Photoisomerization of merocyanine 540 in polymer–surfactant aggregate

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Abstract. Photoisomerization of merocyanine 540 (MC540) in a polymer–surfactant aggregate is studied using picosecond time resolved emission spectroscopy. The aggregate consists of the polymer, poly(vinylpyrrolidone) (PVP) and the surfactant, sodium dodecyl sulphate (SDS). With increase in the concentration of SDS in an aqueous solution of MC540 containing PVP, the emission quantum yield and lifetime of MC540 increase markedly. This indicates marked retardation in the nonradiative photoisomerization process of MC540, when it binds to the polymer-surfactant aggregate. The critical association concentration of SDS for binding to PVP has been found to be 0·5 mM. This is about 16 times lower than the CMC of SDS in pure water (8 mM).

Keywords. Dynamics of photoisomerization; polymer–surfactant aggregate.

1. Introduction

Many biological and technological processes involve polymer-surfactant interaction [1–17]. Such interactions have been studied by fluorescence correlation spectroscopy [2], surface tension [5], fluorescence [8,15–17], light scattering [10], NMR [12], neutron scattering [14], conductivity [15], as well as by many theoretical models [1,4,8,10]. According to the 'necklace model' (figure 1), structure of the polymer-surfactant aggregate is like a necklace with spherical micelles as beads which are surrounded and separated by polymer strands, as threads [2–4,8–17]. In aqueous solution, polymer-surfactant aggregates are formed above a particular surfactant concentration, known as the critical association concentration (CAC). The CAC of a surfactant is often much lower than its critical micellar concentration (CMC). Among the various polymer-surfactant aggregates, the one made up of poly(vinylpyrrolidone) (PVP) and sodium dodecyl sulphate (SDS) has been very well studied [2–4,7–12]. The critical association concentration (CAC) corresponds to the break in the plot of size of aggregates against surfactant concentration. According to a recent fluorescence correlation study, for PVP-SDS system CAC is ~0·3 mM of SDS which corresponds to the onset in the increase in size of the aggregates [2]. CAC is found to be independent of polymer concentration [2]. This is far below the CMC of SDS (8 mM) in water. Above CAC, the polymer chains wrap around the micelles and remove some water

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from the Stern layer of micelle and thus, lowers the polarity of the Stern layer of the micelle.

The photophysical property of a fluorescent probe, merocyanine 540 (MC540, figure 2) is very much sensitive to environment and hence, has been used to study many organized media [23,24]. The main nonradiative pathway of MC540 is photoisomerization about a central double bond [18–22]. The dynamics of isomerization of MC540 and other cyanine dyes have been used earlier to probe many organized media such as water surface, micelles, reverse micelles, nanomaterials [20,23–26]. In an aqueous solution the emission quantum yield and lifetime of MC540 increases as the probe binds to these organized assemblies. This indicates suppression of the nonradiative photoisomerization process. In the present work, we extend our investigation on the photoisomerization of MC540 in a new environment, namely polymer-surfactant aggregate.

2. Experimental

The dye merocyanine 540 (Sigma), SDS (Aldrich) and PVP (Mol. wt. 29000 Da, Aldrich), were used as received. The steady-state absorption and emission spectra were recorded in a JASCO 7850 spectrophotometer and a Perkin–Elmer 44B spectro-
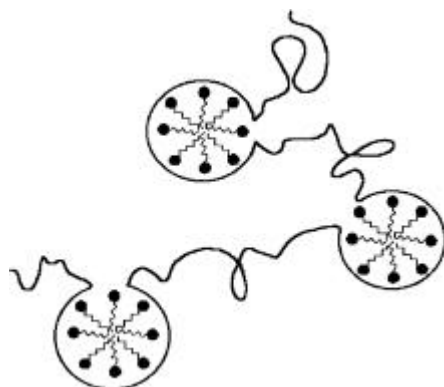

Figure 1. Schematic representation of the 'necklace model' of polymer-surfactant aggregates.
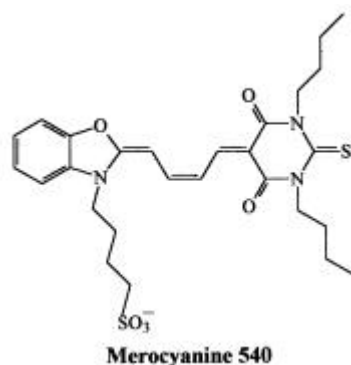

Merocyanine 540

Figure 2. Structure of merocyanine 540.

fluorimeter, respectively. For lifetime measurement, the sample was excited at 570 nm by a cavity-dumped dual jet Rhodamine 6G/DODCI dye laser (Coherent 702-1) pumped by a cw mode-locked Nd:YAG laser (Coherent Antares 76s). The emission was detected at magic angle polarization using a Hamamatsu MCP photomultiplier (2809U). The fluorescence decays were deconvoluted using a global lifetime analysis software (PTI). The quantum yield is calculated with respect to the reported value of MC540 in water at room temperature ($f_f = 0.04$)[24].

