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Photoisomerization of a Carbocyanine Derivative in the Reverse Phases of a Block Copolymer: Evidence for the Existence of Water Droplets

K. S. Mali, G. B. Dutt,* and T. Mukherjee

Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

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In an attempt to understand the nature of water present in the reverse phases of aggregates formed with the triblock copolymer poly(ethylene oxide)₂₀-poly(propylene oxide)₇₀-poly(ethylene oxide)₂₀ (P123) and also investigate how these confined environments influence the rates of photoisomerization, fluorescence lifetimes and quantum yields of a carbocyanine derivative—3,3'-diethyloxadicarbocyanine iodide (DODCI)—were measured in these systems over the temperature range of 293–318 K. Three different copolymer–oil–water compositions were chosen such that the mole ratio of water to copolymer (*W*) spans the range of 50–150. In these systems, butyl acetate was used as the oil or the nonpolar component. It has been noticed that in all three systems the fluorescence decays of DODCI comprise a long component whose contribution is 85–90%, and this has been ascribed to the fraction of solute solubilized in the core region where hydrated poly(ethylene oxide) units are present. A short-decay component is associated with the remaining fraction, and its values match with those measured in water, indicating that the water present in these reverse phases is in the form of droplets. The photoisomerization rate constants of DODCI located in the core regions of the reverse phases are identical in the three systems at a given temperature and similar to the ones obtained in normal phases of P123. The reasons for the observed behavior have been discussed.

1. Introduction

Considerable effort has been directed toward understanding the interiors of reverse micelles because they offer compartmentalized polar environments for carrying out chemical reactions in an oil continuous medium. Aqueous reverse micelles formed with the surfactant Triton X-100 (TX-100) are among the widely explored nonionic systems.^{1–11} These systems are interesting because the hydration of the poly(ethylene oxide) headgroups and the subsequent formation of water droplets depend on the polarity of the oil and also its ability to penetrate inside the polar cores. It has been entrenched that TX-100 forms reverse micelles in nonpolar solvents such as cyclohexane, benzene–*n*-hexane mixtures, and toluene.^{1–6} However, the sizes of the aggregates, the amount of water these systems can accommodate, and the nature of water present are vastly different. For example, the maximum value of the mole ratio of water to surfactant (*W*) that can be attained in the TX-100/cyclohexane system is only 4.2 at 298 K, and there is no water droplet formation because the added water merely hydrates the poly(ethylene oxide) groups. However, in the system comprising TX-100/benzene–hexane (30:70 v/v), the value of *W* can reach as high as 9, and water droplet formation takes place from *W* = 2.5. The TX-100/toluene system, in contrast, does not form reverse micelles in the absence

of water, and the aggregates are found only at *W* > 7. For this system, it has been observed that the size of the water droplet increases with an increase in the water content.¹ The examples presented here are by no means exhaustive but illustrate the diverse nature of the reverse micelles that can be obtained with the same surfactant by simply changing the oil or the nonpolar component.

In recent times, aggregates formed with triblock copolymers have received significant attention^{12–28} because of their rich structural polymorphism and numerous industrial applications. Triblock copolymers of the type poly(ethylene oxide)_{*x*}-poly(propylene oxide)_{*y*}-poly(ethylene oxide)_{*x*}, where *x* and *y* represent the numbers of PEO and PPO groups, respectively, display interesting phase behavior because of the preferential solubility of one block over the other in a given solvent. Besides forming reverse micelles (*L*₂),^{22,24,25} some of the systems also display reverse micellar cubic phases (*I*₂).^{24,25} These block copolymers

* To whom correspondence should be addressed. E-mail: gbdutt@barc.gov.in.

