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Do ionic and hydrophobic probes sense similar microenvironment in Triton X-100 nonionic reverse micelles?

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Rotational diffusion of two structurally similar ionic probes, rhodamine 110 and fluorescein, has been examined in nonionic reverse micellar system of Triton X-100/benzene–*n*-hexane/water as a function of mole ratio of the water to surfactant, *W*. This study has been undertaken to find out whether ionic and hydrophobic probes experience similar microenvironment in these reverse micelles. Experimental results indicate that, from $W=0$ to 3, the average reorientation time, which is a measure of the microviscosity experienced by the probe molecule, increases by 90% and 40% for rhodamine 110 and fluorescein, respectively, and from $W=3$ to 8, it decreases by 20% for both the probes. The increase in the average reorientation time with *W* has been rationalized on the basis of the flexible oxyethylene chains of the TX-100 surfactant being hydrogen bonded by the water molecules, which makes the core region less fluid. However, once the hydration of the oxyethylene chains is complete, further addition of water results in formation of water droplet; which renders the micelle-water interface in the core region less compact leading to a marginal decrease in the average reorientation time of the probe molecules. These explanations are consistent with the location of the probes and the structure of the Triton X-100/benzene–hexane/water reverse micelles. To compare how the microenvironment experienced by these ionic probes is different from the hydrophobic ones, results from our earlier work [J. Phys. Chem. B **108**, 7944 (2004)] have been considered. Such a comparison revealed that both ionic and hydrophobic probes experience similar microenvironment in these reverse micelles until the hydration of the oxyethylene chains is complete. In case of hydrophobic probes, however, the onset of water droplet formation does not alter their microenvironment, which is due to their location in the reverse micellar cores. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2946705]

I. INTRODUCTION

The cores of nonionic reverse micelles represent an "interesting" case of compartmentalized polar microenvironments due to their ability to contain water in hydrated and droplet forms.[1–6] These systems can be utilized for carrying out chemical reactions and synthesis of colloidal particles.[7] Typical examples of such systems include the reverse micelles formed with the nonionic surfactant Triton X-100 (TX-100) in cyclohexane,[1,2] mixed solvents of benzene–*n*-hexane,[3,4] and toluene.[5,6] It must, however, be noted that in aqueous TX-100/cyclohexane reverse micelles only the hydrated form of water exists, whereas aqueous TX-100/benzene–hexane and TX-100/toluene systems contain both forms of water depending on the mole ratio of water to surfactant, *W*. In view of their utility as microreactors, it is essential to explore the dynamics of probe molecules solubilized in these systems. Thus, rotational diffusion studies have been carried out to understand how the hydration of the oxyethylene chains of TX-100 surfactant in these reverse micelles influences the mobility of the probe molecules.[8,9] Solvation dynamics measurements have also been employed to understand the effect of confinement on the dynamical aspects of these micellar interiors.[10]

Rotational diffusion of a probe molecule in an organized assembly is essentially governed by its location and ability to interact with the surroundings. The charge and chemical nature of the probe molecule are important parameters in determining its site of solubilization. In nonionic micelles, ionic probes are usually located at the interface and the hydrophobic ones in the palisade layer. Due to their distinct locations, the microenvironments experienced by ionic and hydrophobic probes in these systems are vastly different. Our recent studies[11,12] have shown that an ionic probe can be used to monitor the microenvironment at the micelle-water interface, whereas a hydrophobic probe can be employed to assess the hydration levels in the palisade layer of a nonionic micelle. However, the site of solubilization of a probe molecule in a nonionic micelle can be altered in presence of additives such as ionic surfactants. It has been demonstrated that the migration of a cationic probe from the interface to palisade layer is possible when negatively charged surfactants molecules are embedded in pluronic micelles.[12]

Although the location and mobility of probe molecules is reasonably well understood in nonionic micelles, these aspects have received relatively little attention in nonionic reverse micelles. In a recent study,[9] rotational diffusion of two structurally similar hydrophobic probes, 2,5-dimethyl-1, 4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DMDPP) and 1,4-dioxo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DPP) has been