3. Results

3.1 *Steady state spectra*

In an aqueous solution, MC540 shows a broad absorption peak around 500 nm which is ascribed to the formation of nonfluorescent dimmers[27]. On addition of 4 mg PVP per ml, absorption spectrum of MC540 remains identical to that in aqueous solution. When SDS is added to the solution of MC540 containing 4 mg PVP per ml the absorption spectra remains same up to 0·5 mM SDS. When concentration of SDS exceeds 0·5 mM a sharp absorption peak appears at around 560 nm (figure 3). The 560 nm peak of MC540 corresponds to the monomer[27]. This shows that, for SDS concentration greater than 0·5 mM, the nonfluorescent dimers of MC540 break and MC540 remains in the form of highly fluorescent monomers in the polymer-surfactant aggregate. In the absence of PVP, the emission properties of MC540 remains unchanged on addition of SDS up to the CMC, i.e., 8 mM. Thus the remarkable change observed at a much lower SDS concentration of 0·5 mM, in the presence of PVP, may be attributed to polymer (PVP)-surfactant (SDS) aggregates.
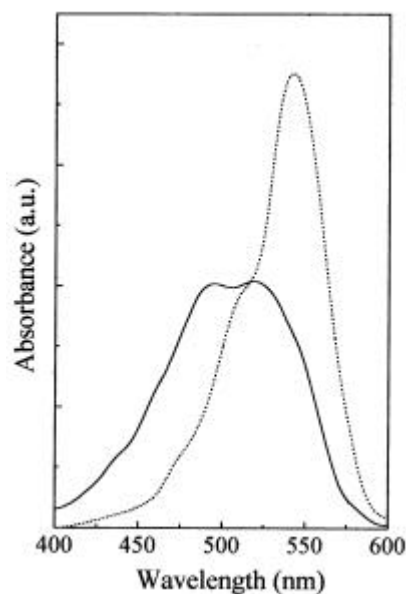

Figure 3. Absorption spectra of merocyanine 540 in (i) water (——), (ii) an aqueous solution containing 4 mg PVP per ml and 12 mM SDS (······).

On addition of SDS to an aqueous solution of MC540 containing 4 mg PVP per ml, the emission maximum of MC540 shows a red shift from 580 nm in the absence of SDS to 585 nm in 12 mM SDS (figure 4a). This red shift of the emission maximum of MC540 on addition of SDS clearly indicates that, inside the polymer-surfactant aggregate the probe experiences an environment less polar than that in the aqueous polymer solution in absence of SDS. In an aqueous polymer solution of MC540 containing 4 mg PVP per ml, the emission quantum yield (f_f) is 0·10 which is slightly greater than that (0·04) in pure water. On addition of SDS to an aqueous PVP solution containing MC540, the emission quantum yield (f_f) of MC540 increases to 0·375 in 12 mM SDS (figure 4b). The plot of f_f of MC540 against SDS concentration shows a sharp break at around 0·5 mM. This clearly suggests that the CAC of PVP-SDS aggregate is at about 0·5 mM. The onset of increase in f_f appears at a concentration of 0·5 mM SDS which is close to the concentration corresponding to onset of increase in size of aggregates reported by Narenberg *et al.* (0·3 mM)[2]. The increase in quantum yield with the increase in concentration of SDS is a clear evidence of the suppression of the main nonradiative pathway i.e. the photoisomerization of MC540 in the PVP-SDS aggregate.

3.2   *Time resolved studies*

The fluorescence decays of MC540 in aqueous solution of PVP as well as in PVP-SDS aggregate is multiexponential. The multiexponential nature of the decay is due to the microscopical heterogeneity of the medium with a marked variation in polarity and viscosity over a small distance[28]. To get an average picture we fitted the decays to a biexponential e.g. $a_1 \exp(-t/t_1) + a_2 \exp(-t/t_2)$ and used the average fluorescence lifetime, $\langle t_f \rangle = a_1 t_1 + a_2 t_2$. The components ($t_i$), their amplitudes ($a_i$) and $\langle t_f \rangle$ are listed in table 2. In pure water, the fluorescence decay of MC540 is single exponential with a lifetime, 110 ps. In an aqueous solution containing 4 mg PVP per ml, the average fluorescence lifetime, ($\langle t_f \rangle$) of MC540 is 600 ps. With increase in concentration of SDS in this polymer

Table 1.   Variation of quantum yield (f_f), average lifetime (t_f) and isomerization rate constant (k_{iso}) of merocyanine 540 (MC 540) with change in concentration of sodium dodecyl sulphate (SDS) in an aqueous solution of 4 mg polyvinyl pyrrolidone (PVP) per ml.

