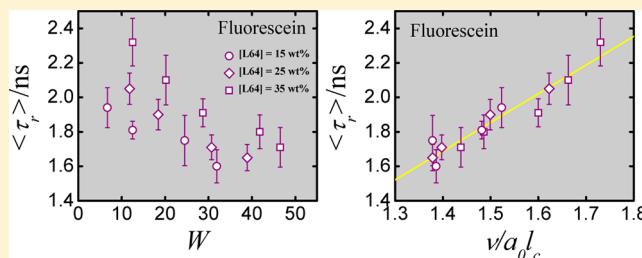


Can Critical Packing Parameter Depict Probe Rotation in Block-Copolymer Reverse Micelles?

Sugosh R. Prabhu and G. B. Dutt*

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

ABSTRACT: Rotational diffusion of two ionic probes, cationic rhodamine 110 (R110) and anionic fluorescein (FL), has been examined in reverse micelles formed with the triblock copolymer (EO)₁₃–(PO)₃₀–(EO)₁₃ (L64), where EO and PO represent ethylene oxide and propylene oxide units, respectively, with small amounts of water in *p*-xylene. This study has essentially been undertaken to explore the influence of mole ratio of water to copolymer (*W*) as well as copolymer concentration on probe rotation. On the basis of fluorescence lifetimes and reorientation times, it has been established that both R110 and FL are located in the interfacial region of L64/water/*p*-xylene reverse micellar system. The average reorientation time decreases by 10–35% with an increase in *W* for both the probes at a given copolymer concentration. However, for a particular *W*, the average reorientation time increases by 10–30% as the concentration of the copolymer is enhanced. From the micellar structural parameters available in the literature, critical packing parameters have been calculated for the L64/water/*p*-xylene reverse micellar system, and it has been noticed that the average reorientation times of both the probes scale linearly with the critical packing parameter. In essence, the results of this study indicate that the probe mobility in the interfacial region of block copolymer reverse micelles is governed by the micellar packing.



INTRODUCTION

Self-assembly behavior of triblock copolymers has aroused a great deal of interest in recent times because of their ability to display a rich structural polymorphism in addition to their widespread industrial applications.^{1–18} Triblock copolymers have the structural formula (EO)_{*m*}–(PO)_{*n*}–(EO)_{*m*}, where EO and PO represent ethylene oxide and propylene oxide units, respectively, with *m* and *n* denoting the numbers of the corresponding EO and PO units. They attain amphiphilic character because of the preferential solubility of one block over the other in water. In other words, the solubility of PO block in water diminishes above 288 K, whereas EO block is hydrophilic in the temperature range of 273–373 K.² As a consequence of the temperature-dependent solubility of the PO block, these block copolymers aggregate to form micelles above a critical micelle temperature (cmt) and critical micelle concentration (cmc). The exact values of cmc and cmt, however, depend on the number of EO to PO units present in the block copolymer. The cmts and cmcs of many block copolymers are available in the literature.^{3,5} Apart from forming normal micelles (L₁), ternary systems comprising block copolymer, water, and oil form many types of organized assemblies. As many as nine different morphologies have been reported for the ternary system of (EO)₁₉–(PO)₄₃–(EO)₁₉, water, and *p*-xylene.⁶

Reverse micellar phase (L₂) is one of the intriguing morphologies that has been formed by block copolymers in the presence of water and oil, and they are somewhat akin to the reverse micelles formed with conventional nonionic surfactants. Reverse micelles formed with the block copolymer, (EO)₁₃–(PO)₃₀–(EO)₁₃ whose trade name is L64, have been

extensively investigated.^{12–18} In a recent study, Arleth et al.¹⁷ have carried out a detailed structural investigation of L64/water/*p*-xylene system using small-angle neutron scattering technique at three different copolymer concentrations and also at several mole ratios of water to L64 (*W*). L64 is completely soluble in *p*-xylene, and small amounts of water (*W* = 5.2) are required to induce the formation of reverse micelles. The reverse critical micellar concentration is 10 wt % in *p*-xylene.¹⁸ According to the findings of Arleth et al.¹⁷ at a fixed copolymer concentration, an increase in *W* has only a small effect on micellar size but induces a significant enhancement in the total number of micelles, which leads to a decrease in the total unimer concentration. In contrast, increasing the copolymer concentration at fixed *W* gives rise to a significant decrease in the micellar size.

Apart from the structural studies mentioned above, microenvironments of the organized assemblies formed with these block copolymers have also been investigated.^{19–32} Processes such as rotational diffusion, solvation dynamics, and to a lesser extent photoisomerization of probe molecules solubilized in these systems have been employed to understand the microenvironments of micelles, reverse micelles, gels, and surfactant–polymer assemblies. Rotational diffusion studies, in particular, enable us to get a clear insight into the microenvironment offered by these organized systems. Barring a couple of studies from our group,^{21,26} the microenvironments

Received: March 6, 2013

Revised: April 10, 2013

Published: April 19, 2013



of reverse micelles formed with triblock copolymers have not been explored extensively. Thus, in the present work, rotational diffusion of two ionic probes, cationic rhodamine 110 (R110) and anionic fluorescein (FL) (see Figure 1 for the molecular

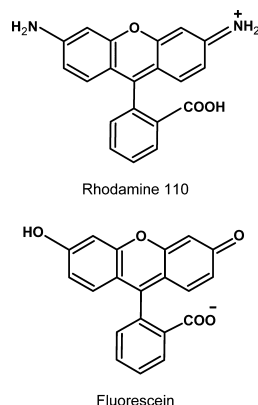


Figure 1. Molecular structures of the probes.