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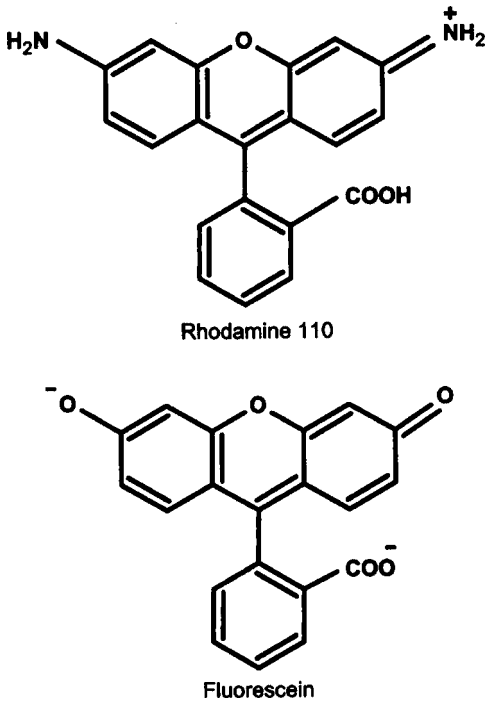

FIG. 1. Molecular structures of the ionic probes used in the study.

investigated in TX-100/benzene–hexane/water reverse micelles as a function of W. It has been observed that from $W=0$ to 3, there is a significant enhancement in the average reorientation time of both the probes and further increase in W from 3 to 8 resulted in its saturation. These observations have been rationalized on the basis of structure of the TX-100/benzene–hexane/water reverse micelles and the site of solubilization of the probe molecules. In an attempt to find out whether or not a similar pattern will be observed in case of ionic probes, the present investigation has been undertaken. For this purpose rotational diffusion of two structurally similar ionic probes has been studied in TX-100/benzene–hexane/water reverse micelles as a function of W. Figure 1 gives molecular structures of the probes rhodamine 110 and fluorescein used in this work and it is evident from the figure that rhodamine 110 is a cationic probe whereas fluorescein exits as a dianion in the reverse micellar system chosen for the present study. The strategy that is being adopted in this work involves the measurement of time-resolved fluorescence anisotropy decays of rhodamine 110 and fluorescein in TX-100/benzene–hexane/water reverse micelles as a function W, which will be varied in steps of one unit. The anisotropy decay parameters of the two ionic probes will be compared to that of the hydrophobic ones from our earlier work.[9] Thus, it would be interesting to find out whether ionic and hydrophobic probes experience a similar microenvironment in this nonionic reverse micellar system.

II. EXPERIMENT

The probes rhodamine 110 (chloride salt) and disodium fluorescein are from Exciton. The surfactant TX-100 is from Riedel–deHaën with a water content of 0.5 wt %. Spectroscopic grade benzene and n-hexane are from Sisco Research Laboratories Pvt. Ltd. and Thomas Baker, respectively. All these chemicals are of the highest available purity and were used as such. De-ionized water from Millipore A-10 was used in the preparation of the micellar samples. Reverse micelles with desired W values were prepared by weighing appropriate amounts of TX-100 and water in volumetric flasks, and the remaining volumes of the flasks were made up with 30:70 (v/v) mixture of benzene and hexane. The concentration of TX-100 was kept at 0.27 mol dm^{-3} and that of the probes maintained in the range of $10^{-5}-10^{-6}$ mol dm^{-3}.

