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The interaction of anionic micelle sodium dodecyl sulfate (SDS) and amphiphilic block copolymers polyethylene-b-polyethylene glycol (PE-b-PEG) and the sharp change of excited-state charge-transfer complex photophysics of 2-(4-(dimethylamino)styryl)-1-methylpyridinium iodide (DASPMI) inside of the supramolecular assembly have been addressed in the paper. The dramatic enhancement of emission intensity of DASPMI incorporated inside of the nanostructure formed by micellar and polymeric chains indicates a completely different environment compared to that in the water and micellar system. A huge increase in the rotational relaxation time obtained from time-resolved anisotropy decay and the value of the order parameter is indicative of a very restrictive regime in the self-assembly system. The wobbling and translational motion of the probe is also restricted inside of the micelle–polymer aggregate due to the presence of polymer chains. The translational diffusion coefficient is drastically reduced due to the aggregation.

Introduction

The interaction of a polymer with surfactants in aqueous solution is an interesting and engaging subject as many formulations and industrial process, like formulations in skin care and cosmetic product and pharmaceutical compounds,1−5 make simultaneous use of polymers and surfactants for their complementary or even synergistic roles.6 The detailed investigation of this interaction using fluorescence correlation spectroscopy,7 conductivity,8 fluorescence light scattering,9−11 NMR,12 and neutron scattering13 has been done by several groups. The first quantitative model of a polymer−surfactant interaction14,15 was based on two independent cooperative equilibria of the surfactant, namely, surfactant aggregate formation on the polymer chain and free micelle formation. It is well established16 that if anionic surfactant is added to the aqueous micellar solutions of amphiphilic diblock copolymers (PE-b-PEG), the surfactants will penetrate into the hydrophobic core of the block copolymers (Scheme 1). The interaction between the hydrophilic homopolymer and SDS can be strengthened by hydrophobic modification.17 Because of the hydrophobic effect,18 the polymer can readily form aggregates with surfactant in aqueous solution above a particular surfactant concentration, known as the critical aggregation concentration (CAC). The value of CAC is much smaller than the CMC (critical micellar concentration) of the surfactant.8,9,12,19−22 Due to this interaction, the environments around the micelles get modified by the copolymer in the shape of a bead,23 as shown in Scheme 1. The mixed micellar structure thus formed by the polymer and SDS micelle creates a more hydrophobic region than that by SDS alone, and the probe in this region can experience a more restricted regime.

This type of formation of an aggregation copolymer is more advantageous than the polymer because surfactant−copolymer mixtures may associate into different nanostructures, which can be designed by simply changing the composition of the species of the system or the medium condition. The ionic styryl dye 2-(4-(dimethylamino)styryl)-1-methylpyridinium iodide (DASPMI) has many applications due to its interesting multibond rotation. The three-state photophysics of DASPMI is dependent on both the polarity and microviscosity of the medium.26 The quantum yield of intramolecular charge transfer (ICT) fluorescence is influenced by the polarity of the environment, and the dissipation through the twisted intramolecular charge transfer (TICT) state is determined by the microviscosity of the environment.27 This simultaneous dependence of styryl dye photophysics on viscosity and polarity has offered several applications in polymer science and cell biology.28,29

The fluorescence anisotropy decay of the dye molecule in a micelle can be described by the wobbling-in-cone model, according to which there are three independent motions, (i) translational motion of dye on the surface, (ii) wobbling of the probe in a cone of angle θ, and (iii) overall rotation of the whole micelle. For polymer−surfactant medium, the values of these motions could be varied. The microscopic friction in many organized assemblies such as DNA and protein,30−32 micelles,33−35 reverse micelle,36 and cyclodextrins37,38 has been studied using rotational relaxation of a suitable probe. Despite some work in this emerging area of surfactant−copolymer interaction, no work regarding the molecular behavior inside of the core area of the surfactant−copolymer aggregate wrapped by a block copolymer could be observed. We were really intrigued to explore in this paper the behavior of DASPMI in the new supramolecular assembly of the anionic micelle (SDS) in the presence of amphiphilic block copolymers polyethylene-b-polyethylene glycol (PE-b-PEG) and also the nature of the assembly through the spectra and dynamics of the probe, as revealed from steady-state and time-resolved emission studies.

