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ARTICLES

Fluorescence Anisotropy Decay in Polymer−Surfactant Aggregates

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The fluorescence anisotropy decay of two dyes merocyanine 540 and oxazine 1 has been studied in a polymer−surfactant aggregate containing poly(vinylpyrrolidone) (PVP) and sodium dodecyl sulfate (SDS). The results are analyzed in terms of the necklace model of the polymer−surfactant aggregate. The rotational motion of the probe is assumed to involve "wobbling-in-cone" along with translational motion along the micellar surface. It is observed that the presence of the polymer chains around the spherical SDS micelles causes significant retardation of both the wobbling motion as well as the translational motion of the two dyes. As a result, the wobbling and translational diffusion of the dyes in the PVP−SDS aggregate are slower than those in SDS micelle.

1. Introduction

There has been a lot of recent interest to estimate the friction experienced by a probe molecule during orientational motion within a restricted environment. The microscopic friction in many organized assemblies such as DNA and protein,[1−3] micelles,[4−6] reverse micelle,[7] and cyclodextrin[8] has been studied using rotational relaxation of suitable probes. The rotational or reorientational motion of an organic dye molecule gives rise to fluorescence depolarization and, hence, is followed by the fluorescence anisotropy decay. In a homogeneous solution, the rotational diffusion coefficient is inversely related to viscosity. This is used in many works on fluorescence depolarization to estimate the microviscosity of confined environments. However, it has been pointed out that the rotational dynamics of a probe in an organized assembly are complex and involve more than one kind of motion.[4−7] According to the "wobbling-in-cone" model,[4−7] fluorescence depolarization in a micelle arises as a result of three independent motions: (a) wobbling of the probe in a cone of angle θ, (b) translational motion of the probe along the surface of the spherical micellar aggregates, and (c) overall tumbling of the micelles. Because of the involvement of different kinds of motion, the decay of rotational function, $r(t)$, deviates from a single exponential decay. Recently several authors have analyzed the biexponential decay of $r(t)$ and estimated the diffusion coefficients arising from different kind of motions.[4−7]

In the present work, we wish to extend these works to a new environment, namely, polymer−surfactant aggregate. Several polymers are known to form relatively well-defined aggregates with selected surfactants. According to the necklace model, the polymer−surfactant aggregates consist of a series of spherical micelles surrounded by polymer segments and connected by polymer strands (Figure 1).[9−15] In such a polymer−surfactant aggregate, the structure and composition of the surface region of the micelles is seriously perturbed because of the surrounding polymer chain. According to the small angle neutron scattering study, in the absence of polymers, a micelle consists of a "dry" core surrounded by a thin Stern layer containing water molecules, polar or ionic headgroups, and counterions.[16] The water molecules confined in the Stern layer show significantly slow solvation dynamics compared to those of bulk water.[17] As demonstrated in a recent study, in a polymer−surfactant

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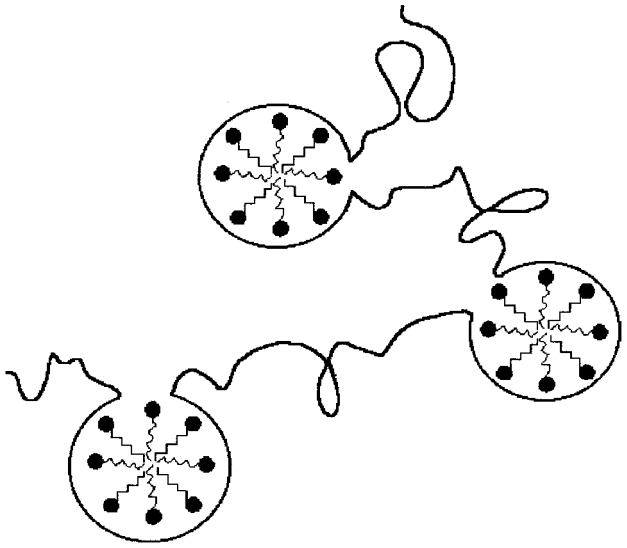


Figure 1. Schematic representation of the "necklace model" of polymer−surfactant aggregates.