Absorption and fluorescence spectra were recorded using a Shimadzu UV-160A spectrophotometer and a Hitachi F-4010 spectrofluorometer, respectively. Steady-state anisotropies of the probes in the reverse micelles were measured with the aid of the above-mentioned spectrofluorometer and the experimental details have been described elsewhere.[13] The probes rhodamine 110 and fluorescein were excited at 440 nm and emission was monitored in the range of 530–580 nm. Time-resolved fluorescence measurements were carried out using time-correlated single-photon counting[14] facility at the Tata Institute of Fundamental Research, Mumbai, and details of the system have been described elsewhere.[15] The excitation source was a frequency-doubled output of a picosecond Ti:sapphire laser (Tsunami, Spectra Physics). The samples containing the probes rhodamine 110 and fluorescein were excited at 440 nm and the emission was monitored at 530 nm. The decays measured in this manner are convoluted with the instrument response function (IRF), which was measured by replacing the sample with a solution that scatters light. Nondairy coffee creamer dispersed in water served as the scattering medium. The full width at half maximum of the IRF is about 50 ps. All the measurements were carried out at 298 K. Each measurement was repeated at least two to three times and the average values are reported. Fluorescence lifetimes and anisotropy decay parameters were obtained from the magic angle and anisotropy decays, respectively, with the help of iterative reconvolution methods as described in literature.[16,17] Details concerning the analysis of the fluorescence and anisotropy decays have been mentioned in our earlier publication.[18]

III. RESULTS AND DISCUSSION

The absorption and emission spectra of rhodamine 110 and fluorescein in TX-100/benzene–hexane reverse micelles at $W=0$ and $W=8$ are given in Fig. 2. The spectra of the probes in water are also given in the figure for the sake of comparison. In these reverse micelles, at $W=0$, the absorption spectrum of rhodamine 110 displays a peak around 525 nm with a shoulder at 505 nm and in contrast, at $W=8$, the spectrum has single peak at 505 nm. The emission spectrum of rhodamine 110 is also redshifted by 10 nm at $W=0$ compared to the one at $W=8$. At $W=0$, rhodamine 110 is predominantly in the neutral form and the shoulder observed in the absorption spectrum at 505 nm is due to the cationic form. The other probe used in the study, fluorescein is in the form of dianion in these reverse micelles at $W=0$ as well as $W=8$. The absorption band of the monoanion form of fluorescein in water is structured with the maxima centered

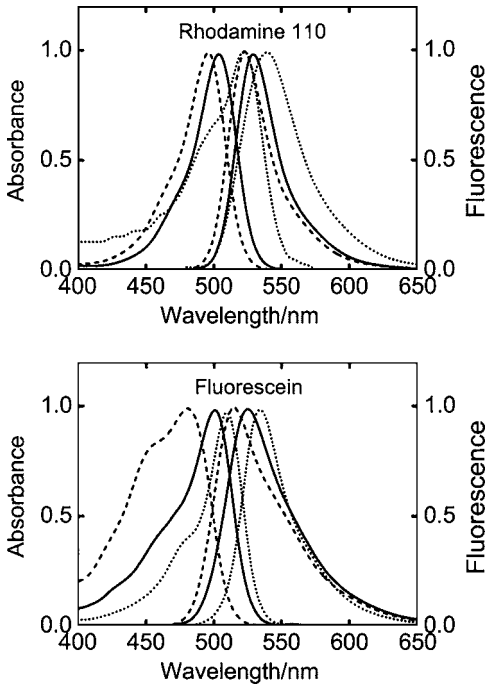

FIG. 2. Absorption and emission spectra of rhodamine 110 and fluorescein in TX-100/benzene–hexane reverse micelles at $W=0$ (dotted line), $W=8$ (solid line), and in water (dashed line). The concentrations of the probes are in the range of $10^{-5}-10^{-6}$ mol dm^{-3}.

around 450 and 480 nm. Both the forms of fluorescein emit in the range of 480–650 nm, but the emission spectrum of the monoanion has a shoulder at around 550 nm.[19] Since the spectra presented in the figure resemble that of a dianion reported in literature and also due to the fact that they lack the characteristic features of the monoanion, it is reasonable to conclude that fluorescein exists as dianion in TX-100/benzene–hexane reverse micelles. The presence of fluorescein dianion in this system is somewhat surprising because in AOT/isooctane reverse micelles the monoanion form of the dye prevails.[20] However, it must be noted that excited state proton transfer is possible in case of both the probes used in this study and this aspect has been discussed in our earlier publication.[20]