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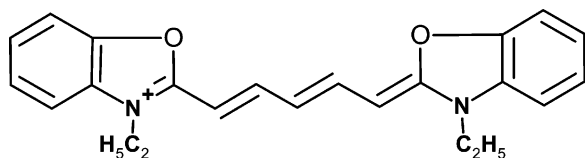


Figure 1. Molecular structure of DODCI.

are similar to nonionic surfactants in the sense that both of these amphiphiles possess poly(ethylene oxide) headgroups. Even though the interiors of nonionic reverse micelles have been reasonably well understood, not much is known about the core regions of the reverse phases formed with block copolymer aggregates. One of the objectives of the present work is to address this issue, which is to find out whether the water present in these reverse phases exists as water droplets.

For this purpose, we have measured the fluorescence lifetimes and quantum yields of a carbocyanine derivative—3,3'-diethyloxadicyanin iodide (DODCI)—(see Figure 1 for molecular structure) in reverse phases of the triblock copolymer poly-(ethylene oxide)₂₀-poly(propylene oxide)₇₀-poly(ethylene oxide)₂₀ (P123) at three different *W* values over the temperature range of 293–318 K. P123 has been chosen for this purpose because the phase diagram of the ternary system constituting P123–butyl acetate–water has been determined in detail.²⁵ DODCI was selected for these studies because it is a charged solute and is expected to be located in the water-rich regions of the reverse micelles, hence glean information pertinent to the nature of the water present in these systems. Moreover, it is a polyene, which undergoes isomerization upon photoexcitation, and thus the same solute can be used to achieve our second objective, which is to understand the isomerization rates in the confined environments of the reverse phases. Recently, we have investigated the photoisomerization of DODCI in normal micellar (*L*₁) and normal micellar gel (*I*₁) phases of P123.^{29,30} It has been observed that a major fraction of DODCI is located in the palisade layer and that the isomerization rate constants were found to be identical in both phases. This result indicates that despite the significant differences in the macroscopic viscosities of *L*₁ and *I*₁ the microviscosities offered by the palisade layers in both the phases are the same. Another interesting finding from this study is that the isomerization rate constants are lower by a factor of 3 compared to those in water, which is due to the enhanced friction offered by the micellar media. Thus, it would be interesting to find out how the photoisomerization of DODCI is going to be affected in the reverse phases of a block copolymer in addition to exploring the nature of the water present in these systems.

2. Experimental Section

The probe DODCI (laser grade), the triblock copolymer P123, and the solvent *n*-butyl acetate were obtained from Exciton, Aldrich, and S. D. Fine-Chem Ltd., respectively, and were used without further purification. Deionized water from Millipore A-10 was used in the preparation of the samples. Appropriate amounts of P123 were weighed in glass bottles, and to these requisite quantities of butyl acetate were added. The bottles were closed with a cap, and the copolymer was dissolved in butyl acetate by gentle shaking. To these samples, water was added such that the weight ratios of P123–butyl acetate–water were 14:80:6, 36:58:6, and 36:52:12. Some of the P123 was precipitated upon the addition of water to these samples, which was dissolved by gentle heating in a water bath. The first two samples are the reverse micellar phases, which can be designated as *L*₂ and ¹*L*₂, whereas the third one is a reverse micellar cubic phase, *I*₂. The water content was estimated by Karl Fischer titration with

the aid of a Metrohm 831 KF coulometer and was found to be 1400 and 6800 ppm, respectively, in butyl acetate and P123. From the weight ratios mentioned earlier, the mole ratios of water to copolymer for the three samples were calculated by taking into consideration the added water and also the water present in the butyl acetate and the copolymer, which resulted in *W* values of 144, 57, and 111, respectively, for *L*₂, ¹*L*₂, and *I*₂. Small aliquots of the stock solution of DODCI in ethanol were taken in 5 mL volumetric flasks, and the ethanol was evaporated. To these volumetric flasks, ternary mixtures of P123–butyl acetate–water (*L*₂, ¹*L*₂, and *I*₂) were added. It was ensured that DODCI was completely solubilized in these mixtures.