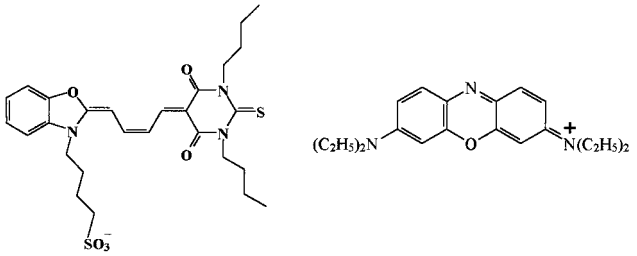


Figure 2. Structure of MC540 and OX-1.

aggregate, the dynamics of excited-state proton transfer is very different from that at a micelle surface.[10] It is obviously interesting to find out how the rotational dynamics of a probe is affected in such a polymer−surfactant aggregate. For this purpose, we have chosen perhaps the most well characterized polymer−surfactant system consisting of the polymer poly(vinylpyrrolidone) (PVP) and the anionic surfactant sodium dodecyl sulfate (SDS). As the probe, we have used two dyes, merocyanine 540 (MC540) and oxazine 1 (OX-1; Figure 2).

2. Experimental Section

The dyes MC540 (Sigma) and OX-1 (Exciton), the surfactant SDS (Aldrich), and the polymer PVP (Aldrich, $M_w = 29\,000$ Da) were used as received. The picosecond laser setup is described elsewhere.[17,18,21] For rotational relaxation studies, the polarization of the exciting light ($\lambda_{ex} = 570$ nm for MC540 and 600 nm for OX-1) was rotated by 90° using a half-wave plate at regular intervals to get the perpendicular ($I_\perp$) and parallel ($I_\parallel$) components. Then, $r(t)$ was calculated using the formula

$$r(t) = \frac{I_\parallel(t) - GI_\perp(t)}{I_\parallel(t) - 2GI_\perp(t)} \quad (1)$$

The G value of the setup was determined using a probe whose rotational relaxation time is very fast, e.g., nile red in methanol. The fluorescence lifetime was determined by recording the decay at magic angle polarization.

3. Results

In aqueous solution, MC540 exhibits a broad absorption peak at ∼500 nm which is assigned to the nonfluorescent dimers.[18,19] On addition of SDS, the dimers break and the monomers show a sharp absorption peak at ∼560 nm.[18,19] In the absence of SDS, in a solution containing 4 mg PVP per mL, the absorption spectrum of MC540 remains water-like with a dimer peak at ∼500 nm. In a solution containing 4 mg PVP per mL and 15 mM SDS, the absorption spectrum of MC540 consists of a sharp peak at 560 nm (Figure 3a). This suggests that MC540 molecules do not form dimers inside the PVP−SDS aggregates.