Fluorescence lifetime (τ_f) measurements of rhodamine 110 and fluorescein were carried out to assess the location the probe molecules in TX-100/benzene–hexane reverse micelles. Fluorescence decays of both the probes from $W=0$ to 8 could be fitted with a single-exponential function. There is no variation in the lifetime of rhodamine 110 with W, which is 3.7 ± 0.1 ns and the corresponding number in water is 4.1 ns.[20] On the other hand, the lifetimes of fluorescein decrease from 4.6 to 4.2 ns as W increases from 0 to 8. The lifetime of fluorescein in water is 3.5 ns when 440 nm excitation wavelength is employed and this corresponds to the lifetime of the monoanion from. Thus, from the lifetime data it can be inferred that both the probes are not solubilized in water and waterlike environments in these reverse micelles. The most probable site of solubilization is either the micelle-water interface or the hydrated oxyethylene chains within the core of the reverse micelles.

Steady-state anisotropies ($\langle r\rangle$) of rhodamine 110 and

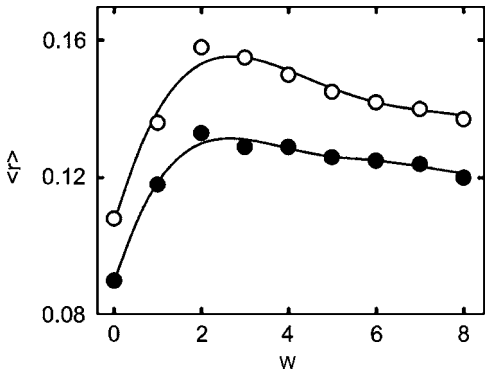

FIG. 3. Variation of steady-state anisotropies of rhodamine 110 (○) and fluorescein (●) in TX-100/benzene–hexane reverse micelles with W. The lines passing through the data points are drawn as visual aid.

fluorescein were measured in the reverse micellar system to obtain preliminary information about the microenvironment experienced by the probe molecules. Figure 3 displays plots of $\langle r\rangle$ versus W and it is evident from the figure that $\langle r\rangle$ increases from $W=0$ to 2 for both the probes and from $W=2$ to 8, it decreases by 15% and 10%, respectively, for rhodamine 110 and fluorescein. These results indicate that there is a change in the microenvironment experienced by both the probe molecules with W, but the variation is not uniform. To get a better appreciation of the microenvironment experienced by rhodamine 110 and fluorescein in TX-100/benzene–hexane reverse micelles and how it varies with W, fluorescence anisotropy decays of the probes were measured. The anisotropy decays $r(t)$ of both the probes could be fitted with a biexponential function 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 time constants associated with the decay of the anisotropy, β is the fraction of the contribution of τ_{r1}, and r_0 is anisotropy at $t=0$, whose value depends on the angle between absorption and emission transition dipoles of the probe molecule. The microenvironment experienced by the probe molecule can be quantified by the parameter, the average reorientation time $\langle\tau_r\rangle$, which is given by the following equation:

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

Figure 4 displays the anisotropy decays of rhodamine 110 and fluorescein in the reverse micelles at $W=0$ and 3 and it is evident from the figure that the anisotropy decays of both the probes become slower with an increase in the water content. The parameters obtained from the analysis of the anisotropy decays of rhodamine 110 and fluorescein in TX-100/benzene–hexane reverse micelles as a function of W are given in Tables I and II, respectively, along with the average reorientation times. It can be noticed from the tables that, for both probes, the parameters τ_{r1} and $\langle\tau_r\rangle$ increase significantly from $W=0$ to 3 and decrease marginally from 3 to 8. On the other hand, no systematic variation has been observed in case of the shorter component τ_{r2}, which is probably due to the inherent limitations associated with the recovery of all the parameters from the anisotropy decays accurately. Figure