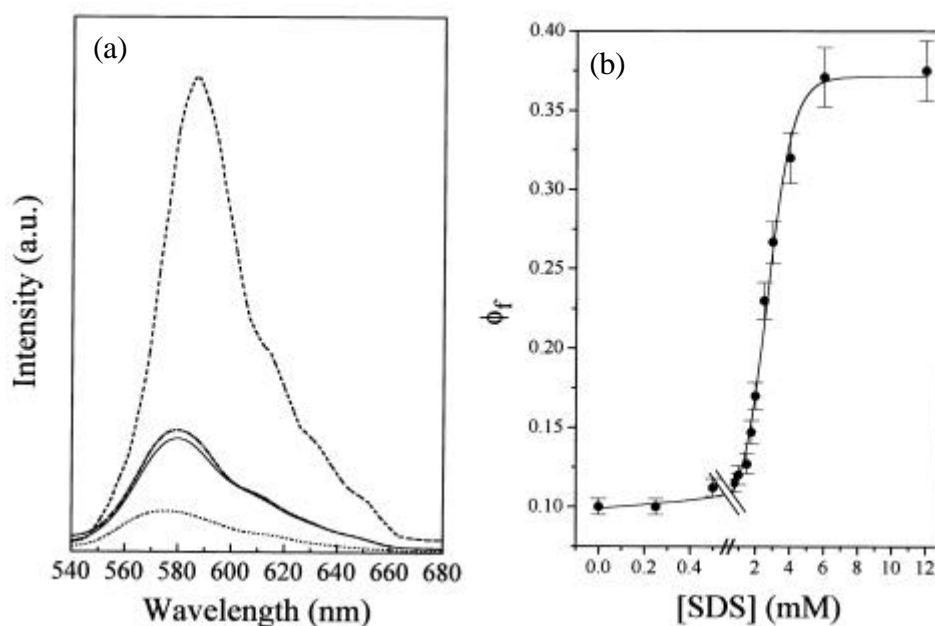| Concentration of SDS (mM)	f_f*	$\langle t_f \rangle$* (ps)	$k_{iso} \times 10^{-9}$ (s^{-1})	$k_r \times 10^{-9}$ (s^{-1})
0·00	0·100	600	1·50	0·17
0·25	0·100	600	1·50	0·17
0·50	0·112	605	1·47	0·18
0·75	0·115	630	1·41	0·18
1·00	0·120	640	1·38	0·19
1·50	0·127	710	1·23	0·18
1·75	0·147	800	1·07	0·18
2·00	0·170	940	0·88	0·18
2·50	0·230	1140	0·68	0·20
3·00	0·267	1190	0·62	0·22
4·00	0·320	1210	0·56	0·26
6·00	0·371	1250	0·50	0·30
12·00	0·375	1250	0·50	0·30

* ± 5%

Figure 4. (a) Emission spectra of MC540 in water (······), aqueous solution of PVP (4 mg/ml) (——), PVP (4 mg/ml) and 0.5 mM SDS (-·-·-), PVP (4 mg/ml) and 12 mM SDS (----). (b) Variation of quantum yield (f_f) of merocyanine 540 in an aqueous solution containing 4 mg PVP per ml with increasing concentrations of SDS.

solution, $\langle t_f \rangle$ of MC540 increases from 600 ps in 0 mM SDS to 1250 ps in 12 mM SDS. The average fluorescence lifetimes ($\langle t_f \rangle$) of MC540 in the presence of PVP and different SDS concentrations are listed in table 1 and fluorescence decays are shown in figure 5a. The sigmoidal nature of the plot of $\langle t_f \rangle$ against the concentration of SDS and a sharp break at 0·5 mM (figure 5b) indicates that the CAC of PVP-SDS aggregate is 0·5 mM. This result is consistent with the increase in f_f and is surely due to the inhibition of the photoisomerization process of MC540.