structures of the probes), has been examined in reverse micellar system of L64/water/*p*-xylene, and the motivation for undertaking such an endeavor is discussed here. Recent studies from our laboratory indicate that the rates of friction-dependent processes such as solute rotation and photoisomerization in ionic reverse micelles can be correlated with the critical packing parameter of the organized assemblies.^{33,34} It has been noticed that the rate constants for the above-mentioned processes decrease as the interfacial packing becomes more compact. Although such a correlation holds for ionic reverse micelles, it has not been explored in the case of nonionic systems whose interfacial regions are vastly different because of the presence of ethylene oxide headgroups. We believe that the present study will allow us to realize whether probe rotation in the reverse micelles formed with block copolymers can be correlated with their critical packing parameters. For this purpose, fluorescence anisotropies and lifetimes of R110 and FL have been measured in L64/water/*p*-xylene reverse micellar system as a function of mole ratio of water to the block copolymer (*W*) and also at different copolymer concentrations.

EXPERIMENTAL SECTION

The block copolymer L64 and anhydrous *p*-xylene were obtained from Aldrich, whereas the probes R110 and FL were from Exciton. All the chemicals used in this study are of the highest available purity and were used without further purification. Deionized water from Millipore A-10 was used in the preparation of the samples. Reverse micellar solutions were prepared by weighing appropriate amounts of L64, water, and *p*-xylene. L64 was dissolved by sonicating the samples after gently heating them in a water bath. The concentrations of the probes in the reverse micellar solutions were maintained in the range of 10^{-5} to 10^{-6} mol dm⁻³.

Time-resolved fluorescence measurements were carried out with a setup that works on the principle of time-correlated single-photon counting.³⁵ The setup used in the present study was purchased from IBH, United Kingdom, and employs a diode laser as the excitation source. The instrumental details have been described in our earlier publication.³⁶ Samples containing the probes R110 and FL were excited with a 450 nm diode laser, and the emission from the samples was collected at

550 nm. The decays were collected in 4096 channels with a time increment of 13.8 ps/channel. The instrument response function (IRF) of the setup was measured by collecting the scattered light from a TiO₂ suspension in water, and the full width at half-maximum was found to be around 150 ps. For lifetime measurements, decays were collected by keeping the emission polarizer at magic angle (54.7°) with respect to the polarization of the excitation laser to ensure the complete depolarization of the fluorescence. Anisotropy decay measurements were carried out by collecting parallel and perpendicular decay components with respect to the polarization of the excitation laser. The two decay components were acquired for at least 900 s each such that a good signal-to-noise ratio was obtained. To account for the discrepancies in transmission efficiency of the monochromator, the perpendicular component was corrected for the G-factor of the spectrometer. All the anisotropy measurements were performed at 298 K. The temperature of the sample was controlled with the aid of a thermoelectric controller (model DS) from IBH. Each measurement was repeated two to three times, and the average values are reported. The analyses of fluorescence and anisotropy decays were performed using the software supplied by IBH.

RESULTS AND DISCUSSION

The fluorescence decays of R110 and FL in L64/water/*p*-xylene reverse micellar system were fit to single-exponential functions, and the resulting lifetimes are 3.60 ± 0.08 ns and 3.67 ± 0.07 ns, respectively. These lifetimes are more or less independent of water and copolymer concentrations. In contrast, anisotropy decays of the probes were fit to a biexponential function of the form described by eq 1.

$$r(t) = r_0[\beta \exp(-t/\tau_{r1}) + (1 - \beta)\exp(-t/\tau_{r2})] \quad (1)$$

In the above equation, τ_{r1} and τ_{r2} are the two time constants associated with the decay of the anisotropy, and β is the percentage contribution of τ_{r1} . r_0 is the limiting anisotropy, which is characteristic of the probe. Average reorientation times ($\langle\tau_r\rangle$) have been calculated using eq 2, which is given below.

$$\langle\tau_r\rangle = \beta\tau_{r1} + (1 - \beta)\tau_{r2} \quad (2)$$

The anisotropy decay parameters and the average reorientation times of the two probes R110 and FL in L64/water/*p*-xylene reverse micellar system at various values of *W* and three copolymer concentrations are listed in Tables 1 and 2, respectively. The uncertainties on the average reorientation times, represented as standard deviations, are in the range of 4–8%. From the tables, it is evident that there is a marginal decrease in the copolymer concentration with an increase in *W* at 25 and 35 wt % of L64; these concentrations have been taken from ref 17. Inspection of the tables also reveals that $\langle\tau_r\rangle$ decreases marginally with an increase in *W* at a given copolymer concentration for both R110 and FL. Similarly, at a fixed *W*, a small increase in $\langle\tau_r\rangle$ can be noticed when [L64] increases from 15 to 35 wt %. Figure 2 displays the anisotropy decays of R110 and FL in L64/water/*p*-xylene reverse micellar system at *W* = 12 for 15 wt % and 35 wt % of L64, and it is evident from the figure that the decays at higher copolymer concentration are slower compared to the ones at lower concentration. A visual portrayal of all the data collected in this work is presented in the form of plots of $\langle\tau_r\rangle$ versus *W* for both the probes at the three concentrations of L64 in Figure 3. It can

Table 1. Anisotropy Decay Parameters of R110 in L64/Water/*p*-Xylene Reverse Micellar System at Three Copolymer Concentrations and Various Values of *W*