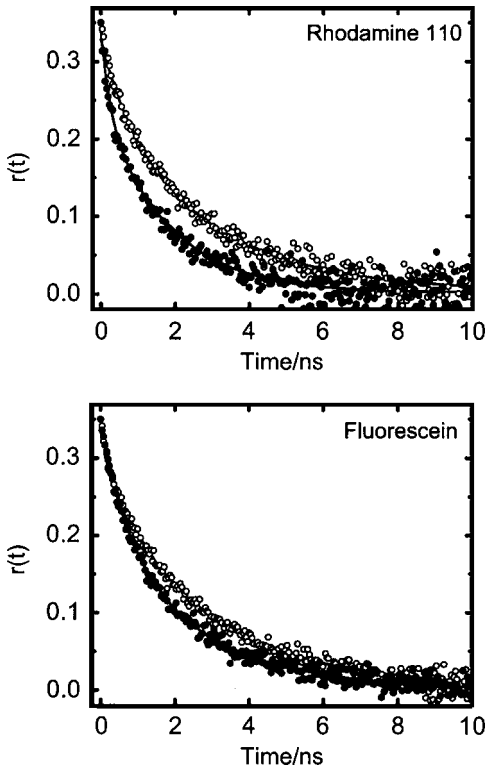

FIG. 4. Anisotropy decay curves of rhodamine 110 and fluorescein in TX-100/benzene–hexane reverse micelles at $W=0$ (●) and $W=3$ (○). The anisotropy decays of both the probes become slower as the water content increases from 0 to 3. The smooth curves passing through the data points were obtained by biexponential fits.

5 depicts plots of $\langle\tau_r\rangle$ versus W for rhodamine 110 and fluorescein, in this reverse micellar system.

To rationalize these experimental results, the structure of the TX-100/benzene–hexane reverse micelles needs to be considered. Dynamic light scattering studies carried out by Zhu *et al.*[3] indicate that a 0.27 mol dm^{-3} solution of TX-100 in 30% (v/v) benzene and 70% (v/v) *n*-hexane forms reverse micelles with a hydrodynamic diameter D_h of 7.2 nm at 298 K. The size of these reverse micelles increases with W and D_h reaches close to 90 nm at $W=9$. Spectrophotometric investigations[4] with the probes methyl orange and 1-methyl-8-oxyquinolonium betaine reveal that in the absence of water, benzene penetrates the cores of these reverse micelles. At low water content ($W=1$ and 2), the added water hydrates the oxyethylene chains of the surfactant by replacing benzene

TABLE I. Anisotropy decay parameters of rhodamine 110 in reverse micelles of TX-100/benzene–hexane as function of the water content at 298 K.

W	β	τ_{r1} (ns)	τ_{r2} (ns)	$\langle\tau_r\rangle$ (ns)
0	0.61 ± 0.01	1.85 ± 0.08	0.24 ± 0.05	1.22
1	0.71 ± 0.01	2.54 ± 0.10	0.30 ± 0.06	1.89
2	0.68 ± 0.01	2.98 ± 0.10	0.63 ± 0.04	2.23
3	0.80 ± 0.02	2.72 ± 0.10	0.68 ± 0.05	2.31
4	0.82 ± 0.01	2.70 ± 0.09	0.33 ± 0.04	2.27
5	0.75 ± 0.03	2.80 ± 0.08	0.28 ± 0.06	2.17
6	0.76 ± 0.01	2.62 ± 0.10	0.42 ± 0.04	2.09
7	0.80 ± 0.02	2.43 ± 0.09	0.33 ± 0.03	2.01
8	0.72 ± 0.02	2.50 ± 0.08	0.37 ± 0.05	1.90

TABLE II. Anisotropy decay parameters of fluorescein in reverse micelles of TX-100/benzene–hexane as function of the water content at 298 K.

W	β	τ_{r1} (ns)	τ_{r2} (ns)	$\langle\tau_r\rangle$ (ns)
0	0.55 ± 0.02	2.65 ± 0.05	0.79 ± 0.05	1.81
1	0.71 ± 0.03	2.86 ± 0.10	0.82 ± 0.05	2.27
2	0.72 ± 0.02	3.11 ± 0.09	0.85 ± 0.05	2.48
3	0.71 ± 0.02	3.19 ± 0.06	0.87 ± 0.12	2.52
4	0.74 ± 0.01	3.09 ± 0.05	0.71 ± 0.09	2.47
5	0.70 ± 0.01	3.06 ± 0.05	0.86 ± 0.05	2.40
6	0.71 ± 0.01	2.91 ± 0.09	0.81 ± 0.04	2.30
7	0.73 ± 0.01	2.73 ± 0.06	0.66 ± 0.04	2.17
8	0.77 ± 0.03	2.49 ± 0.09	0.74 ± 0.06	2.09

and once the hydration is complete, water droplet formation takes place at $W=2.5$. These studies also reveal that the water droplet present in these reverse micelles does not attain the properties of bulk water even at the highest value of W, which is 9. Another point, which needs to be noted here, is that there is no estimate on the size of the water droplets present in this system.