Materials and Method

2-(4-(Dimethylamino)styryl)-1-methylpyridinium iodide (DASPMI) was received from Aldrich Chemical, U.S.A., and purified by vacuum sublimation. Sodium dodecyl sulfate (SDS) and the polymer PE-b-PEG (Mw = 575) were used as received.
from Aldrich Chemicals, U.S.A. For measuring absorption and fluorescence spectra, deionized water (Millipore) was used. The absorption spectra at 300 K were recorded with a Shimadzu spectrophotometer (Model UV-2104 PC), and emission spectra were obtained with a Hitachi F-4500 fluorescence spectrophotometer. The concentration of DASPMI used in all fluorescence experiments was about $5 \times 10^{-5}$ M, and the emission was corrected for all of the optical components.

The fluorescence picosecond lifetime measurement was done with a Horiba Jobin Yvon Fluoro Cube 01-NL time-resolved fluorescence lifetime spectrometer with a TBX-04 detector, Data Station measurement software, and a DSA6 foundation package, and the excitation was carried out at 440 nm (diode laser). The instrument response function was $\sim 80$ ps. The same software was also used for the anisotropy. The decay was fitted for multiexponential decay with a $\chi^2$ value very near to unity.

Time-resolved emission spectra TRES were calculated from the fit parameters of the biexponential decays detected from 500 to 650 nm at intervals of 5 nm and the corresponding steady-state intensities. The TRES were fitted by log-normal functions.39

Results and Discussion

Steady-State Absorption and Emission Spectra. The absorption spectra of DASPMI in water, in SDS micelles, and in polymer–surfactant aggregates are shown in Figure 1. In aqueous solution, DASPMI exhibits an absorption band at 435 nm. Upon SDS addition, we observe a red shift ($\sim 462$ nm) in the absorption spectra possibly due to excess excited-state stabilization compared to that of ground state in SDS. The red shift may be due to hydrogen bonding between the surfactant head group and the $\text{-NH}_2$ group. In the absence of SDS, the solution containing 1 mg/mL polymer shows a peak which is very similar to that with the water solution (at $\sim 435$ nm); possibly here, the dye does not go into the copolymer. However, the solution containing SDS and 1 mg/mL polymer absorption spectrum shows an increased peak at $\sim 462$ nm.

Like absorption spectra, when the copolymer is added in a water solution of DASPMI, the intensity of the charge-transfer emission band at 570 nm remains unchanged, although the diblock copolymer forms a micelle, keeping hydrophobic part (polyethylene) in the core region and the hydrophilic part (polyethylene glycol) in water environments. However, surprisingly, the intensity of the 570 nm emission band gradually increases with SDS concentration in the presence of copolymer (1 mg/mL). This enhancement of the intensity maximum is enormous at 15 mM of SDS (Figure 2). The magnitude of the emission enhancement caused by 15 mM SDS alone is much

\begin{equation}
r(t) = \frac{[I_{vv} - GI_{vh}]}{[I_{vv} + 2GI_{vh}]}
\end{equation}

where $G$ is the ratio between the fluorescence intensity at parallel and perpendicular polarizations of the emission with respect to the excitation beam. The value of $G$ has been used as 0.56, as identified for the instrument.

The Nano-ZS (Malvern) instrument (5 mW He–Ne laser, $\lambda = 632$ nm) was used for dynamic light scattering (DLS) experiments. The sample was poured in a DTS0112 low-volume disposable cuvette of 1.5 mL (path length 1 cm). Before the DLS study, samples (typical concentration $\sim 10^{-5}$ M) were passed through a 0.2 Am filter. The operating procedure was programmed (using the DTS software supplied with the instrument) such that there was an average of runs, and each run was averaged for 15 s, with an equilibration time of 3 min at 25 °C.

Field emission scanning electron microscopy (FESEM) (JSM-6700F, from JEOL, Japan) was used to record the scanning electron micrograph images of PE-$b$-PEG and SDS micellar aggregates.

![Figure 1](image_url)
less than that in the presence of both polymer and SDS. It is to be mentioned here that in the absence of copolymer, the emission intensity of DASPMI shows a jump at 8 mM SDS,
indicating a CMC (critical micellar concentration) of SDS. In a polymer solution of DASPMI with the addition of SDS, the emission intensity starts to increase (critical aggregation concentration, CAC, for the polymer–surfactant system) at a concentration at least 10 times smaller than the CMC of the surfactant SDS. In the present system, the value of CAC is 0.7 mM. However, for a high SDS concentration in the polymeric micellar solution, the rate of increment of the fluorescence intensity of DASPMI gradually decreases compared to the same concentration of the SDS solution alone. This result indicates that in the presence of copolymer, DASPMI experiences a microenvironment which is very different from that in neat SDS micellar aggregates. A dramatic increase in fluorescence intensity in the complex micelle–copolymer system over that in micellar environment alone may be attributed to the drastic cut in the nonradiative channel in the absence of water. Therefore, this composite system (supramolecular assembly) creates a water-tight environment in which the probe dye shows a completely different emission characteristic than that only in neat water, in micelle, and in PE-b-PEG polymer alone. When the SDS concentration increases beyond the CAC value, it may be surmised that a new type of aggregate (supramolecular assembly) due to the interaction of the PEG chains in the corona region and SDS micelles is formed. As SDS is added gradually in the mixed polymer–surfactant micelles, the disruption of the mixed polymer–surfactant micelles arises, and this disruption leads to a decrease of the binding rate due to electrostatic repulsions of SDS head groups resulting in the change in emission intensity. The formation of a supramolecular assembly is confirmed by the SEM picture (Figure 3a,b), like the simulated picture of diblock copolymer.