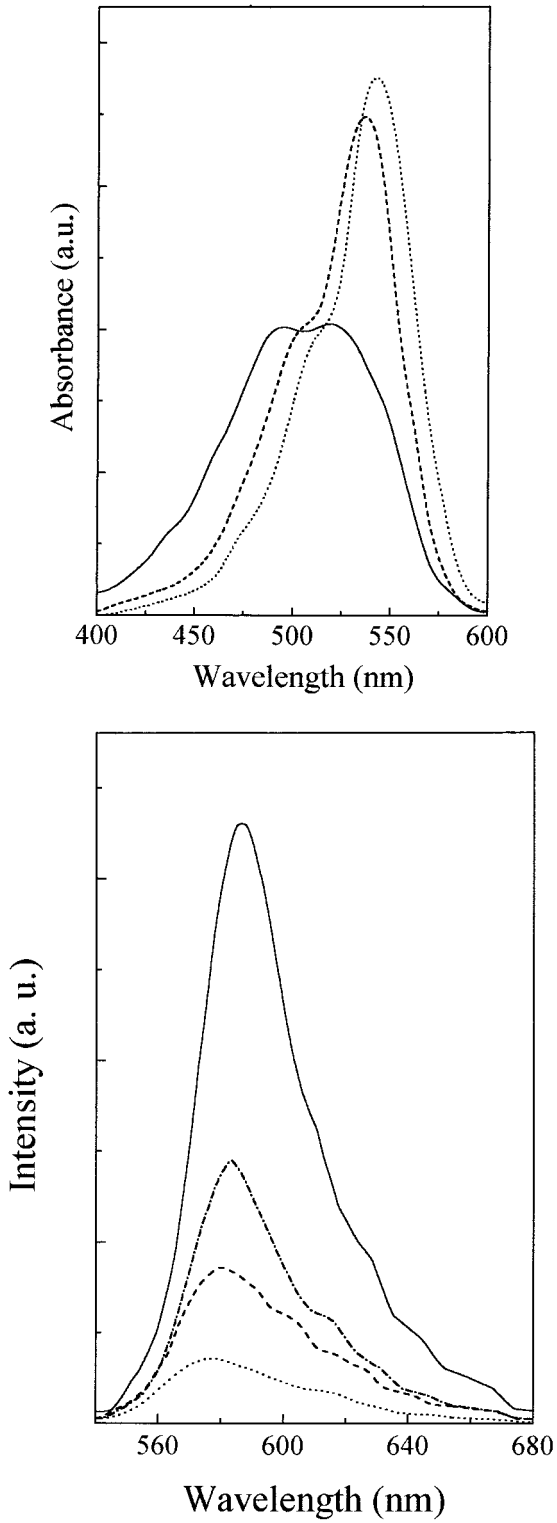


Figure 3. (a) Absorption spectra of MC540 in (i) aqueous solution of PVP (4 mg/mL; —), (ii) 15 mM SDS solution (- - -), and (iii) PVP (4 mg/mL) and 15 mM SDS solution (···). (b) Emission spectra of MC540 in (i) water (···), (ii) an aqueous solution of PVP (4 mg/mL; - - -), (iii) 15 mM SDS (-·-·-), and (iv) PVP (4 mg/mL) and 15 mM SDS (—).

TABLE 1: Fluorescence Decay Parameters of Dyes in Micelle and in the Polymer−Surfactant Aggregate at 21 °C

dye	medium	a_1	τ_1 (ps)	a_2	τ_2 (ps)	$\langle\tau_f\rangle^a$ (ps)
MC540	15 mM SDS	1.00	560			560
MC540	15 mM SDS+PVP (4 mg/mL)	0.54	825	0.46	1950	1340
OX-1	15 mM SDS	1.00	1200			1200
OX-1	15 mM SDS+PVP (4 mg/mL)	0.25	900	0.75	1300	1200

[a] Average fluorescence lifetime, $\langle\tau_f\rangle = a_1\tau_1 + a_2\tau_2$, for a biexponential decay, $a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)$.

The emission spectra of MC540 in different media are shown in Figure 3b. The emission quantum yield (ϕ_f) of MC540 increases from 0.04 in pure water to 0.1 in 4 mg PVP per mL and 0 mM SDS and to 0.15 in 15 mM SDS and 0 mg PVP. ϕ_f of MC540 in an aqueous solution containing 4 mg PVP per mL and 15 mM SDS is 0.375, which is much higher than that in PVP alone or SDS alone. This indicates that in an SDS−PVP aggregate MC540 experiences a microenvironment very different from that in pure SDS or in PVP alone.