Absorption and fluorescence spectra were recorded using a Spectrascan UV 2600 spectrophotometer and a Hitachi F-4010 spectrofluorometer, respectively. For the purpose of quantum yield measurements, samples containing the probe DODCI were excited at 555 nm, and the corrected emission spectra were recorded from 560 to 700 nm. The integrated areas in this wavelength region were calculated and compared with that of a reference. DODCI in ethanol was used as the reference whose quantum yield is 0.42 at 298 K.^{31,32} The absorbance values of the sample and the reference were matched up to the third decimal, and it was ensured that these values were in the range of 0.05–0.10 at the wavelength of excitation. Fluorescence decays were measured using the single-photon counting³³ facility at the Tata Institute of Fundamental Research, Mumbai, India, and the details of the system have been described elsewhere.³⁴ The only modification that has been carried out to the earlier system is the replacement of the pump laser with a newer one, which is a Spectra Physics (Vanguard) CW mode-locked Nd:YAG laser with a repetition rate of 80 MHz. The frequency-doubled and attenuated (from 2 to 0.6 W) output of this laser was used to pump the dye laser. The samples were excited at 588 nm, and the emission was monitored at 620 nm. The average power of the dye laser at 588 nm is about 15 mW. Under this condition, it is safe to assume that the effects of local heating of the samples by the excitation source are negligible. For fluorescence decay measurements, 10 000 peak counts were collected in 512 channels with a time increment of 20 ps/channel, and each measurement was repeated 3 times. In both time-resolved and steady-state equipment, the desired sample temperature was achieved with the help of a thermocouple-based temperature controller, which is regulated by a microprocessor (Eurotherm). The measured fluorescence decays were analyzed using the iterative reconvolution method with the aid of the Marquardt algorithm as described by Bevington.³⁵ The criteria for a good fit were judged by statistical parameters such as the reduced χ^2 being close to unity and the random distribution of the weighted residuals.

3. Results

Figure 2 displays normalized absorption spectra of DODCI in water, micellar solution (*L*₂), and butyl acetate. The absorption maxima are centered around 575, 587, and 591 nm in water, *L*₂, and butyl acetate, respectively. The polarity of the medium is responsible for the observed shifts in the three cases. The absorption spectra of DODCI in *L*₂, ¹*L*₂, and *I*₂, however, overlap (not shown in the Figure), indicating that the microenvironment experienced by DODCI is the same for the three values of *W* used in this study. Fluorescence decays of DODCI in butyl acetate, *L*₂, ¹*L*₂, and *I*₂ over the temperature range of 293–318 K could be adequately described by a two-exponential function as described below:

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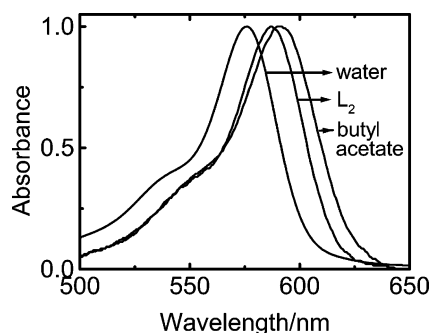


Figure 2. Absorption spectra of DODCI in water, butyl acetate, and L_2 . Notice that the absorption maxima shift to the red side with a decrease in the polarity of the medium.

$$f(t) = a \exp\left(\frac{-t}{\tau_{f1}}\right) + (1 - a) \exp\left(\frac{-t}{\tau_{f2}}\right) \quad (1)$$