The fluorescence lifetime acts as a sensitive parameter for exploring the local environment around a fluorophore, and it is sensitive to excited-state interactions. The different extent of solvent relaxations around a fluorophore could also be expected to give rise to differences in its lifetime. The increase in average lifetime values of multiexponential decay of DASPMI in the composite medium compared to SDS is ~2 times (Table 1). The multiexponential decay arises due to the superposition of many decays of slightly different lifetimes, as discussed by many workers. To get an average picture, we fitted the fluorescence decays to a biexponential, for example, $a_1 \exp(-t/\tau_1) + a_2 \exp(t/\tau_2)$, and the averaged lifetime comes as

$$\langle \tau_0 \rangle \geq a_1 \tau_1 + a_2 \tau_2$$

The fluorescence lifetimes and amplitudes of the probe in different media are shown in Table 1 (Figure 4). The average fluorescence lifetime of DASPMI in a polymer–surfactant aggregate is nearly double of that in SDS alone, possibly due to the supramolecular assembly between the polymer and micelle and the complete isolation of the supramolecular assembly from water. The dramatic increase in emission intensity, as revealed from the steady-state experiments due to the diminished nonradiative hydrogen bonding channel caused...
by estrangement of DASPMI from water, also corroborates the increase in lifetime. The location of the probe molecules can be measured by the time-resolved anisotropy measurement in water molecules and in polymer–surfactant aggregates.

Decay parameters were calculated from the mono- and biexponential fitting procedure. They were used together with the steady-state intensities at the corresponding wavelengths to calculate the TRES. Figure 5 shows that the emission spectra shift progressively to longer wavelengths at longer times, and the band shape shows no variation with a time variation of $0.3$–$15$ ns. The solvent relaxation time is comparable to the fluorescence lifetime of the fluorophore, which produces the emission band shift to the lower energies at longer times. These facts are in agreement with the continuous model for a spectral relaxation, which can explain TRES that comes from a multitude of solvent fluorophore interactions.46

\[
\begin{align*}
    r(t) = a_1 \times e^{-t/\tau_1} + a_2 \times e^{-t/\tau_2} = r_0 \left[ \beta \exp\left(\frac{-t}{\tau_{\text{slow}}}\right) + (1 - \beta) \exp\left(\frac{-t}{\tau_{\text{fast}}}\right) \right]
\end{align*}
\]

where $a_1$ and $a_2 = \beta$ are the fast and the slow components with time constants $\tau_1 = \tau_{\text{fast}}$ and $\tau_2 = \tau_{\text{slow}}$, respectively. Figure 6 shows the fluorescence anisotropy decay of DASPMI in micelle and polymer–surfactant aggregates. In Table 2, the fitted results of fluorescence anisotropy decays of DASPMI in pure water, micelles, and polymer–surfactant aggregates are shown. Table 2 shows that the molecules have a higher rotational relaxation time in micelle and polymer–surfactant aggregates compared to that of water. The large value in rotational relaxation time in micelle and polymer–surfactant aggregates indicates that the molecule bound to the Stern layer experiences a restricted environment. It is interesting that the rotational relaxation time in polymer–surfactant aggregates is larger than that in micelles, which indicates a more restricted environment due to presence of the excess polymer surrounding the micelle and thus shielded from outside water.