The fluorescence decay of MC540 in water is single-exponential with a lifetime of 110 ps. In the PVP−SDS aggregate, the fluorescence decay of MC540 is found to be multiexponential. It should be emphasized that, in such a complex medium involving surfactants, polymer, and water, probes in different locations may give rise to different lifetimes. If the diffusion coefficient of the probe in the aggregate is the same as that in bulk water, within its lifetime of about 1 ns, the probe may undergo excursion over a region of radius $\approx$ 1 nm and may experience different environments.[20c] Even if we assume that inside the polymer−surfactant aggregate the diffusion or excursion of the probe is rather slow, there is a possibility that probes in different locations or sites are excited simultaneously. This may also give rise to a multiexponential decay. At this stage, it is difficult to study unequivocally the dynamics of the probe in a selected location within a microheterogeneous environment, like a polymer−surfactant aggregate. Several authors have discussed that the multiexponential decay can be fitted to a biexponential.[20] To get an average picture, we fitted the fluorescence decays to a biexponential, e.g., $a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)$, and used the average lifetime, $\langle\tau_f\rangle = a_1\tau_1 + a_2\tau_2$. The fluorescence lifetimes, amplitudes, and average lifetimes of the probes in different media are listed in Table 1. The average fluorescence lifetime of MC540 in PVP−SDS aggregate is 1340 ps which is different from that of MC540 in pure water (110 ps), in SDS micelle (560 ps), or in 4 mg PVP per mL without SDS (590 ps).

The fluorescence anisotropy decays of MC540 in different media (in SDS solution and in PVP−SDS) are shown in Figure 4. In PVP (4 mg/mL) and SDS micelles (15 mM), the anisotropy decay of MC540 is found to be biexponential with components 170 ± 20 and 3550 ± 50 ps (Table 2). For SDS micelles, in the absence of PVP, the anisotropy decay consists of two components 80 ± 10 and 1660 ± 50 ps.[4] In a solution that contains 4 mg PVP per mL and 0 mM SDS, the anisotropy decay components for MC540 are 30 and 2100 ps. It is obvious that the anisotropy decays of MC540 in the PVP−SDS aggregate are very different from that in SDS micelles or in aqueous PVP solution without SDS.

Similar results are obtained with OX-1. Because OX-1 is a cationic dye, it binds strongly to the anionic micelle, SDS. This is evidenced by the increase in fluorescence lifetime and average rotational relaxation time. At 21 °C, the fluorescence lifetime

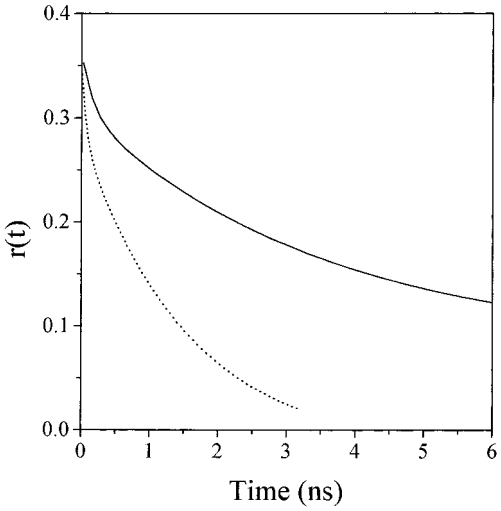


Figure 4. Decays of fluorescence anisotropy of MC540 in (i) 15 mM SDS (···) and (ii) PVP (4 mg/mL) and 15 mM SDS (—).

TABLE 2: Parameters of Rotational Dynamics of Dyes in Micelle and in the Polymer−Surfactant Aggregate at 21 °C

dye	medium	b	τ_{slow} (ps)	τ_{fast} (ps)
MC540	15 mM SDS	0.83	1600	80
MC540	15 mM SDS+PVP (4 mg/mL)	0.81	3550	170
OX-1	15 mM SDS	0.82	850	100
OX-1	15 mM SDS+PVP (4 mg/mL)	0.86	1100	170

of OX-1 increases from 520 ± 20 ps in water to 1200 ± 20 ps in SDS micelle, whereas rotational relaxation time increases from 125 ± 25 ps in water to a biexponential decay consisting of two components of 100 ± 20 and 850 ± 20 ps.[22] In PVP−SDS aggregates rotational dynamics of OX-1 becomes slower than that in SDS alone. The rotational dynamics of OX-1 in PVP−SDS aggregates are found to be biexponential with two components of 170 ± 10 and 1100 ± 20 ps. The rotational dynamics data of OX-1 is included in Table 2. Figure 5a shows the anisotropy decay of OX-1 in different environments, whereas Figure 5b shows the raw data for relaxation in PVP−SDS aggregates.