[L64]/wt%	<i>W</i>	β	τ_{r1}/ns	τ_{r2}/ns	$\langle\tau_r\rangle/\text{ns}^a$
14.7	6.7	0.94	2.25	0.47	2.14 ± 0.08
14.7	12.5	0.92	2.28	0.60	2.15 ± 0.03
14.7	24.5	0.90	2.15	0.59	1.99 ± 0.08
14.7	31.9	0.90	2.10	0.55	1.95 ± 0.06
26.2	11.8	0.94	2.32	0.58	2.22 ± 0.05
25.2	18.4	0.91	2.33	0.65	2.18 ± 0.04
25.2	30.7	0.90	2.13	0.57	1.97 ± 0.05
24.2	38.9	0.91	2.02	0.50	1.88 ± 0.06
36.7	12.5	0.96	2.60	0.57	2.52 ± 0.13
35.7	20.2	0.94	2.43	0.62	2.32 ± 0.07
35.7	28.7	0.91	2.35	0.67	2.20 ± 0.08
34.7	41.8	0.89	2.19	0.64	2.02 ± 0.09
33.6	46.5	0.90	2.14	0.59	1.98 ± 0.04

^aCalculated using eq 2.

Table 2. Anisotropy Decay Parameters of FL in L64/Water/*p*-Xylene Reverse Micellar System at Three Copolymer Concentrations and Various Values of *W*

[L64]/wt%	<i>W</i>	β	τ_{r1}/ns	τ_{r2}/ns	$\langle\tau_r\rangle/\text{ns}^a$
14.7	6.7	0.95	2.03	0.37	1.95 ± 0.12
14.7	12.5	0.92	1.93	0.44	1.81 ± 0.05
14.7	24.5	0.90	1.90	0.40	1.75 ± 0.15
14.7	31.9	0.89	1.75	0.39	1.60 ± 0.10
26.2	11.8	0.95	2.14	0.43	2.05 ± 0.09
25.2	18.4	0.93	2.02	0.41	1.91 ± 0.09
25.2	30.7	0.91	1.84	0.39	1.71 ± 0.07
24.2	38.9	0.89	1.81	0.42	1.65 ± 0.08
36.7	12.5	0.95	2.41	0.46	2.32 ± 0.14
35.7	20.2	0.94	2.21	0.46	2.10 ± 0.14
35.7	28.7	0.94	2.01	0.40	1.91 ± 0.08
34.7	41.8	0.88	1.98	0.48	1.80 ± 0.10
33.6	46.5	0.87	1.89	0.43	1.70 ± 0.12

^aCalculated using eq 2.

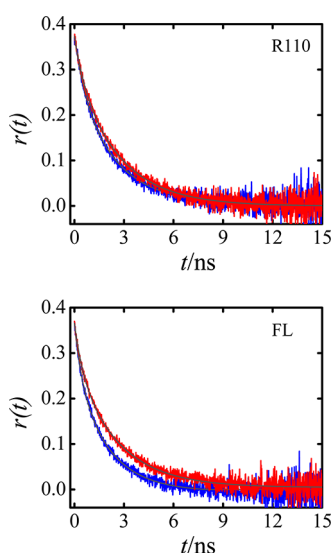


Figure 2. Anisotropy decays of R110 and FL in L64/water/*p*-xylene reverse micellar system at *W* = 12 for copolymer concentrations of 15 wt % (blue) and 35 wt % (red). The decays of both the probes are marginally slower at higher copolymer concentration for a given *W*.

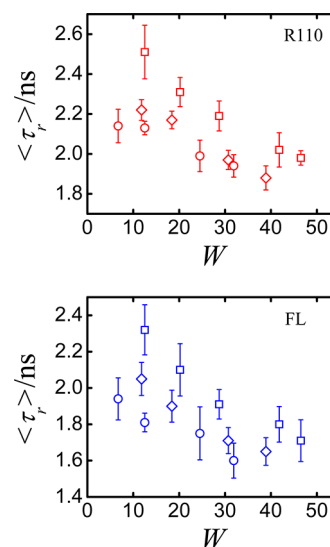


Figure 3. Plots of $\langle\tau_r\rangle$ versus *W* for R110 and FL in L64/water/*p*-xylene reverse micellar system at 15 (○), 25 (◇), and 35 (□) weight percent of copolymer. It is evident from the figure that for a particular *W*, the probe rotation becomes slower as the copolymer concentration increases.

be noticed from the figure that *W* is not the sole parameter, which governs the probe rotation since $\langle\tau_r\rangle$ also varies with [L64]. To understand these results, the structure of these reverse micelles and the location of the probes in them have been considered.

According to the structural details elucidated by Arleth et al.,¹⁷ a 15 wt % L64 forms reverse micelles in the presence of water and *p*-xylene at *W* = 6.24. *W* has been defined as mole ratio of water to per mole of EO group in ref 17. However, for the sake of convenience, in the present study, we have reported values of *W* that are multiplied by 26, which is the number of EO groups present in L64. In other words, *W* is defined as the mole ratio of water to the mole ratio of the copolymer in this work. Upon increasing the *W* from 6.24 to 32, the reverse micelles swell in size and the aggregation number (*N_a*) increases from 88 to 138 and the core radius (*r_c*) and hard-sphere radius (*r_h*) also increase marginally. Moreover, it has also been noticed that an increase in the concentration of L64 from 15 wt % to 35 wt % leads to a significant reduction in *N_a*.¹⁷ Essentially, L64 reverse micelles comprise a core with a water droplet and hydrated EO headgroups and a corona made up of PO groups, which are dispersed in *p*-xylene.