In the above equation, τ_{f1} and τ_{f2} are the two lifetimes associated with the fluorescence decay, and a is the percentage contribution of τ_{f1} to the decay. Typical fluorescence decays of DODCI in butyl acetate and the L_2 phase measured at 298 K are displayed in Figure 3. In the case of reverse micellar phases, the origin of the two lifetimes of the probe can be understood with respect to its location; however, the recovery of two decay components in butyl acetate is somewhat surprising. The contribution of the second component in butyl acetate is 10–20%, whose value is around 300 ps, and it was found to be independent of temperature. At this moment, we do not have an explanation for this observation. However, τ_{f2} values of DODCI in the L_2 , 1L_2 , and I_2 phases are identical to the ones measured in water, and their contributions are in the range of 10–15%. The fluorescence decay parameters of DODCI in butyl acetate and in the L_2 , 1L_2 , and I_2 phases are given in Table 1 together with the ones measured in water, which were taken from our earlier work,²⁹ for the sake of comparison. A quick glance at the Table reveals that the decay parameters of DODCI in the L_2 , 1L_2 , and I_2 phases are identical at a particular temperature. Figure 4 gives plots of fluorescence quantum yields of DODCI in water, butyl acetate, L_2 , 1L_2 , and I_2 phases of P123 as a function of temperature. The quantum yields of DODCI are significantly lower in water and butyl acetate compared to the reverse micellar phases. As with the case of lifetimes, the quantum yields of DODCI in the L_2 , 1L_2 , and I_2 phases are identical at a given temperature.

4. Discussion

According to the information available in the literature,²⁴ reverse micellar phase L_2 is formed with butyl acetate concentration as low as 40% and P123 up to 50%, which can accommodate no more than 10% water. However, reverse micellar cubic phase I_2 is formed in the concentration range of 30–40% P123 and 42–58% butyl acetate, which can hold a maximum water content of 10–20%. It has been established that in the I_2 phase reverse micelles are arranged in a face-centered cubic structure. Even though the amount of water present in these systems appears to be low, the mole ratios of water to copolymer are quite large owing to the high molecular weight of P123. Nevertheless, the nature of the water present in these systems has not been explored. As already mentioned, an inquisitiveness to investigate this issue forms one of the motives for the present study.

However, before this issue can be addressed, the location of the probe in the reverse phases must be ascertained. For this purpose, the lifetime and quantum yield data have been employed

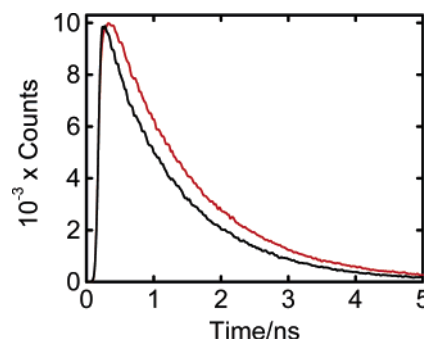


Figure 3. Fluorescence decays of DODCI in butyl acetate (black line) and L_2 (red line) at 298 K. It is evident that DODCI decays faster in butyl acetate than in L_2 . Both of these decays could be fitted with biexponential functions. However, the fitted curves and the instrument response function are not shown for the sake of clarity.

because these parameters for DODCI are sensitive to local polarity and viscosity. An inspection of Table 1 indicates that the τ_{f2} values of DODCI in the L_2 , 1L_2 , and I_2 phases of P123 are identical to the ones measured in water. This indicates that 10–15% of the probe is solubilized in a water-like environment, and this aspect will be discussed thoroughly in due course. Concomitantly, a fast decay component whose amplitude is similar to that observed in the reverse micellar phases has been recovered in butyl acetate as well. Thus, it might be possible that the second component obtained in the L_2 , 1L_2 , and I_2 phases could be due to a fraction of the solute solubilized in butyl acetate surrounding the reverse micelles. However, this possibility can be ruled out because the recovered τ_{f2} values in butyl acetate are lower than those obtained in the reverse micellar phases of P123. Moreover, there is no systematic variation in the recovered values of τ_{f2} or in the corresponding amplitude parameters of DODCI in butyl acetate with temperature (Table 1). Another important point, which is to be noted from Table 1, is that the τ_{f1} values of DODCI in the L_2 , 1L_2 , and I_2 phases are almost identical and are only marginally higher (5–10%) than the corresponding numbers in butyl acetate. Hence, it is plausible that this component arises from the fraction of the solute solubilized in butyl acetate. For this argument to be realistic, the quantum yields of DODCI should be identical in the micellar phases as well as in butyl acetate. However, the measured quantum yields of the probe in the micellar phases are higher by nearly a factor of 3 compared to the ones in butyl acetate. Thus, it is safe to conclude that the slow component (τ_{f1}) obtained in the reverse micellar phases of P123 arises because a major fraction of the solute is located in the cores of the reverse micelles where hydrated poly(ethylene oxide) chains are present.