The rate constant of isomerization in the excited state of MC540 (k_{iso}) was calculated from the observed f_f and $\langle t_f \rangle$, using the relation

$$k_{iso} = (1 - f_f)/\langle t_f \rangle.$$

The values of k_{iso} of the probe in the presence of 4 mg PVP per ml and different concentration of SDS are tabulated in table 1. The plot of k_{iso} against the concentration of SDS is also sigmoidal (figure 6). In an aqueous solution of PVP, the rate constant of isomerization process of MC540 decreases about three times from $1·5 \times 10^9$ s^{-1} in 0 mM SDS to $0·5 \times 10^9$ s^{-1} in 12 mM SDS.

The increase in $\langle t_f \rangle$ and decrease in k_{iso} clearly shows that the isomerization process of MC540 is inhibited to a greater extent in PVP-SDS aggregate than that in an aqueous PVP solution without SDS. The plot of emission quantum yield, average life time and rate constant of isomerization process against SDS concentration clearly indicates that, CAC of PVP-SDS aggregate is 0·5 mM.
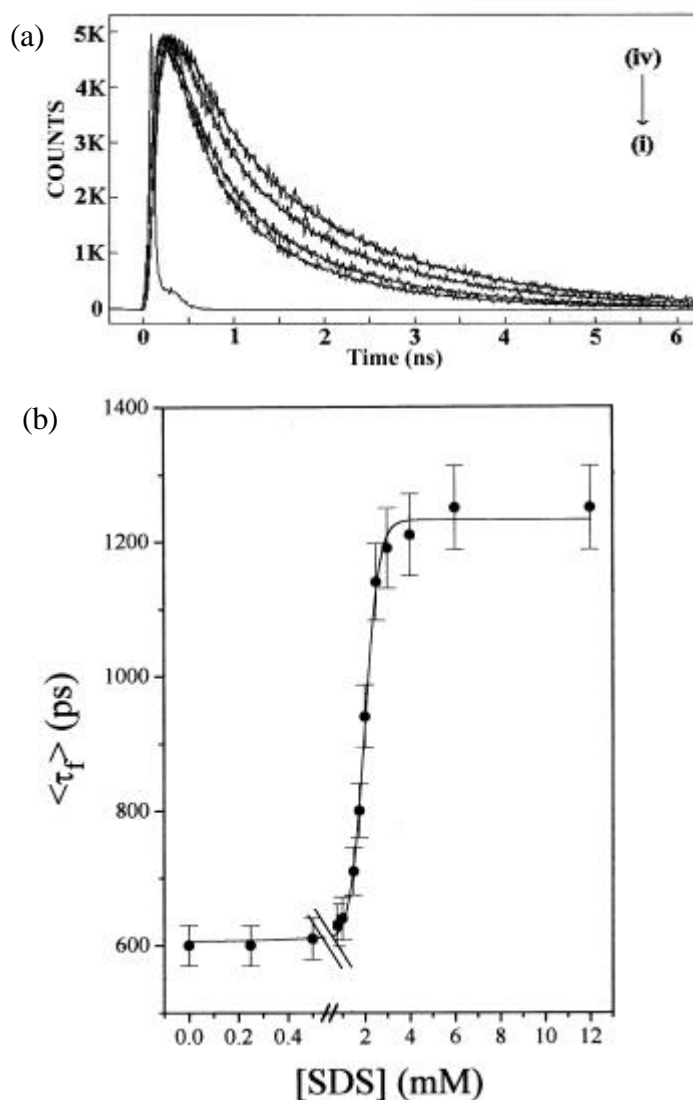
(a)

(b)

Figure 5. (a) Fluorescence decays of merocyanine 540 in an aqueous solution containing 4 mg PVP per ml and (i) 0·5 mM SDS, (ii) 1·5 mM SDS, (iii) 2·0 mM SDS, (iv) 12 mM SDS. (b) Variation of average fluorescence lifetime ($\langle t_f \rangle$) of merocyanine 540 in an aqueous solution containing 4 mg PVP per ml with SDS concentration.

4. Discussions

The most fascinating observation in this work is the sharp increase in f_f and $\langle t_f \rangle$ and the sharp decrease in k_{iso} in PVP-SDS aggregate around a SDS concentration of 0·5 mM. In a 4 mg PVP per ml solution f_f and $\langle t_f \rangle$ of MC540 increases about 3·75 times and 2 times respectively from 0 mM SDS to 12 mM SDS. k_{iso} of MC540 decreases about 3 times from 0 mM SDS to 12 mM SDS. In all cases, the sigmoidal curves show a break at about

0.5 mM SDS concentration. This is about 16 times lower than the CMC of SDS in water (8 mM).

