle is not very different from...
that of other dyes. The slow wobbling (and similarly slow translational diffusion) for rhodamine-DPPE indicates that covalent linking with the lipid chain does affect the diffusive dynamics of the dye molecule. The comparison of the diffusion coefficients for the same dye in different micelles indicates a consistent observation that the wobbling diffusion coefficient is less in TX than in SDS and CTAB for the same dye irrespective of their structural differences. Similar observations of lower wobbling diffusion coefficient in the TX micelle have also been observed for other fluorescent molecules: porphyrins and merocyanine 540 and octadecylrhodamine B. A similar but opposite trend is observed for $D_t$ (see below).

**Translational (Lateral) Diffusion Coefficient.** The translational diffusion coefficient of the dye molecule on the micellar surface is lowest for rhodamine-DPPE, which is to be expected. For other dye molecules the value is in the range $(1.4–5.0) \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$. These values are comparable to or larger than the lateral self-diffusion coefficient $(0.2–1.5) \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ of surfactant molecules in SDS or CTAB micelle. One interesting observation is the consistently larger diffusion coefficient for all dyes (except rhodamine-DPPE) in TX than in SDS or CTAB. This is exactly opposite of that observed for the wobbling diffusion coefficient and is discussed further in a later section.

**Temperature Effects on $D_o$, $D_t$, $S$, and $\theta_0$.** The micellar structure is compact but fluidlike, as indicated by the wobbling and lateral diffusion of the dye molecules. The variation of the structural and dynamical fluidity parameters of nile red in SDS micelle was investigated at different temperatures (15–50 °C). The fluorescence decay of nile red in SDS micelle at magic angle polarization was fitted adequately ($g^2$ varying from 0.9 to 1.1) to a single-exponential function at all temperatures. This indicated that the partitioning of nile red in aqueous phase was negligible even at 50 °C, which is not surprising since the dye is neutral and insoluble in water. It was observed however that the fluorescence lifetime of the dye in the micelle decreased with increasing temperature. Such a decrease of lifetime with temperature is usually associated with an increase in nonradiative rate with temperature. Nile red has a diethyl amino group which can undergo torsional motion about the C–N bond, which can increase the nonradiative rate. Interestingly, the temperature dependence of the lifetime of nile red in butanol was only marginal (3.90 ns at 25 °C and 3.72 ns at 50 °C) compared to the temperature dependence in the micelle (2.43 ns at 25 °C and 1.92 ns at 50 °C). This is an indication that the temperature dependence of the torsional motion of nile red in the micelle is quantitatively different than in butanol; that is, the torsional motion appears to be faster in the micelle, which is in qualitative agreement with a similar strong temperature dependence of $D_o$ (see below). The experimentally determined fluorescence anisotropy parameters for nile red in SDS at different temperatures (Table 3) were used to calculate $D_o$, $D_t$, $S$, and $\theta_0$. It is assumed that the aggregation number and radius of the micelle remain unchanged in this temperature range. The variation of $D_o$, $D_t$, $S$, and $\theta_0$ with temperature is shown in Table 3. It is observed that $D_o$ and $D_t$ increase with temperature. However, the value of $D_o$ increases by a factor of 4.5, whereas $D_t$ increases by only 1.9 in the above temperature range. The order parameter decreases with temperature, and the cone semiangle calculated from the order parameter increases from 41° to 56.7° in the temperature range 15–50 °C. Increased mobility of the dye molecule seems to have the effect of increasing the cone angle. These results indicate that an increase in diffusion coefficient is correlated with a decrease in order parameter.

**Microviscosity.** In the classical model of the micelle the interior region of the micelle is considered to be liquidlike and the physical properties of the interior would resemble that of an oil drop. The fact that all organic substances that are insoluble in water could be solubilized in aqueous micellar solutions had a facile explanation that organic molecules seek the interior hydrocarbon region of the micelle. This led to the assumption that the physical properties of the “oil drop” (viscosity, dielectric constant, etc.) could be determined using the solubilized organic molecule as the probe. Shinitzky et al. used the steady-state fluorescence anisotropy (which is larger in micellar solutions than in water or alcohol) of several organic molecules and calculated the “microviscosity” of the interior region of the micelle. The crucial assumptions involved were (a) the organic molecule is solubilized in the interior region, (b) the molecule tumbles freely in the micelle as in a pure solvent, and (c) the Stokes–Einstein equation for the rotational diffusion coefficient and correlation time $(D_r = kT/8\pi\eta r^3)$ for a spherical particle in liquid is valid for the micellar interior. The microviscosity for several micelles (including SDS and CTAB) was in the range 15–50 cP at room temperature, and the value for the same micelle depends on the probe. The microviscosity of the micelle was also determined using other spectroscopic properties of the solubilized molecules and their relationship to lateral or rotational diffusion coefficient of the molecule. To give a few examples, ESR of organic free radicals trapped in micelles was used to determine the diffusion coefficient in the micelle, which gives the microviscosity for SDS to be approximately 5 cP. Intermolecular excimer formation kinetic data of pyrene in micelles were used, and the microviscosities of SDS and CTAB were determined to be 193 and 151 cP, respectively, whereas intramolecular excimer formation kinetics led to a value of 4 cP. The discrepancy in the results was substantially large, and the value of “microviscosity” is technique-dependent and also probe-dependent. It is evident that one or more of the basic assumptions stated above concerning the diffusive dynamics of the solubilized molecule in micelles is not valid.