Having established the location of the solute in the L_2 , 1L_2 , and I_2 phases of P123 from the fluorescence lifetime and quantum yield data of DODCI, we now turn our attention to addressing the important issues of this investigation, which are to understand the nature of water present in these reverse phases and also the photoisomerization of DODCI in confined systems. As already mentioned, a major fraction of the solute is located in the cores of the reverse micelles. However, the surprising observation from these measurements is the presence of a short component (10–15%) whose values match those obtained in water, which is an indication that water present in the interiors of the L_2 , 1L_2 , and I_2 phases of P123 has the properties of bulk water. In other words, this observation confirms the existence of water droplets in these reverse phases. It must be noted that fluorescence measurements monitor only those micelles that contain the fluorophore or the probe. Because the solubilization of probes in micelles follows the Poisson distribution, not all micelles

Table 1. Fluorescence Lifetimes of DODCI in Water, Butyl Acetate, L₂, I₂, and I₂ as a Function of Temperature^a

<i>T</i> /K	water ^b		butyl acetate		L ₂		I ₂		I ₂		I ₂	
	τ_f /ns	ϕ_f	τ_{f1} /ns	τ_{f2} /ns	τ_{f1} /ns	τ_{f2} /ns	τ_{f1} /ns	τ_{f2} /ns	τ_{f1} /ns	τ_{f2} /ns	τ_{f1} /ns	τ_{f2} /ns
293	0.69	0.82	1.23	0.29	0.89	1.40	0.68	0.90	1.43	0.70	0.90	1.37
298	0.64	0.78	1.17	0.31	0.89	1.29	0.64	0.91	1.32	0.64	0.93	1.27
303	0.57	0.84	1.08	0.27	0.86	1.20	0.58	0.88	1.23	0.58	0.90	1.19
308	0.51	0.87	1.00	0.36	0.83	1.10	0.50	0.86	1.13	0.52	0.85	1.09
313	0.46	0.91	0.91	0.31	0.85	1.00	0.45	0.89	1.03	0.45	0.87	0.99
318	0.41	0.83	0.85	0.27	0.80	0.92	0.40	0.89	0.94	0.42	0.87	0.90

^a The uncertainties in the τ_f values are about 5%. ^b From ref 29.

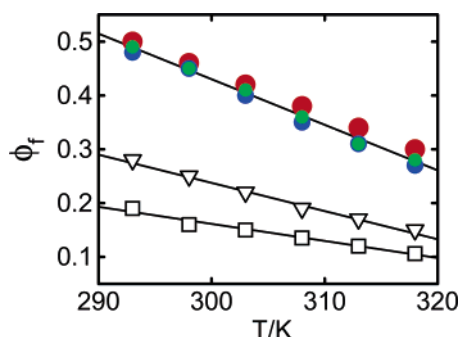


Figure 4. Plots of quantum yield vs *T* for DODCI in water (inverted triangles), butyl acetate (open squares), L₂ (red circles), I₂ (blue circles), and I₂ (green circles). The lines passing through the data points were obtained by linear least-squares fits.

contain fluorophores. The probe used in the present study is ionic in nature, and as a consequence, it may be able to draw more water into the water pools of the reverse micelles as compared to the ones without a probe. This in turn can portray a somewhat incorrect picture of the investigated system. If the probe molecule were to experience a higher water content in the reverse micellar water pools, then it has to draw water from the hydrated poly(ethylene oxide) chains. However, the water present in the poly(ethylene oxide) chains is thermodynamically bound and is held to these chains through hydrogen bonding interactions. Hence the scenario where the micelles containing the ionic probe are likely to have a higher water content compared to the ones without the probe is unlikely. Even if such a situation were to arise, the number of water molecules that the sole ionic probe can draw from the hydrated poly(ethylene oxide) chains will be negligible. Although we could provide evidence for the existence of water droplets resembling the properties of bulk water in the cores of P123–butyl acetate–water reverse micellar systems, no indication can be given regarding the size of these droplets from the measurements performed in this study. As already mentioned, the data available in the literature²⁴ essentially offers information about phase boundaries for the L₂ region.