4. Discussion

As noted earlier, the anisotropy decay of probes in micelles may be explained in terms of the "wobbling-in-cone" model.[4−7] According to this model, the decay of the rotational anisotropy function $r(t)$ is biexponential as[4−7]

$$r(t) = r_0[\beta \exp(-t/\tau_{slow}) + (1 - \beta) \exp(-t/\tau_{fast})] \quad (2)$$

According to the model involving wobbling-in-cone and translational diffusion along micelle surfaces, the anisotropy decay $r(t)$ arises as a result of three independent motions: (i) wobbling motion, $r_w(t)$ of the dye molecule in a cone; (ii) translational motion, $r_t(t)$ of the dye along the surface of the spherical micelle; and (iii) rotation, $r_M(t)$ of the micelle as a whole.[4−7] As a result

$$r(t) = r_w(t)\, r_t(t)\, r_M(t) \quad (3)$$

If r_0 denotes the initial anisotropy (at $t = 0$) and τ_R, τ_D, and τ_M are the time constants for wobbling of the dye molecule,

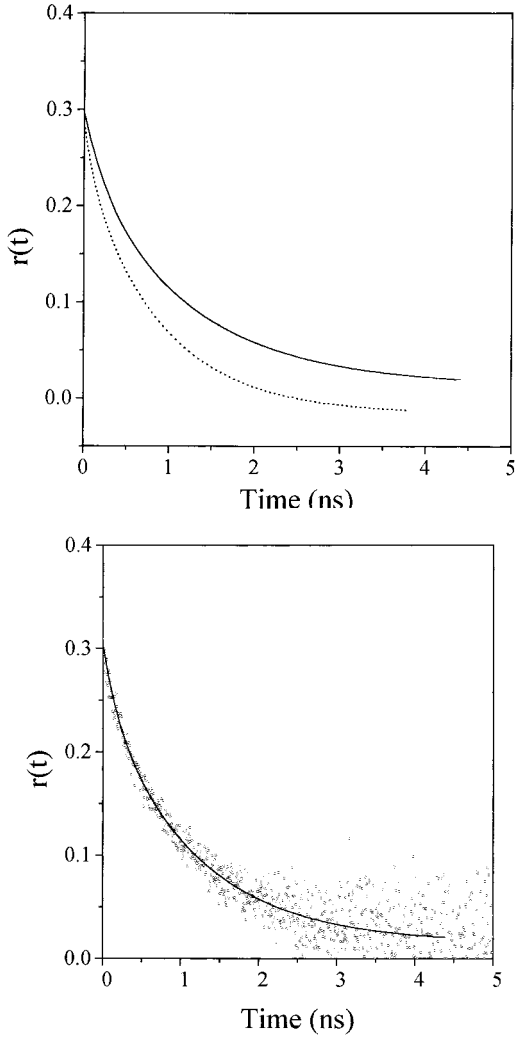


Figure 5. (a) Decays (fitted curve) of fluorescence anisotropy of OX-1 in (i) 15 mM SDS (···) and (ii) PVP (4 mg/mL) and 15 mM SDS (—). (b) Raw data along with fitted curve for rotational relaxation of OX-1 in PVP−SDS aggregates.

translation of the dye molecule and overall rotation of the spherical micelle[4−7]

$$r(t) = r_0[S^2 + (1 - S^2)\exp(-t/\tau_R)]\exp\{-t(1/\tau_D + 1/\tau_M)\} \quad (4)$$

where S is the order parameter related to the semicone angle θ in the wobbling in a cone model as[4−7]

$$S = 0.5\cos\theta\,(1 + \cos\theta) \quad (5)$$

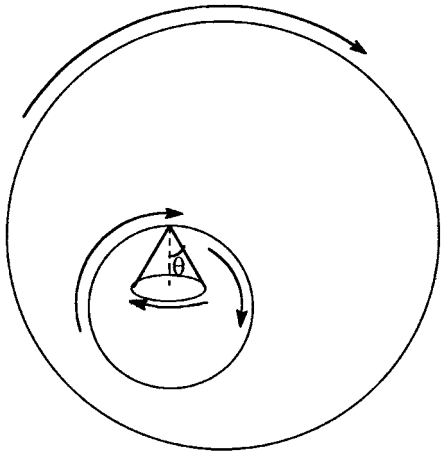
When the probe is attached to a spherical particle, τ_M is given by[4−6]