In view of these structural details, the two time constants (τ_{r1} and τ_{r2}) recovered from the anisotropy decay can be rationalized in the following manner. Since the probes used in the study are of ionic character, they are not soluble in benzene-hexane mixture, which is the bulk phase surrounding the reverse micelles. The short component (τ_{r2}) obtained for both the probes at all values of W is considerably longer compared to the reorientation times of the probes measured in water at 298 K.[20] This rules out the possibility that the probes being solubilized in the water droplet present in these reverse micelles. Thus, it is logical to conclude that the probes can reside at either the micelle-water interface or near the hydrated oxyethylene chains within the core of the reverse micelles and the exact location will be established in due course. It has been well documented that, when the probe molecules are located at or near the interfacial region of the micelles, they cannot experience isotropic rotation as in homogeneous solutions; instead, they undergo somewhat restricted rotation. They endure slow translational diffusion on or inside the curved surface of the micellar aggregates,

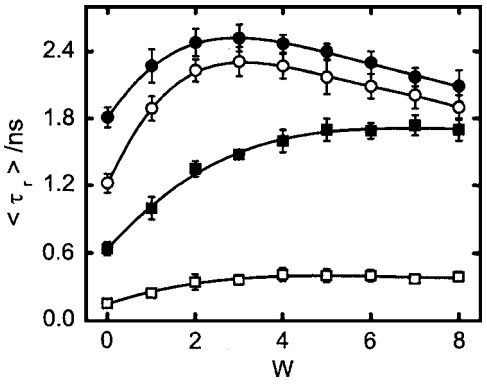

FIG. 5. Variation of average reorientation times of ionic probes rhodamine 110 (○) and fluorescein (●) in TX-100/benzene–hexane reverse micelles with W. For the sake of comparison, $\langle\tau_r\rangle$ values of hydrophobic probes DPP (■) and DMDPP (□), which have been taken from Ref. 9 are also shown in the figure. The lines passing through the data points are drawn as visual aid.

which is also known as lateral diffusion and a fast wobbling motion in an imaginary cone. The lateral diffusion and wobbling motion are coupled to the overall rotation of the micelle and the model that describes these two distinct types of motions of the probe molecule is known as the two-step model.[21–24] This model has extensively been used[8,9,12,20,25–31] to explain the rotational diffusion of organic probe molecules in different kinds of organized assemblies including reverse micelles. According to this model, the experimentally measured reorientation times τ_{r1} and τ_{r2}, and the parameter β are related to the model parameters by the following equations:[25]

$$\tau_{r1} = \left[\frac{1}{\tau_L} + \frac{1}{\tau_M}\right]^{-1}, \tag{3}$$

$$\tau_{r2} = \left[\frac{1}{\tau_W} + \frac{1}{\tau_L} + \frac{1}{\tau_M}\right]^{-1}, \tag{4}$$

$$\beta = S^2. \tag{5}$$

In these expressions, the parameters τ_L, τ_W, and τ_M represent the time constants for lateral diffusion, wobbling motion, and the rotation of the micelle as a whole. The entity S is the order parameter, which follows the inequality $0 \leqslant S^2 \leqslant 1$ and the magnitude of S determines the extent of restriction in the rotation of the probe.[25] Since the hydrodynamic radius of the micelles is known,[3] time constant for the overall rotation of the micelles can be calculated using Stokes–Einstein–Debye (SED) relation with stick boundary condition[32] and subsequently obtain the values of τ_L and τ_W. However, the main focus of the present study is to compare the trends in the microenvironments experienced by the ionic and hydrophobic probes in TX-100/benzene–hexane reverse micelles as a function of the water content and hence elaborate execution of the two-step model is not being undertaken.