To ascertain the location of the probes in these reverse micelles, lifetimes and anisotropy decay parameters of R110 and FL have been considered. Single-exponential lifetimes observed for R110 and FL indicate that the site of solubilization of the probes is unique in the L64/water/*p*-xylene reverse micellar system. From the lifetime data presented earlier, it is evident that FL is in the form of a monoanion.³⁷ Because both the probes are ionic, they cannot be solubilized in the bulk region surrounding the reverse micelles, which is *p*-xylene. Because of their ionic character, it is likely that R110 and FL are located in the interfacial region of the reverse micelles and also in the water droplet present in the core. However, a close look at the values of τ_{r2} from Tables 1 and 2 indicates that these numbers are significantly higher than the reorientation times of R110 and FL in water. The reorientation times of R110 and FL are identical in water at 298 K, which is 110 ps.³⁸ On the basis

of these arguments, it can be concluded that R110 and FL are located in the interfacial region of L64/water/*p*-xylene reverse micellar system. Biexponential anisotropy decay can also result from anisotropic rotational diffusion of the probe molecule.³⁹ However, recent work from our laboratory dealing with the rotational diffusion of R110 and FL in low viscosity ionic liquids indicates that the anisotropy decays of these probes can be described by single-exponential functions.⁴⁰ If the probes were to display anisotropic rotational diffusion, then biexponential anisotropy decays would have been observed in ionic liquids as well. Thus, it is safe to conclude that the observed biexponential anisotropy decays of R110 and FL in L64/water/*p*-xylene reverse micellar system are not due to anisotropic rotational diffusion of the probe molecules. It has been well-established that a probe molecule located in the interfacial region of these reverse micelles cannot undergo isotropic rotation; instead, it experiences somewhat restricted rotation. Such a restricted rotation results in biexponential anisotropy decays, which have been reported in the case of micelles,^{41–48} reverse micelles,^{33,38,49–54} gels,²⁰ and polymer–surfactant aggregates.^{22,23} The two time constants are often interpreted using the two-step model.^{55–59} According to this model, the probe molecule located at the interface of a spherical aggregate undergoes a slow lateral diffusion on or inside the curved surface and a fast wobbling motion in an imaginary cone, and both these motions are coupled to the overall rotation of the supramolecular aggregate. Under the assumption that the slow and fast motions are separable, the experimentally measured anisotropy decay parameters, τ_{r1} and τ_{r2} , are related to the model parameters by eqs 3–5.⁴¹

$$\frac{1}{\tau_{r1}} = \frac{1}{\tau_L} + \frac{1}{\tau_M} \quad (3)$$

$$\frac{1}{\tau_{r2}} = \frac{1}{\tau_W} + \frac{1}{\tau_L} + \frac{1}{\tau_M} \quad (4)$$

$$\beta = S^2 \quad (5)$$

In the above equations, τ_L , τ_W , and τ_M are the time constants for lateral diffusion, wobbling motion, and overall rotation of the reverse micelles, respectively. β is the square of the order parameter S , which follows the inequality $0 \leq S^2 \leq 1$, and the magnitude of S determines the extent of restriction in the rotation of the probe.⁴¹ Because r_h of the L64/water/*p*-xylene reverse micelles is known,¹⁷ time constants for the overall rotation of the micelles can be calculated using Stokes–Einstein–Debye (SED) relation with stick boundary condition⁶⁰ and τ_L and τ_W with the aid of eqs 3 and 4. However, the main focus of the present study is to understand the influence of W and the concentration of L64 on probe rotation, and hence, we refrain from the detailed execution of the two-step model. Instead, we try to rationalize $\langle\tau_r\rangle$ in terms of micellar packing. The viscosity of *p*-xylene is 0.603 mPa s at 298 K, and the r_h values of L64/water/*p*-xylene reverse micellar system are in the range of 4.5–7.0 nm.¹⁷ τ_M values calculated using these numbers with the aid of SED relation are in the range of 56–210 ns, which is significantly longer than the average reorientation times observed for the two-probe molecules. Thus, the contribution of the overall rotation of the reverse micelles to average reorientation time is almost negligible.

As mentioned earlier, the average reorientation time of the probe depends on W as well as [L64], and to rationalize the

observed behavior, micellar packing has been taken into consideration. For this purpose, the critical micellar packing parameter, which is defined as ν/a_0l_c , has been calculated for the L64/water/*p*-xylene reverse micellar system from the structural parameters available in the literature.¹⁷ In the expression ν/a_0l_c , the terms ν , a_0 , and l_c are effective volume of the hydrophobic tail, optimum surface area of the headgroup, and fully extended chain length of the hydrophobic tail, respectively.⁶¹ These quantities are related to the micellar structural parameters by the following relations.⁶²

$$\nu = \frac{4\pi}{3N_a}[r_h^3 - r_c^3] \quad (6)$$

$$a_0 = \frac{4\pi r_c^3}{N_a} \quad (7)$$

$$l_c = [r_h - r_c] \quad (8)$$

For the L64/water/*p*-xylene reverse micellar system, the critical packing parameters have been calculated, and they are in the range of 1.38–1.73, which indicates that the variation in ν/a_0l_c is about 25%. This variation is meager compared to ones noticed in the case of reverse micelles formed with ionic surfactants such as bis(2-ethylhexyl) sodium sulfosuccinate (AOT) and sodium dodecyl sulfate (SDS) where ν/a_0l_c decreases from as high as 4.5 to 1.5.^{33,34} Nonetheless, the important point is that the critical packing parameter should be greater than one for the formation of stable reverse micelles.⁶²

To find out how the probe rotation correlates with micellar packing, $\langle\tau_r\rangle$ is plotted as a function of ν/a_0l_c in Figure 4 for the probes R110 and FL. It can be noticed from the figure that $\langle\tau_r\rangle$ increases linearly with an increase in ν/a_0l_c for both the probes. Linear least-squares fits of the data give the following relationships between $\langle\tau_r\rangle$ and ν/a_0l_c .