$$\tau_M = 4\pi\eta r_h^3/3KT \quad (6)$$

where η is the viscosity of water and r_h is the hydrodynamic radius of the spherical particle. For SDS, $r_h = 20$ Å and, at 25 °C, $\tau_M = 8.3$ ns.[5]

According to necklace model, the polymer−surfactant aggregate consists of several beads of spherical SDS micelles.[9−15] Obviously it is reasonable to assume that the individual spherical SDS micelles rotates inside the "necklace" formed by the polymer, PVP, and the surfactant, SDS. The hydrodynamic radius of the spherical SDS aggregates should be very close to

SCHEME 1: Model of the rotational dynamics in polymer−surfactant aggregates



that in SDS micelles, i.e., 20 Å. So, to a very good first approximation, one may assume τ_M for PVP−SDS aggregates same as that of τ_M in SDS, i.e., 8.3 ns (at 25 °C). In the present case, apart from the wobbling-in-cone, translational diffusion, and overall motion of micelle, there is an additional motion $r_A(t)$ due to the overall rotation of the polymer−surfactant aggregate (Scheme 1). Thus, in the model of wobbling-in-cone (r_w), translation of the probe dye along the micelle surface (r_t), overall rotation of micelle (r_M), and overall rotation of polymer-surfactant aggregate (r_A), eq 3 is modified as

$$r(t) = r_w(t)\, r_t(t)\, r_M(t)\, r_A(t) \quad (7)$$

If τ_A denotes time constant of the overall rotation of the aggregate, on inclusion of rotation of the aggregate, eq 4 becomes

$$r(t) = r_0[S^2 + (1 - S^2)\exp(-t/\tau_R)]\exp\{-t(1/\tau_D + 1/\tau_M + 1/\tau_A)\} \quad (8)$$

Comparing eq 8 with eq 2, one immediately gets

$$\beta = S^2 \quad (9)$$

$$1/\tau_{fast} = 1/\tau_R + 1/\tau_D + 1/\tau_M + 1/\tau_A \quad (10)$$

$$1/\tau_{slow} = 1/\tau_D + 1/\tau_M + 1/\tau_A \quad (11)$$

Recent light scattering experiment indicates that for low molecular weight PVP the hydrodynamic radius is approximately 60 Å.[9] Thus, if the polymer−surfactant aggregate rotates as a whole, $\tau_M^{PVP-SDS}/\tau_M^{SDS} \approx (60/20)^3 \times 8.3$ ns, so that in PVP−SDS aggregates, τ_A is nearly 224.1 ns at 25 °C. Calculating the value of τ_A and τ_M for PVP−SDS aggregates using eq 6, τ_D and τ_R may be immediately calculated from eqs 10 and 11. The results are tabulated in Table 3. Once all of the decay parameters are known the diffusion coefficients for wobbling and translational motion may be calculated as follows. The wobbling diffusion coefficient (D_w) is given by[4−6]

$$D_w = \{\tau_R(1 - \beta)\}^{-1}[-x^2(1 + x)^2\{\ln(1 + x/2) + (1 - x/2)\}\{2(1 - x)\}^{-1} + (1 - x)(6 + 8x - x^2 - 12x^3 - 7x^4)/24] \quad (12)$$

TABLE 3: Values of Parameters for the Model (Wobbling-in-Cone + Translational Diffusion + Overall Motion of the Aggregate) Derived from the Experimental Results at 21 °C

dye	medium	τ_R (ps)	τ_D (ps)	τ_M (ns)	τ_A (ns)	$D_W \times 10^{-8}$ (s^{-1})	$D_t \times 10^{10}$ ($m^2 s^{-1}$)	θ
MC540	15 mM SDS	84	1950	9.36		4.07	3.42	20.0°
MC540	15mM SDS+PVP (4 mg/mL)	179	5860	9.36	252.7	2.16	1.14	21.3°
OX-1	15mM SDS	110	940	9.36		3.29	7.09	20.7°
OX-1	15mM SDS+PVP (4 mg/mL)	200	1250	9.36	252.7	1.38	5.30	18.1°