Because of the presence of the anionic sulfonate group, MC540 is constrained to remain at the interface between the micellar aggregate and bulk water with the sulfonate group projected into bulk water. The dramatic decrease in k_{iso} appears to be due to the increase in viscosity as well as the decrease in polarity in the microenvironment of PVP-

Table 2. Fluorescence decay parameters of merocyanine 540 (MC540) in an aqueous solution containing 4 mg PVP per ml and different concentrations of SDS.

Concentration of SDS (mM)	a_1	t_1 (ps)	A_2	t_2 (ps)	$\langle t_f \rangle$* (ps)
0·00	0·62	290	0·38	1110	600
0·25	0·63	290	0·37	1120	600
0·50	0·62	280	0·38	1140	605
0·75	0·62	300	0·38	1170	630
1·00	0·60	270	0·40	1190	640
1·50	0·58	310	0·42	1270	710
1·75	0·55	360	0·45	1330	800
2·00	0·50	400	0·50	1480	940
2·50	0·46	490	0·54	1700	1140
3·00	0·40	470	0·60	1670	1190
4·00	0·38	450	0·62	1680	1210
6·00	0·35	490	0·65	1660	1250
12·00	0·45	560	0·55	1820	1250

*$\langle t_f \rangle = a_1 t_1 + a_2 t_2, \pm 5\%$
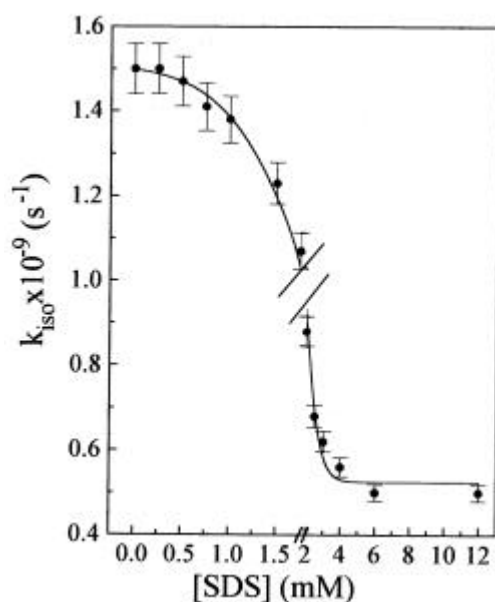

Figure 6. Variation of rate of isomerization (k_{iso}) of merocyanine 540 in an aqueous solution containing 4 mg PVP per ml with SDS concentration.

SDS aggregate around the probe. In aqueous PVP solution the emission maximum of MC540 shifts from 580 nm in the absence of SDS to 585 nm in 12 mM SDS. The red shift clearly indicates relatively lower polarity of the microenvironment of MC540 in the PVP-SDS aggregate compared to bulk water or that experienced by MC540 in aqueous PVP solution in the absence of SDS. In an earlier work[24], we have shown that, the nonradiative isomerization rate of MC540 decreases with decrease in polarity about 27 times as one goes from water to dioxane. The observed retardation of the isomerization process and the consequent increase in f_f and $\langle t_f \rangle$ of MC540 in polymer-surfactant aggregate is attributed to both the lower polarity and higher friction of the microenvironment of aggregate compared to that in bulk water or in micelles or that experienced by MC540 in aqueous PVP solution. In the absence of PVP, and in the presence of SDS at a concentration greater than CMC the lifetime of MC540 is 560 ps[26] which is much lower than the observed $\langle t_f \rangle$ (1250 ps) in the PVP-SDS aggregate. This indicates that inside the PVP-SDS aggregate MC540 experiences a microenvironment different from that in SDS micelles or PVP solutions. Thus it may be concluded that the increase in quantum yield and average lifetime of MC540 in PVP-SDS aggregate above CAC is due to the decrease in polarity as well as the increase in viscosity of the microenvironment.

5. Conclusions

The present work indicates photoisomerization of MC540 is a sensitive probe to study interaction of a polymer, PVP with a surfactant, SDS. On addition of SDS to an aqueous solution containing MC540 as a fluorescent probe, the fluorescence quantum yield and lifetime of MC540 increases and the rate constant of photoisomerization decreases sharply at a concentration of 0·5 mM SDS. This indicates critical association concentration (CAC) of SDS to PVP is 0·5 mM. The CAC determined in this way is significantly lower than the CMC of SDS. The microenvironment of MC540 in PVP–SDS complex is found to be different from that in either SDS micelles or in aqueous PVP solutions.

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