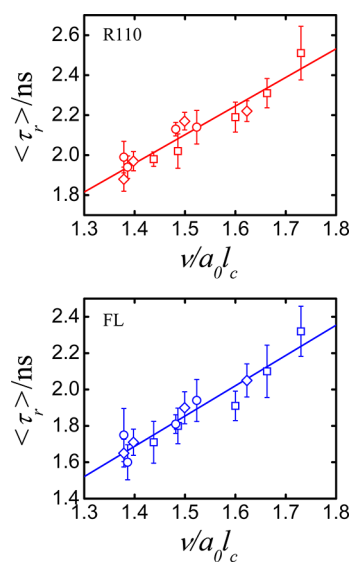


Figure 4. Plots of $\langle\tau_r\rangle$ versus critical packing parameter for R110 and FL in L64/water/*p*-xylene reverse micellar system at 15 (○), 25 (◇), and 35 (□) weight percent of the copolymer. The lines passing through the data points have been obtained by linear least-squares fits. The figure presents conclusive evidence that the average reorientation times of both the probes scale linearly with ν/a_0l_c .

$$\text{R110-L64/water}/p\text{-xylene} \quad \langle \tau_r \rangle = -0.05 + 1.43(\nu/a_0 l_c) \\ (N = 13, R = 0.955)$$

$$\text{FL-L64/water}/p\text{-xylene} \quad \langle \tau_r \rangle = -0.64 + 1.67(\nu/a_0 l_c) \\ (N = 13, R = 0.957)$$

In these expressions, N and R are the number of data points and regression coefficients, respectively. The slope of $\langle \tau_r \rangle$ versus $\nu/a_0 l_c$ plot depends on the nature of the probe for a particular reverse micellar system employed. Thus, it can be deduced that the slope is essentially a combination of the terms appearing in the Stokes–Einstein–Debye hydrodynamic equation,⁶⁰ and the critical packing parameter can be termed as a “correction factor” to account for the changes associated with the local viscosity. A quick glance at Figure 4 reveals the presence of some scatter in the data, which probably arises as a consequence of small changes associated with $\langle \tau_r \rangle$ and also the constraints involved in the estimation of structural parameters of L64 reverse micelles that have been employed in the calculation of $\nu/a_0 l_c$. If one takes these limitations into consideration, the correlation obtained here appears reasonable. Even though W increases by nearly a factor of 7 in the case of L64/water/ p -xylene reverse micellar system employed in the present study, $\langle \tau_r \rangle$ varies only by a factor of 1.3 and 1.4 for R110 and FL, respectively. This is because the variation in the critical packing parameter is only 25%. Thus, from the findings of the study, it is evident that the rotation of a probe molecule solubilized in the interfacial region of a block copolymer reverse micelle is essentially governed by the micellar packing.

CONCLUSIONS

The friction experienced by a probe molecule in an organized assembly is dictated by the local viscosity, which is often referred to as microviscosity. Of late, our efforts have been channelized toward understanding this friction in reverse micelles in terms of their structural parameters. The present work is one such attempt in that direction, and the conclusions are summarized in this section. Fluorescence anisotropy measurements carried out with two structurally similar ionic probes R110 and FL, which are located in the interfacial region of L64/water/ p -xylene reverse micellar system, indicate that their average reorientation times are dependent on water content as well as on the concentration of the copolymer. To rationalize these observations, critical packing parameters have been calculated with the aid of aggregation number, core radius, and hard-sphere radius for the L64 block copolymer reverse micelles. The important finding from the study is that the average reorientation times of both the ionic probes scale linearly with the critical packing parameters of the reverse micellar system, which essentially indicates that the interfacial friction experienced by the probe molecules can be depicted by a combination of micellar structural parameters in the form of $\nu/a_0 l_c$.

AUTHOR INFORMATION

Corresponding Author

*E-mail: gbdutt@barc.gov.in.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Dr. Rajib Ganguly for fruitful discussions on L64 reverse micellar system employed in this study. Sugosh Prabhu would like to acknowledge University Grants Commission for the award of Junior Research Fellowship.