TABLE 4: Temperature Dependence of Fluorescence Decay Parameters of MC540 in the Polymer−Surfactant Aggregate

temp (K)	a_1	τ_1 (ps)	a_2	τ_2 (ps)	$\langle\tau_f\rangle$ (ps)
288	0.40	690	0.60	2050	1500
294	0.53	800	0.47	1950	1340
298	0.38	480	0.62	1710	1250
318	0.46	370	0.54	1170	800
328	0.54	360	0.46	1050	680

Where, $x = \cos\theta$. The values of D_w at 21 °C for MC540 and OX-1 in PVP−SDS aggregates are tabulated in Table 3.

The translational diffusion coefficient is given by[4−6]

$$D_t = r_M 2/6\tau_D \tag{13}$$

The translational diffusion coefficients are tabulated in Table 3.

From the results summarized in Table 3, it is evident that because of the interaction with the polymer chains the wobbling motion of the dye molecule at the surface of the micelle is retarded by a factor of about 2, as indicated by the increase in τ_R and decrease in D_w. The translational motion, on the other hand, is also retarded by a factor of 1.3−3 depending on the probe. It is evident that in the PVP−SDS aggregates the presence of the polymer chains around the spherical SDS micelles hinder both the wobbling and translational motion of the two probes. It should be pointed out that in our analysis we have assumed that the orientation of the transition dipole of the dye is normal to the micelle surface. Krishna et al.[21] have studied in detail the effect of the orientation of the transition dipole near a micelle surface.

Finally, we have studied the effect of temperature on the anisotropy decay of MC540 in the PVP−SDS aggregate. It is observed that the fluorescence lifetime of MC540 decreases with an increase in temperature (Table 4) and the anisotropy decay becomes faster (Figure 6 and Table 5). From Table 5, it is evident that both D_w and D_t increase with temperature in the range of 15−55 °C. This qualitatively indicates increased mobility of the dye in the aggregate. Though the structure of the PVP−SDS aggregate has not been studied as a function of temperature, it is highly unlikely that the structure will change drastically over such a small temperature change. According to the Stokes−Einstein equation, D_w, D_t, and their ratio are related to the microviscosity (microscopic friction) as

$$D_w = \xi kT/6\eta V \tag{14}$$

$$D_t = \xi' kT/6\pi\eta r \tag{15}$$

$$\frac{D_t}{D_w} = \frac{\xi'}{\xi}\frac{4r^2}{3} \tag{16}$$

where ξ and ξ' 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. According to eq 16, D_t/D_w should be independent of temperature. However, as shown in Figure 7, we found a slight decrease of the ratio with an increase in temperature. It may be noted that a similar decrease of D_t/D_w with rise in temperature is also noted by Periasamy et al.[5]

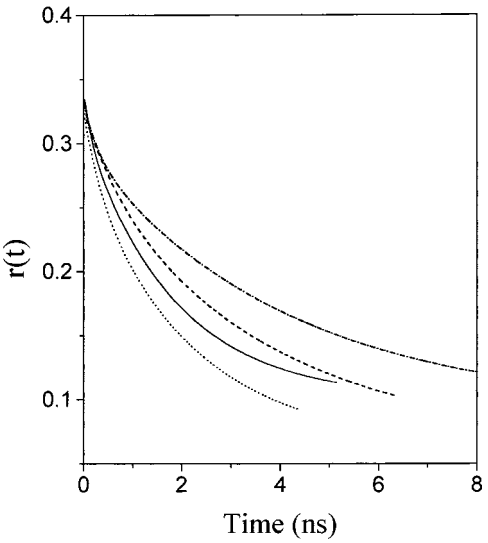


Figure 6. Decays of fluorescence anisotropy of MC540 in PVP (4 mg/mL) and 15 mM SDS at 15 (-·-·-), 25 (- - -), 45 (—), and 55 °C (···).