At this juncture, it would be worthwhile to compare somewhat similar results obtained by Schelly and co-workers⁵ and Qi and Ma⁷ in the case of aqueous reverse micelles formed with TX-100/benzene–hexane (30:70 v/v) and TX-100/*n*-hexanol/cyclohexane. Schelly and co-workers⁵ have measured the shift in the absorption maxima (λ_{\max}) of the probe 1-methyl-8-oxyquinolinium as a function of *W* and have found that even at *W* = 9 the properties of the water droplet in the core are not similar to that of bulk water. They attribute this observation to the size of the water droplet, which is too small to have bulk properties. In contrast, Qi and Ma⁷ have measured the shift in λ_{\max} of the probe methylene blue in the aqueous TX-100/*n*-hexanol/cyclohexane reverse micellar system with increasing *W* and have observed that at *W* = 5.3 the properties of the water droplet resemble that of bulk water. Although the property that has been monitored by us is different, our results are similar to

the ones obtained by Qi and Ma.⁷ The water droplet properties at three different values of *W* (144, 57, and 111 in L₂, I₂, and I₂, respectively) are identical to that of bulk water, which is evident from the similarities in the lifetime (τ_{f2}) values with the ones measured in water. This result indicates that the water droplets present in the reverse phases of P123, even at the lowest value of *W* used in this study, are probably large enough to possess the properties of bulk water. In a recent study, Fayer and co-workers³⁶ have examined the properties of water droplets present in the reverse micelles formed with anionic surfactant aerosol-OT (AOT) in isooctane using linear and nonlinear infrared spectroscopy and have found that at *W* > 20 (corresponding to a water pool diameter of 7.0 nm) the water pool in AOT reverse micelles displays the properties of bulk water. However, it must be noted that the linear relationship, which exists between *W* and the water pool diameter in AOT reverse micelles does not hold in the case of nonionic systems. In addition to the above-mentioned study,³⁶ numerous photophysical studies^{37–41} have been carried out in AOT reverse micellar systems as a function of *W*. In all of these studies, variation in the measured property, such as excited-state reaction rates and solvation times, with *W* has been observed. This is because the *W* values were chosen such that the water pools in these systems are small and did not attain the properties of bulk water. Compared to the AOT system, very low values of *W* cannot be employed with the block copolymer system used in the present study because the L₂ region is formed over a narrow range of water concentration. Moreover, we have observed the degradation of DODCI at *W* = 0.

Now turning our attention to the photoisomerization of DODCI in the reverse phases of P123, which is the second objective of this work, the nonradiative (k_{nr}) and radiative (k_r) rate constants were calculated from the measured quantum yields and lifetimes with the aid of the following relations:⁴²

$$\phi_f = \frac{k_r}{k_r + k_{nr}} \quad (2)$$

$$\tau_f = \frac{1}{k_r + k_{nr}} \quad (3)$$

Usually, k_r and k_{nr} are obtained from eqs 2 and 3. However, in the present situation, the measured quantum yield (ϕ_f) of DODCI in the reverse phases of P123 is a combination of the quantum yield of the probe solubilized in the hydrated poly(ethylene oxide)