REFERENCES

- (1) Brown, W.; Schillén, K.; Hvidt, S. Triblock Copolymers in Aqueous Solution Studied by Static and Dynamic Light Scattering and Oscillatory Shear Measurements. Influence of Relative Block Sizes. *J. Phys. Chem.* **1992**, *96*, 6038–6044.
- (2) Mortensen, K.; Pedersen, J. S. Structural Study on the Micelle Formation of Poly(ethylene oxide)-Poly(propylene oxide)-Poly(ethylene oxide) Triblock Copolymer in Aqueous Solution. *Macromolecules* **1993**, *26*, 805–812.
- (3) Alexandridis, P.; Holzwarth, J. F.; Hatton, T. A. Micellization of Poly(ethylene oxide)-Poly(propylene oxide)-Poly(ethylene oxide) Triblock Copolymers in Aqueous Solutions: Thermodynamics of Copolymer Association. *Macromolecules* **1994**, *27*, 2414–2425.
- (4) Chu, B. Structure and Dynamics of Block Copolymer Colloids. *Langmuir* **1995**, *11*, 414–421.
- (5) Chu, B.; Zhou, Z. Physical Chemistry of Polyoxyalkylene Block Copolymer Surfactants. In *Nonionic Surfactants*; Nace, V. M., Ed.; Surfactant Science Series; Marcel Dekker: New York, 1996; Vol. 60, pp 67–142.
- (6) Alexandridis, P.; Olsson, U.; Lindman, B. A Record Nine Different Phases (Four Cubic, Two Hexagonal, and One Lamellar Lyotropic Liquid Crystalline and Two Micellar Solutions) in a Ternary Isothermal System of an Amphiphilic Block Copolymer and Selective Solvents (Water and Oil). *Langmuir* **1998**, *14*, 2627–2638.
- (7) Holmqvist, P.; Alexandridis, P.; Lindman, B. Modification of the Microstructure in Block Copolymer–Water–“Oil” Systems by Varying the Copolymer Composition and the “Oil” Type: Small-Angle X-ray Scattering and Deuterium-NMR Investigation. *J. Phys. Chem. B* **1998**, *102*, 1149–1158.
- (8) Ganguly, R.; Aswal, V. K.; Hassan, P. A.; Gopalakrishnan, I. K.; Yakhmi, J. V. Sodium Chloride and Ethanol Induced Sphere to Rod Transition of Triblock Copolymer Micelles. *J. Phys. Chem. B* **2005**, *109*, 5653–5658.
- (9) Jansson, J.; Schillén, K.; Olofsson, G.; da Silva, R. C.; Loh, W. The Interaction between PEO-PPO-PEO Triblock Copolymers and Ionic Surfactants in Aqueous Solution Studied Using Light Scattering and Calorimetry. *J. Phys. Chem. B* **2004**, *108*, 82–92.
- (10) Jansson, J.; Schillén, K.; Nilsson, M.; Söderman, O.; Fritz, G.; Bergmann, A.; Glatter, O. Small-Angle X-ray Scattering, Light Scattering, and NMR Study of PEO-PPO-PEO Triblock Copolymer/Cationic Surfactant Complexes in Aqueous Solution. *J. Phys. Chem. B* **2005**, *109*, 7073–7083.
- (11) Ganguly, R.; Aswal, V. K.; Hassan, P. A.; Gopalakrishnan, I. K.; Kulshreshtha, S. K. Effect of SDS on the Self-Assembly Behavior of the PEO-PPO-PEO Triblock Copolymer (EO)₂₀(PO)₇₀(EO)₂₀. *J. Phys. Chem. B* **2006**, *110*, 9843–9849.
- (12) Wu, G.; Zhou, Z.; Chu, B. Water-Induced Micelle Formation of Block Copoly(oxyethylene-oxypropylene-oxyethylene) in *o*-Xylene. *Macromolecules* **1993**, *26*, 2117–2125.
- (13) Wu, G.; Chu, B. Light-Scattering Studies of a Block Poly(oxyethylene-oxypropylene-oxyethylene) Copolymer in Water/*o*-Xylene Mixtures. *Macromolecules* **1994**, *27*, 1766–1773.
- (14) Wu, G.; Chu, B.; Schneider, D. K. Small-Angle Neutron Scattering Study of Polymeric Micellar Structures. *J. Phys. Chem.* **1994**, *98*, 12018–12024.
- (15) Svensson, B.; Olsson, U.; Alexandridis, P.; Mortensen, K. A SANS Investigation of Reverse (Water-in-Oil) Micelles of Amphiphilic Block Copolymers. *Macromolecules* **1999**, *32*, 6725–6733.
- (16) Barreleiro, P. C. A.; Alexandridis, P. ¹³C-NMR Evidence on Amphiphile Lifetime in Reverse (Water-in-Oil) Micelles Formed by a Poloxamer Block Copolymer. *J. Colloid Interface Sci.* **1998**, *206*, 357–360.