Since the probe molecules in TX-100/benzene–hexane reverse micelle system are located at a single site, average reorientation time can be used to quantify the microenvironment experienced by them. Once again turning our attention to Fig. 5, $\langle\tau_r\rangle$ increases with W from 0 to 3 for both the probes, which is due to the flexible oxyethylene chains in the core region being hydrogen bonded by the water molecules. The hydrogen bonding between water and oxyethylene chains makes the core region less fluid. However, from $W=3$ to 8, about 20% decrease has been noticed in $\langle\tau_r\rangle$ for rhodamine 110 as well as fluorescein. This behavior can be rationalized only if the probe molecules are located at the micelle-water interface within the core. Upon the completion of the hydration of oxyethylene chains, a subsequent increase in W results in the formation of droplet inside the core and further addition of water merely contributes to the water pool. Under these circumstances, the interfacial region of the reverse micelle becomes more fluid leading to a decrease in $\langle\tau_r\rangle$.

This result is analogous to the one observed for rhodamine and fluorescein in AOT/isooctane reverse micelles.[20] However, in AOT reverse micelles, the decrease in $\langle\tau_r\rangle$ with water content is significant because W was varied from 1 to 20. Another point, which needs to be mentioned here, is that, for AOT reverse micelles, a direct correlation exists between the water droplet size and W. In case of TX-100/benzene–hexane reverse micelle system, phase separation occurs after W reaches a value of 9.5 and there is no direct relation between W and droplet size.[3] In view of these limitations, one to one comparison of the rotational diffusion of rhodamine 110 and fluorescein in TX-100 and AOT reverse micelles is not possible. Another point that is to be noted here is that the average reorientation times of fluorescein are longer compared to those of rhodamine 110 by 10% except at $W=0$. This is because dianion form of fluorescein interacts more strongly with the hydroxyl groups of the TX-100 surfactant compared to the positively charged rhodamine. At $W=0$, however, the rotation of rhodamine 110 is faster than fluorescein by 20%, which is due to rhodamine 110 being in the neutral form and neutral form of the dyes that contain amino groups are known to rotate marginally faster compared to their protonated counterparts.[33,34]

To find out whether or not the ionic and hydrophobic probes experience similar microenvironments in TX-100/benzene–hexane reverse micelles, which is the main objective of the present study, data from our earlier work has been considered.[9] $\langle\tau_r\rangle$ versus W data for the hydrophobic probes DMDPP and DPP are also plotted in Fig. 5. Inspection of the figure reveals that essentially there is no difference in the microenvironment experienced by the ionic and hydrophobic probes until the hydration of oxyethylene chains is complete. Nonetheless, once the water droplet formation takes place, there is no change in the microenvironment experienced by the hydrophobic probes DMDPP and DPP, which is evident from the saturation of $\langle\tau_r\rangle$ versus W plots after $W=3$. This trend is in contrast to the one observed for the ionic probes rhodamine 110 and fluorescein where a 20% decrease has been noticed in $\langle\tau_r\rangle$. For the microenvironment of the probes to remain invariant with W in this system, they have to be solubilized near the hydrated oxyethylene chains within the core. In this region, once the hydration is complete, there is no change in the microenvironment with W as the added water merely contributes to the water pool. Thus, this study essentially reveals that both ionic and hydrophobic probes get solubilized in the core of the nonionic reverse micelles; the former at the micelle-water interface, whereas the latter within the hydrated oxyethylene chains. It must, however, be noted that the microenvironment experienced by them is not significantly different even after the formation of the water droplet. Based on the insights gained from this work, the respective locations of ionic and hydrophobic probes in TX-100/benzene–hexane reverse micelles are depicted in Fig. 6.