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chains (ϕ_{micelle}) and the water pool (ϕ_{water}). From the preexponential factors, which were obtained during the biexponential fluorescence decay analysis, the fraction of the solute (a) solubilized in the micellar phase is known. Thus, ϕ_{micelle} was calculated using the following expression from the measured values of ϕ_f and ϕ_{water} :

$$\phi_f = a\phi_{\text{micelle}} + (1 - a)\phi_{\text{water}} \quad (4)$$

After obtaining the quantum yields of DODCI solubilized in the two environments, the nonradiative rate constants in the respective locations were obtained. The k_{nr} in the case of butyl acetate was obtained from eqs 2 and 3 using the average lifetime ($\langle\tau_f\rangle$), which is given by $\langle\tau_f\rangle = a\tau_{f1} + (1 - a)\tau_{f2}$. The observed changes in the lifetimes and quantum yields of DODCI with temperature in the different systems investigated are due to variation in the nonradiative rate constant. The radiative rate constant, however, has been found to be more or less independent of temperature. It may be recalled that the photoisomerization of DODCI has been extensively investigated in homogeneous^{32,43–47} and microheterogeneous media^{29,30,37,48} and also at the air–water interface.⁴⁹ The nonradiative rate constant of DODCI has been identified as the isomerization rate constant ($k_{\text{nr}} = k_{\text{isomerization}}$) about the double bond,⁴⁴ which can be understood in the following manner. The excited-state isomerization of DODCI involves an activated twisting motion about the double bonds to an intermediate geometry. In the twisted geometry, the excited state becomes close in energy to the ground state, thus it rapidly decays to the twisted ground electronic state by internal conversion. Once on the ground-state surface, branching between the isomer and the normal form occurs. The nonradiative process is dominated by the barrier crossing or the twisting motion because internal conversion from the twisted excited state is very rapid. Hence, photoisomerization rate constants are sensitive to local friction or the microviscosity of the medium in which the solute is solubilized. However, it must be noted that at very high viscosities, when twisting is inhibited, internal conversion becomes the main nonradiative process.

Because the variation of the photoisomerization rate constant with temperature follows the Arrhenius relation, the parameters $\ln(k_{\text{nr}})$ and $1/T$ were plotted as the ordinate and abscissa, respectively, in Figure 5 for the different systems investigated in this study. However, it must be noted that the activation energies or barrier heights of the reaction cannot be estimated from such plots because of the expected influence of temperature on local viscosity. Moreover, because the transition state involved in the isomerization of DODCI has polar character, the micropolarity of the medium also influences the isomerization rate constants. In other words, an increase in the polarity of the medium alters the isomerization process by decreasing the barrier height of the reaction. Nevertheless, it is difficult to disentangle the effects of viscosity and polarity on nonradiative rate constants and obtain the activation energies of the reaction in microheterogeneous systems. However, these problems have been tackled in the case of homogeneous media by measuring the isomerization rate constants under isoviscous and isodielectric conditions and

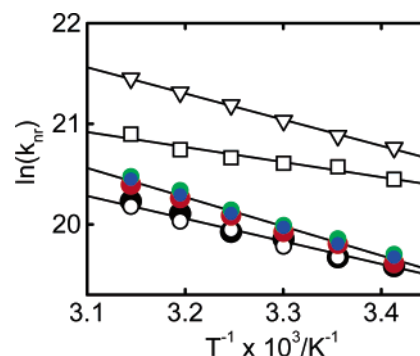


Figure 5. Plots of $\ln(k_{\text{nr}})$ vs $1/T$ for DODCI in water (inverted triangles), butyl acetate (open squares), L_2 (red circles), 1L_2 (blue circles), and I_2 (green circles). The open and filled circles correspond to the data obtained in the L_1 and I_1 phases of P123, which was taken from ref 30. The lines passing through the data points were obtained by linear least-squares fits.