- (17) Arleth, L.; Svensson, B.; Mortensen, K.; Pedersen, J. S.; Olsson, U. Block-Copolymer Micro-emulsion with Solvent-Induced Segregation. *Langmuir* **2007**, *23*, 2117–2125.
- (18) Alexandridis, P.; Andersson, K. Reverse Micelle Formation and Water Solubilization by Polyoxyalkylene Block Copolymers in Organic Solvent. *J. Phys. Chem. B* **1997**, *101*, 8103–8111.
- (19) Dutt, G. B. How Critical Micelle Temperature Influences Rotational Diffusion of Hydrophobic Probes Solubilized in Aqueous Triblock Copolymer Solutions. *J. Phys. Chem. B* **2005**, *109*, 4923–4928.
- (20) Mali, K. S.; Dutt, G. B.; Ganguly, R.; Mukherjee, T. Effect of “Inverse Melting Transition” of Aqueous Triblock Copolymer Solutions on Solute Rotational Dynamics. *J. Chem. Phys.* **2005**, *123*, 144913/1–144913/6.
- (21) Mali, K. S.; Dutt, G. B.; Mukherjee, T. Rotational Diffusion of an Ionic Solute in Polymorphic Environments of a Block Copolymer: Influence of Interfacial Friction on Solute Rotation. *Langmuir* **2007**, *23*, 1041–1046.
- (22) Mali, K. S.; Dutt, G. B.; Mukherjee, T. Rotational Diffusion of Organic Solutes in Surfactant-Block Copolymer Micelles: Role of Electrostatic Interactions and Micellar Hydration. *J. Phys. Chem. B* **2007**, *111*, 5878–5884.
- (23) Mali, K. S.; Dutt, G. B.; Mukherjee, T. Rotational Diffusion of Ionic and Neutral Solutes in Mixed Micelles: Effect of Surfactant to Block Copolymer Mole Ratio on Solute Rotation. *J. Chem. Phys.* **2007**, *127*, 154904/1–154904/7.
- (24) Mali, K. S.; Dutt, G. B.; Mukherjee, T. Polyene Photoisomerization Rates: Are They Distinct in Aqueous Block Copolymer Micellar Solutions and Gels? *J. Chem. Phys.* **2006**, *124*, 054904/1–054904/6.
- (25) Mali, K. S.; Dutt, G. B.; Mukherjee, T. Erratum: Polyene Photoisomerization Rates: Are They Distinct in Aqueous Block Copolymer Micellar Solutions and Gels? *J. Chem. Phys.* **2006**, *124*, 199901/1–199901/2.
- (26) Mali, K. S.; Dutt, G. B.; Mukherjee, T. Photoisomerization of a Carbocyanine Derivative in the Reverse Phases of a Block Copolymer: Evidence for the Existence of Water Droplets. *Langmuir* **2006**, *22*, 6837–6842.
- (27) Jeon, S.; Granick, S.; Kwon, K. C.; Char, K. Microviscosity in Poly(ethylene oxide)-Polypropylene Oxide-Poly(ethylene oxide) Block Copolymers Probed by Fluorescence Depolarization Kinetics. *J. Polym. Sci., Part B: Polym. Phys.* **2002**, *40*, 2883–2888.
- (28) Grant, C. D.; DeRitter, M. R.; Steege, K. E.; Fadeeva, T. A.; Castner, E. W., Jr. Fluorescence Probing of Interior, Interfacial, and Exterior Regions in Solution Aggregates of Poly(ethylene oxide)-Poly(propylene oxide)-Poly(ethylene oxide) Triblock Copolymers. *Langmuir* **2005**, *21*, 1745–1752.
- (29) Grant, C. D.; Steege, K. E.; Bunagan, M. R.; Castner, E. W., Jr. Microviscosity in Multiple Regions of Complex Aqueous Solutions of Poly(ethylene oxide)-Poly(propylene oxide)-Poly(ethylene oxide). *J. Phys. Chem. B* **2005**, *109*, 22273–22284.
- (30) Kumbhakar, M.; Goel, T.; Nath, S.; Mukherjee, T.; Pal, H. Microenvironment in the Corona Region of Triblock Copolymer Micelles: Temperature Dependent Solvation and Rotational Relaxation Dynamics of Coumarin Dyes. *J. Phys. Chem. B* **2006**, *110*, 25646–25655.
- (31) George, S.; Kumbhakar, M.; Singh, P. K.; Ganguly, R.; Nath, S.; Pal, H. Fluorescence Spectroscopic Investigation to Identify the Micelle to Gel Transition of Aqueous Triblock Copolymer Solutions. *J. Phys. Chem. B* **2009**, *113*, 5117–5127.
- (32) Singh, P. K.; Kumbhakar, M.; Pal, H.; Nath, S. Modulation in the Solute Location in Block Copolymer–Surfactant Supramolecular Assembly: A Time-resolved Fluorescence Study. *J. Phys. Chem. B* **2009**, *113*, 1353–1359.
- (33) Dutt, G. B. What Governs Molecular Rotation at the Interfaces of Reverse Micelles? *ChemPhysChem* **2010**, *11*, 1646–1649.
- (34) Gangamallaiiah, V.; Dutt, G. B. Characterizing Interfacial Friction in AOT Reverse Micelles from Photoisomerization Studies of Carbocyanine Derivatives. *J. Chem. Phys.* **2011**, *134*, 024706/1–024706/6.
- (35) O'Connor, D. V.; Phillips, D. *Time-Correlated Single Photon Counting*; Academic Press: London, 1984.
- (36) Dutt, G. B. Influence of Specific Interactions on the Rotational Dynamics of Charged and Neutral Solutes in Ionic Liquids Containing Tris(pentafluoroethyl)trifluorophosphate (FAP) Anion. *J. Phys. Chem. B* **2010**, *114*, 8971–8977.
- (37) Alvarez-Pez, J. M.; Ballesteros, L.; Talavera, E.; Yguerabide, J. Fluorescein Excited-State Proton Exchange Reactions: Nanosecond Emission Kinetics and Correlation with Steady-State Fluorescence Intensity. *J. Phys. Chem. A* **2001**, *105*, 6320–6332.
- (38) Dutt, G. B. Fluorescence Anisotropy of Ionic Probes in AOT Reverse Micelles: Influence of Water Droplet Size and Electrostatic Interactions on Probe Dynamics. *J. Phys. Chem. B* **2008**, *112*, 7220–7226.
- (39) Chung, T. J.; Eiselthal, K. B. Theory of Fluorescence Depolarization by Anisotropic Rotational Diffusion. *J. Chem. Phys.* **1972**, *57*, 5094–5097.
- (40) Gangamallaiiah, V.; Dutt, G. B. Rotational Diffusion of Nonpolar and Ionic Solutes in 1-Alkyl-3-Methylimidazolium bis-(trifluoromethylsulfonyl)imides: Is Solute Rotation Always Influenced by the Length of the Alkyl Chain on the Imidazolium Cation? *J. Phys. Chem. B* **2012**, *116*, 12819–12825.
- (41) Quitevis, E. L.; Marcus, A. H.; Fayer, M. D. Dynamics of Ionic Lipophilic Probes in Micelles: Picosecond Fluorescence Depolarization Measurements. *J. Phys. Chem.* **1993**, *97*, 5762–5769.
- (42) Maiti, N. C.; Krishna, M. M. G.; Britto, P. J.; Periasamy, N. Fluorescence Dynamics of Dye Probes in Micelles. *J. Phys. Chem. B* **1997**, *101*, 11051–11060.
- (43) Dutt, G. B. Rotational Diffusion of Nondipolar Probes in Triton X-100 Micelles: Role of Specific Interactions and Micelle Size on Probe Dynamics. *J. Phys. Chem. B* **2002**, *106*, 7398–7404.
- (44) Dutt, G. B. Rotational Relaxation of Nondipolar Probes in Triton X-100 Micelles in the Presence of Added Salt: Correlation of Lateral Diffusion Coefficient with “Dry” Micelle Radius. *J. Phys. Chem. B* **2003**, *107*, 3131–3136.
- (45) Dutt, G. B. Rotational Diffusion of Hydrophobic Probes in Brij-35 Micelles: Effect of Temperature on Micellar Internal Environment. *J. Phys. Chem. B* **2003**, *107*, 10546–10551.
- (46) Kelepouris, L.; Blanchard, G. J. Dynamics of 7-Azatriptophan and Tryptophan Derivatives in Micellar Media. The Role of Ionic Charge and Substituent Structure. *J. Phys. Chem. B* **2003**, *107*, 1079–1087.
- (47) Hierrezuelo, J. M.; Ruiz, C. C. Rotational Diffusion of Coumarin 153 in Nanoscopic Micellar Environments of *n*-Dodecyl- β -D-maltoside and *n*-Dodecylhexaethylene-glycol Mixtures. *J. Phys. Chem. A* **2012**, *116*, 12476–12485.
- (48) Ruiz, C. C. Rotational Dynamics of Coumarin 153 in Non-ionic Mixed Micelles of *n*-Octyl- β -D-thioglucoside and Triton X-100. *Photochem. Photobiol. Sci.* **2012**, *11*, 1331–1338.
- (49) Wittouck, N.; Negri, R. M.; Ameloot, M.; De Schryver, F. C. AOT Reversed Micelles Investigated by Fluorescence Anisotropy of Cresyl Violet. *J. Am. Chem. Soc.* **1994**, *116*, 10601–10611.
- (50) Dutt, G. B. Rotational Relaxation of Hydrophobic Probes in Nonionic Reverse Micelles: Influence of Water Content on the Location and Mobility of the Probe Molecules. *J. Phys. Chem. B* **2004**, *108*, 805–810.
- (51) Dutt, G. B. Does the Onset of Water Droplet Formation Alter the Microenvironment of the Hydrophobic Probes Solubilized in Nonionic Reverse Micelles? *J. Phys. Chem. B* **2004**, *108*, 7944–7949.
- (52) Dutt, G. B. Do Ionic and Hydrophobic Probes Sense Similar Microenvironment in Triton X-100 Nonionic Reverse Micelles? *J. Chem. Phys.* **2008**, *129*, 014501/1–014501/6.
- (53) Mali, K. S.; Dutt, G. B. Do the Interfacial Fluidities of Cationic Reverse Micelles Enhance with an Increase in the Water Content? *J. Chem. Phys.* **2009**, *131*, 174708/1–174708/8.
- (54) Spry, D. B.; Goun, A.; Glusac, K.; Moilanen, D. E.; Fayer, M. D. Proton Transport and the Water Environment in Nafion Fuel Cell