It has been a well-established fact from numerous studies available in the literature33,36,47 that the biexponential anisotropy decay of the probe observed in the micellar system is neither due to the fact that the probe is solubilized in two distinct regions of the micelle nor due to anisotropic rotations of the probe. On

### Table 1: Fluorescence Lifetime Decay Parameters of Dye in Micelle and in Polymer–Surfactant Aggregates

<table>
<thead>
<tr>
<th>system</th>
<th>$q_i$</th>
<th>$\tau_1$ (ns)</th>
<th>$a_1$</th>
<th>$\tau_2$ (ns)</th>
<th>$a_2$</th>
<th>$\langle \tau_r \rangle$ (ns)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>dye + water</td>
<td>0.018</td>
<td>0.6</td>
<td>0.68</td>
<td>1.4</td>
<td>0.29</td>
<td>0.814</td>
<td>0.986</td>
</tr>
<tr>
<td>dye + 20 mM SDS</td>
<td>0.054</td>
<td>1.01</td>
<td>0.78</td>
<td>10.5</td>
<td>0.2</td>
<td>2.8</td>
<td>1.021</td>
</tr>
<tr>
<td>dye + 20 mM SDS + poly(1 mg/mL)</td>
<td>0.12</td>
<td>0.9</td>
<td>0.6</td>
<td>11.6</td>
<td>0.4</td>
<td>5.2</td>
<td>1.042</td>
</tr>
</tbody>
</table>

### Table 2: Initial Anisotropy ($r_0$) and Rotational Relaxation Time of Dye in Micelle and in Polymer–Surfactant Aggregates

<table>
<thead>
<tr>
<th>system</th>
<th>$r_0$</th>
<th>$\tau_{1r}$ (ns)</th>
<th>$\tau_{2r}$ (ns)</th>
<th>$\langle \tau_r \rangle$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dye + water</td>
<td>0.39</td>
<td>1</td>
<td>0.120</td>
<td>0.120</td>
</tr>
<tr>
<td>dye + 20 mM SDS</td>
<td>0.36</td>
<td>0.36</td>
<td>0.115</td>
<td>0.64</td>
</tr>
<tr>
<td>dye + 20 mM SDS + poly(1 mg/mL)</td>
<td>0.36</td>
<td>0.24</td>
<td>0.112</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Figure 4. Fluorescence decays of a $5 \times 10^{-5}$ M aqueous DASPMI solution containing SDS (15 mM) and diblock copolymer (1 mg/mL) and SDS (15 mM).

Figure 5. The peak-normalized components of time-resolved emission of DASPMI in diblock copolymer (1 mg/mL) and SDS (15 mM). The times are 0.3, 1.3, 4.0, 7.0, 10.0, and 15.0 ns. The spectrum moves toward lower energies with the passage of time.

Figure 6. Fluorescence anisotropy decay of DASPMI ($5 \times 10^{-5}$ M) in (1) SDS (15 mM) with a value of $\chi^2 = 1.01$ and (2) diblock copolymer (1 mg/mL) and SDS (15 mM) with a value of $\chi^2 = 1.06$. 
the other hand, in micelles and micelle–polymer aggregates, the biexponential rotational relaxation time is a consequence of three independent depolarizing motions,\(^33,34,47\) namely, (1) the translational motion \(r(t)\) of the dye, (2) wobbling dynamics \(r_w(t)\) of the dye about the local symmetry axis in the micelle,\(^48,49\) and (3) the rotational dynamics \(r_m(t)\) of the spherical micelle as a whole. The decay time constant associated with the three motions are \(\tau_r\) (translational diffusion), \(\tau_w\) (wobbling dynamics), and \(\tau_m\) (rotation of the micelle).

In the present case, the rotational motion of the SDS micelle is hindered by the polymeric micelle, and apart from the above three motions, there is an additional motion \(r_s(t)\) due to the overall rotation of the polymer–surfactant aggregates (Scheme 2). Therefore, we can write

\[
r(t) = r_w(t)r_r(t)r_m(t)
\]

For the description of the rotational motion in polymer–surfactant aggregates, we use the following equation from the biexponential anisotropy decay (Figure 5)

\[
r(t) = r_0\left[8^2 + (1 + 8^2)\exp\left(-t/\tau_{tr}\right)\exp\left(-t/\tau_0\right)\right]
\]

where \(r_0\) denotes the initial anisotropy and \(\tau_A\) is the time constant of the overall rotation of the aggregates.