TABLE 5: Temperature Dependence of Rotational Dynamics of MC540 in the Polymer−Surfactant Aggregate

temp (K)	r_0	β	τ_{slow} (ns)	τ_{fast} (ns)	τ_M (ns)	τ_A (ns)	τ_D (ns)	$D_W \times 10^{-8}$ (s^{-1})	$D_t \times 10^{10}$ ($m^2 s^{-1}$)
288	0.33	0.80	4.15	0.31	11.2	302.2	6.76	1.20	0.98
294	0.34	0.81	3.55	0.17	9.36	252.7	5.86	2.16	1.14
298	0.34	0.80	2.85	0.15	8.30	224.1	4.43	2.55	1.50
318	0.33	0.80	2.30	0.14	5.10	136.9	4.31	2.71	1.55
328	0.33	0.80	2.00	0.10	4.10	109.8	4.05	3.84	1.65

There could be several reasons for the apparent deviation from the Stokes−Einstein behavior. It should be pointed out that microviscosity or microscopic friction is a measure of coupling or intermolecular interactions between the diffusing solute molecules and the surrounding solvent molecules. In the present complex medium consisting of polymer chains, surfactant assemblies, and bulk water, it is obviously difficult to define a microviscosity. In homogeneous liquids, there have been several attempts to estimate microscopic friction toward reorientational and isomerization motion.[23−25] The Stokes−Einstein equations were originally developed for translational diffusion. However, in many simple solvents, translational diffusion coefficient of aromatic hydrocarbons are observed to exhibit a nonlinear dependence on viscosity.[23−25] Zwanzig and Harrison[24b] argued that this is not due to failure of hydrodynamics. They suggested that the microscopic friction may vary from solvent to solvent, and they took this into account by allowing the effective size of the solute to vary from solvent to solvent. The volume of solvent (or polymer chains and surfactants) swept aside during translation of the probe dye on the spherical surface of the micelle is very different from that swept during wobbling motion. It is therefore quite possible that wobbling and translational motion may experience different microscopic

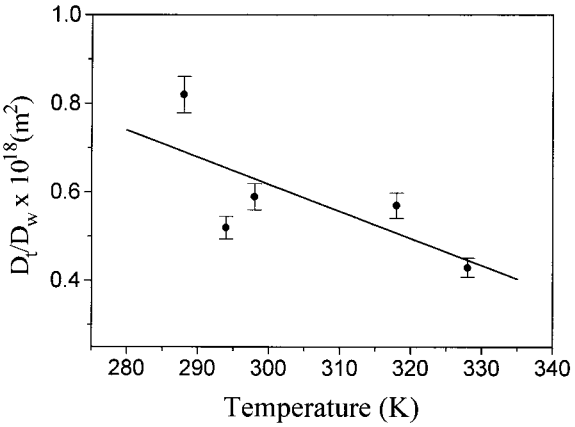


Figure 7. Plot of D_t/D_w vs temperature for MC540 in PVP−SDS aggregate.

friction in the present complex system of PVP−SDS aggregates. This might lead to different microviscosity experienced by the probe for wobbling and translational motion in PVP−SDS aggregates. If the microviscosities and their temperature dependence are different for wobbling and translational motion, the ratio D_t/D_w may not remain constant with temperature.

5. Conclusion

Rotational dynamics of two dyes MC540 and OX-1 in PVP−SDS aggregates is found to be substantially slower than that of the same dyes in a corresponding micelle, SDS. The magnitude of the diffusion coefficients for wobbling and translational motion for the two dyes in PVP−SDS aggregates indicate that the microscopic friction in PVP−SDS aggregates are greater than that in a SDS micelle alone. This is attributed to the interaction of the probe with the polymer chain surrounding the SDS micelles. This is consistent to the so-called "necklace model" of polymer−surfactant aggregates.

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