employing the modified Kramers equation.⁴⁷ From Figure 5, it is evident that the isomerization rate constants in the L_2 , 1L_2 , and I_2 phases of P123 at a particular temperature are almost identical, which indicates that the local friction experienced by DODCI for isomerization is the same. In contrast, these rate constants are lower compared to the ones obtained in water and butyl acetate by factors of 2.6–2.8 and 1.5–2.3, respectively, over the temperature range studied. This observed trend is due to the organized media offering enhanced friction compared to that of simple liquids and thus causing hindrance in the isomerization process. Between the two homogeneous liquids used in the study, the isomerization rate constants in butyl acetate are lower by a factor of 1.4–1.7 compared to those in water. This result is surprising considering the fact that the isomerization rate constants increase with a decrease in the viscosity of the medium. (The viscosity of butyl acetate is lower than that of water.) The probable reason for the observed lower isomerization rate constants of DODCI in butyl acetate compared to those in water could be the low polarity of the organic solvent, which increases the barrier height of the reaction and thus impedes the isomerization process. It is also possible that the biexponential fluorescence decays of DODCI in butyl acetate, which could not be comprehended, may hold the key to the observed behavior. The important result from this study, however, is that the photoisomerization rate constants of DODCI are independent of the water content in the reverse phases and are significantly lower compared to water and butyl acetate. In nonionic reverse micellar systems, the added water initially hydrates the poly(ethylene oxide) chains, and the formation of water droplets transpires only when these chains are completely hydrated. It may be recalled that in L_2 , 1L_2 , and I_2 the W values are 144, 57, and 111, respectively, and water droplets exist in each of the three samples, which means that the hydration of poly(ethylene oxide) chains is complete. Because a major fraction of DODCI is solubilized in the core region where hydrated poly(ethylene oxide) chains are present, it experiences an identical microenvironment in the three reverse phases, thus the photoisomerization rate constants are the same. In such a scenario, the logical question that arises is, what happens to the photoisomerization rate constant if the poly(ethylene oxide) chains are not hydrated? In other words, how would the isomerization of DODCI be affected in the absence of water in these reverse phases? We have made an attempt to address this issue by making the L_2 phase with 14% P123, 86% butyl acetate, and no water. Unfortunately, no measurements could be performed in this system because the solute DODCI degraded instantaneously upon dissolving. To find out how the photoisomerization rate constants of DODCI in these reverse

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phases measure up to the ones obtained in normal phases of P123, we have also plotted data from our earlier work^{29,30} in Figure 5. It is evident from the Figure that the isomerization rate constants are similar in normal and reverse phases, which is not surprising considering the fact that in normal phases the site of solubilization of DODCI is the palisade layer whereas it is situated in the core region in the reverse phases and both of these locales constitute hydrated poly(ethylene oxide) chains. The marginally higher rate constants obtained in the case of the reverse phases are probably due to the penetration of butyl acetate inside the cores of the reverse phases, which increases the fluidity of the surroundings. In the recent past, the photoisomerization of DODCI has been investigated³⁷ in reverse micelles of AOT-*n*-heptane-water at $W = 4$ and 12, and it was observed that the isomerization rate constant is 40% larger at higher water content. Even though these differences were considered to be insignificant by the authors, we do believe that the size of the water pool influences the photoisomerization rates by altering the electrostatic interactions between the cationic probe molecule and the anionic headgroup of the AOT surfactant, especially at low values of W .

Conclusions

Understanding the nature of water present in aqueous reverse micelles is of immense interest to many researchers because this topic has potential implications in many areas of physics, chemistry, and biology. The present investigation has been undertaken with that intention, and the important conclusions

are as follows. In this work, fluorescence lifetimes and quantum yield measurements have been performed on carbocyanine derivative DODCI in the reverse phases of block copolymer P123. It has been observed that a small fraction of the solute is solubilized in the water present in the core region of the reverse micelles. The lifetimes of this fraction are identical to the ones measured in water, which indicates that the water present in the cores of these reverse phases is in the form of a droplet and its properties resemble that of bulk water irrespective of the water content used in this study. The second objective of this study is to understand the role of confinement in the photoisomerization process. For this purpose, nonradiative rate constants of DODCI have been obtained from the measured lifetimes and quantum yields. A major fraction of the solute is solubilized in the core region where hydrated poly(ethylene oxide) chains exist, and its isomerization rate constants were found to be identical for the three water/copolymer mole ratios used in the study. The isomerization rate constants in these confined environments are significantly lower compared to those obtained in homogeneous media such as water and butyl acetate.

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