Comparing this equation with eq 1, we get

\[
\frac{1}{\tau_{slow}} = \frac{1}{\tau_{2r}} = \frac{1}{\tau_{tr}} + \frac{1}{\tau_0}
\]

\[
\frac{1}{\tau_{fast}} = \frac{1}{\tau_{tr}} + \frac{1}{\tau_0} + \frac{1}{\tau_A}
\]

Therefore, the wobbling time of the dye may be obtained from the following equation

\[
\frac{1}{\tau_w} = \frac{1}{\tau_{fast}} - \frac{1}{\tau_{slow}}
\]

Here, we assumed that the probe molecules are attached to the surface of the micelles. The micellar rotation for SDS micelle alone \((\tau_m)\) can be obtained from the Stokes–Einstein–Debye relation\(^50\) with the stick boundary condition

\[
\tau_m = \frac{4\pi\eta r_m^3}{3KT}
\]

where \(r_m\) is the hydrodynamic radius of the micelles, \(\eta\) is the viscosity of the water, and \(K\) and \(T\) are the Boltzmann constant and absolute temperature, respectively. The hydrodynamic radius of SDS micelles is found to be 21 Å.\(^51\) Using this value, the SDS micellar rotational time \(\tau_m\) is 8.09 ns.

The order parameter \(S\) is a measure of the equilibrium orientational distribution of the probe and satisfies the inequalities \(0 \leq S^2 \leq 1\). If the fast motion is isotropic,\(^33\) \(S = 0\), and if it is completely restricted, \(|S| = 1\). \(S\) also can be defined as

\[
S^2 = a_{2r} = \beta
\]

In the present case, the values are \(S \approx 0.87\) for polymer–surfactant aggregates and \(S \approx 0.8\) for the micellar only medium. This indicates that the probe molecules face a more restricted environment inside of the polymer–surfactant aggregates than in the micellar media.

The order parameter is related to the cone semiangle \(\theta_0 = \cos^{-1}(1/2)(1 + 8|S|^{1/2})\). The dynamic light scattering experiment reveals that the hydrodynamic radius of the polymer is approximately 71 Å.\(^6\) For the rotation of polymer–surfactant aggregates as a whole, \((r_A)\) may be written as \(r_{A,poly} = r_m^{poly-SDS}/r_m^{SDS} \approx 1\) \(71/21\), \(\times\) 8.09 ns \(\approx\) 312 ns. Therefore, now, we can get the values of \(\tau_A\), \(\tau_r\), and \(\tau_w\) for polymer–surfactant aggregates (Table 3).

The translational diffusion coefficient \((D_t)\) is related to \(\tau_t\) by the following equation: \(D_t = r^2/6\tau_t\). Now, the wobbling diffusion coefficient\(^52\) is obtained from the following relations:

\[
D_w \tau_w (1 - S^2) = -x_0^2(1 + x_0^2)[\log((1 + x_0)/2) + (1 - x_0)/2]/[2(1 - x_0) + (1 - x_0)(6 + 8x_0 - x_0^2 - 12x_0^2)]
\]

where \(x_0 = \cos \theta_0\)

The values of \(D_t\), \(D_w\), and \(\theta_0\) that were calculated using the above equations are given in Table 3. From 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 1.5, as indicated by the increase in \(\tau_w\) and decrease in \(D_w\). It is evident that in the polymer–surfactant aggregates, the presence of the polymer chains around the spherical SDS micelles hinders both the wobbling and translational motion of the probe. It should be mentioned here that we have assumed that the orientation of the transition dipole of the dye is normal to the micelle surface.

### TABLE 3: Analytical Rotational Parameters for Dye in Micelle and in Polymer–Surfactant Aggregates

<table>
<thead>
<tr>
<th>System</th>
<th>(\tau_m) (ns)</th>
<th>(\tau_A) (ns)</th>
<th>(\tau_w) (ps)</th>
<th>(\tau_r) (ns)</th>
<th>(D_w \times 10^{-8} (S^2))</th>
<th>(D_t \times 10^{20} (m^2 s^{-1}))</th>
<th>(\theta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye + 20 mM SDS</td>
<td>8.09</td>
<td>127</td>
<td>1.4</td>
<td>6.57</td>
<td>5.25</td>
<td>1.4</td>
<td>30.7°</td>
</tr>
<tr>
<td>Dye + 20 mM SDS + poly (1 mg/mL)</td>
<td>312</td>
<td>116</td>
<td>3.1</td>
<td>4.49</td>
<td>1.4</td>
<td>24.2°</td>
<td></td>
</tr>
</tbody>
</table>
Conclusion

Therefore, in conclusion, we have created a completely new water-tight compartment of a micelle–polymer supramolecular assembly, where a different photophysics of dye due to a significant decrease in nonradiative decay through hydrogen bonding can be seen. The aggregation of the polymer and micelle creates a water-tight environment in the core of the micelle. The SEM picture also confirms the formation of assembly between the polymer and the micelle. In polymer surfactant aggregates, the presence of the polymer chains around the spherical SDS micelles hinder both the wobbling and translational motion of the probe. The composite polymer micelle system has a solvent reorientation time.

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References and Notes

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