IV. CONCLUSIONS

Compared to ionic reverse micelles, the microenvironment offered by the core region of the nonionic reverse micelles is not straightforward to comprehend because nonionic surfactants possess repetitive units of oxyethylene head groups, which get hydrated upon the addition of water. The number of water molecules that are needed for the complete hydration of a typical nonionic surfactant such as TX-100 depends on the type of oil used and its ability to penetrate the

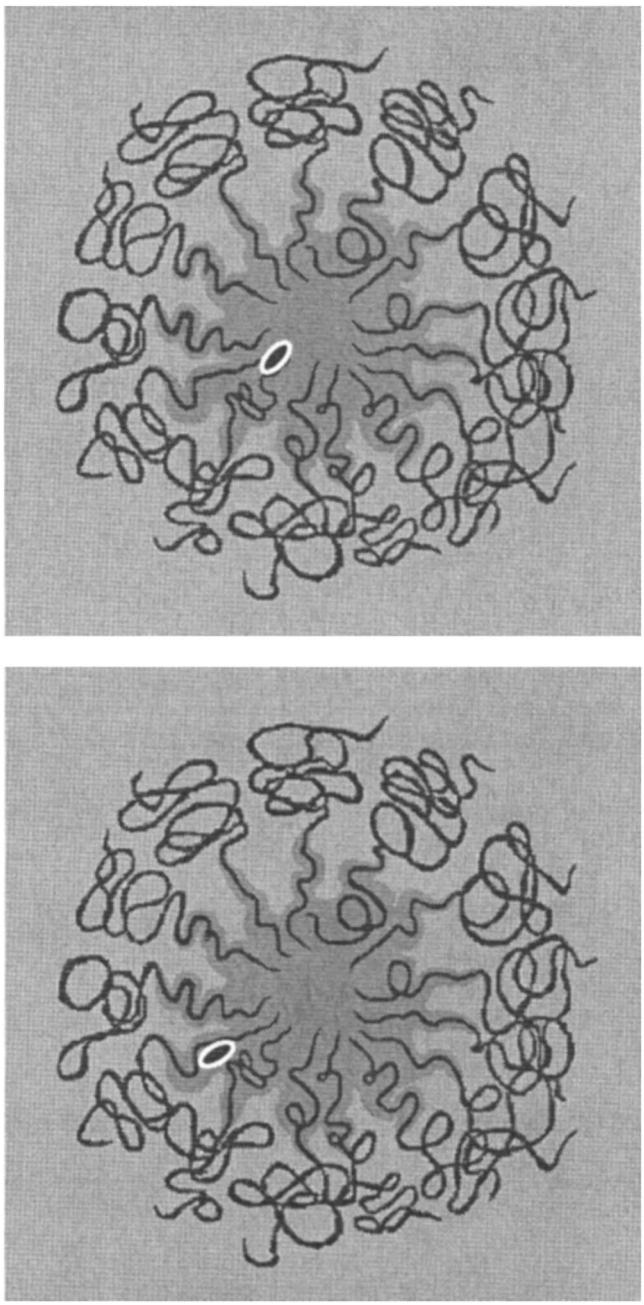

FIG. 6. Pictorial representation of ionic (top) and hydrophobic (bottom) probes in nonionic reverse micellar system of TX-100/benzene–hexane/water. The light gray area in the picture represents the bulk phase (benzene–hexane) whereas the dark gray area represents hydrated oxyethylene chains and the water droplet.

polar core. Thus, in principle, it is possible for the nonionic reverse micelles to offer a variety of microenvironments. This study has been undertaken to compare the microenvironment experienced by ionic and hydrophobic probe molecules in a typical nonionic reverse micellar system. For this purpose rotational diffusion of two structurally similar ionic probes rhodamine 110 and fluorescein has been examined in TX-100/benzene–hexane reverse micellar system as a function of W and compared with that of the hydrophobic probes DMDPP and DPP. The important conclusions of this work have been summarized in this section. The trends observed in the microenvironment experienced by the ionic and hydrophobic probes are similar in reverse micelles at $W=0$ and at low water content, which has been reflected in the variation of average reorientation time with W. However, after the completion of the hydration of oxyethylene chains of the surfactant, there appears to be a difference in the microenvironment sensed by the ionic and hydrophobic probes. These differences, though only marginal, are due to the different locations occupied by the ionic and hydrophobic probes. Thus, in a nutshell, this study reveals that a typical nonionic reverse micellar system such as TX-100/benzene–hexane offers different microenvironments for ionic and hydrophobic probes after the onset of water droplet formation.

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