The sites of solubilization of organic molecules in micelles (usually SDS or CTAB) have been investigated extensively. It appears that practically all organic molecules are solubilized near the surface, even for small aromatic molecules such as benzene. Therefore, organic molecular probes are expected to report the physical properties of the interfacial region and not that of the interior region. Since the interfacial region is structurally heterogeneous (consisting of polar and nonpolar regions separated by a few angstroms), the structure and dynamics of organic probe molecules would be sensitive to the nature of the probe molecule. For example, the dynamics of a charged probe molecule would be different from that of a neutral probe molecule. Moreover, the equilibrium orientational distribution of the probe molecule in the site of solubilization in micelles is not random (nonzero order parameters), and hence the assumption of free tumbling of the probe molecule in micelles is also incorrect. These factors could explain the sensitivity of the microviscosity value to the nature of the probe and the technique used. Thus, it is important that a proper modeling of the diffusive dynamics of the probe and an appropriate experimental technique, preferably the time-resolved technique, are necessary. The question remains whether “microviscosity” itself is meaningful or not for the micelle.
of wobbling of the molecular in a restricted space (wobbling-in-cone), lateral diffusion along the spherical surface, and rotation of the micelle. This model is also consistent with the observation that the dyes are solubilized near the surface. The analysis of data led to the determination of $D_w$ and $D_t$ for the probe molecule. These values can be used to test the usefulness of the concept of “microviscosity” in micelles.

$D_w$ and $D_t$ and the ratio $(D_t/D_w)$ are related to microviscosity by Stokes–Einstein eqs 21 and 22.

$$D_w = \frac{\zeta kT}{6\eta V} \quad (21)$$

$$D_t = \frac{\zeta' kT}{6\pi \eta r} \quad (22)$$

$$\frac{D_t}{D_w} = \frac{\zeta'}{\zeta} \frac{4r^2}{3} \quad (23)$$

Here $\zeta$ and $\zeta'$ are constants that are correction factors for the nonspherical shape of the molecule, $r$ is the radius, and $V$ is the molecular volume of the probe. One expects the ratio $D_t/D_w$ to be independent of temperature for the same probe. Figure 7 shows the plot of $D_t/D_w$ as a function of temperature for the neutral dye probe, nile red, in SDS micelles (data from Table 3). The ratio decreases with increasing temperature even in the small temperature range 288–323 K. Therefore, the Stokes–Einstein equations for $D_t$ and $D_w$ are not valid for the probe solubilized in the micelle. Failure of the Stokes–Einstein equation is an indication of “non-Brownian” dynamics, and we conclude that the “microviscosity” is an ill-defined parameter in such a system.

There are two possible reasons for the failure of the Stokes–Einstein relations to describe correctly the diffusive dynamics of the molecular probe in micelles. First, the Brownian dynamics of collisions between solute (probe) and solvent (surfactant molecule) in micelles and the transfer of linear and angular momenta are fundamentally different (for example, a hopping mechanism for lateral diffusion; see below) from that of liquids because of the nonrandom orientational distribution of the solute in micelles. Second, the length scale of the micelle, especially the interfacial region, is of the same order or possibly smaller than the probe molecule. Therefore, the concept of microviscosity in micelles can be convincingly tested only with a fluorescent probe that is solubilized in the core of the micelle (model 2 in Figure 6), where the fluorescence anisotropy decay is single exponential and the order parameter is zero. It will be interesting if such a fluorophore–micelle system could be identified.

Finally, we comment on the observation of faster lateral diffusion and slower wobbling diffusion of all the dye molecules (neutral and charged), including those reported for other molecules, in neutral TX-100 than in negatively charged SDS or positively charged CTAB. TX-100 is larger in size and the surface is uncharged. It is conceivable that the basic mechanism of lateral diffusion of the solute is different in TX-100. For example, transport of the solute on the surface by a hopping mechanism is possible. Such a hopping is essentially a large amplitude motion of the solute which is confined to a small diffusive volume characteristic of a high-order parameter. Independent experiments and molecular dynamics simulations are necessary to assess the importance of hopping of solutes in micelles.

Conclusions

Fluorescence depolarization dynamics of a few organic dye molecules in three micelles is best described by a model of rotational (wobbling-in-cone) and translational diffusion of the dye coupled with the rotation of the micelle as a whole. The rotational and translational diffusion coefficients, order parameter, and semicone angle were determined. The order parameter is inversely correlated with the diffusion coefficient, which is expected. The rotational and translational diffusion coefficients do not follow the trend predicted by Stokes–Einstein equations, indicating the non-Brownian dynamics of the dye in the micelle.

References and Notes