Membranes and AOT Reverse Micelles. *J. Am. Chem. Soc.* **2007**, *129*, 8122–8130.

(55) Kinoshita, J.; Kawato, S.; Ikegami, A. A Theory of Fluorescence Polarization Decay in Membranes. *Biophys. J.* **1977**, *20*, 289–305.

(56) Lipari, G.; Szabo, A. Effect of Librational Motion on Fluorescence Depolarization and Nuclear Magnetic Resonance Relaxation in Macromolecules and Membranes. *Biophys. J.* **1980**, *30*, 489–506.

(57) Lipari, G.; Szabo, A. Model-Free Approach to the Interpretation of Nuclear Magnetic Resonance Relaxation in Macromolecules. 1. Theory and Range of Validity. *J. Am. Chem. Soc.* **1982**, *104*, 4546–4559.

(58) Lipari, G.; Szabo, A. Model-Free Approach to the Interpretation of Nuclear Magnetic Resonance Relaxation in Macromolecules. 2. Analysis of Experimental Results. *J. Am. Chem. Soc.* **1982**, *104*, 4559–4570.

(59) Wang, C. C.; Pecora, R. Time-Correlation Functions for Restricted Rotational Diffusion. *J. Chem. Phys.* **1980**, *72*, 5333–5340.

(60) Debye, P. *Polar Molecules*; Dover: New York, 1929.

(61) Israelachvili, J. The Science and Applications of Emulsions-An Overview. *Colloids Surf., A: Physicochem. Eng. Aspects* **1994**, *91*, 1–8.

(62) Mitchell, D. J.; Ninham, B. W. Micelles, Vesicles and Microemulsions. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 601–629.