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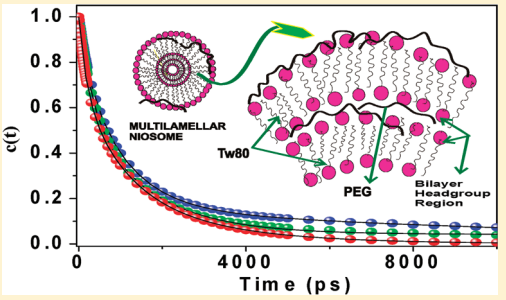
Solvation Dynamics and Rotational Relaxation Study Inside Niosome, A Nonionic Innocuous Poly(ethylene Glycol)-Based Surfactant Assembly: An Excitation Wavelength Dependent Experiment

Chiranjib Ghatak, Vishal Govind Rao, Shirsendu Ghosh, Sarthak Mandal, and Nilmoni Sarkar*

Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, WB, India

Supporting Information

ABSTRACT: Excitation wavelength dependence of solvation and rotational relaxation dynamics has been investigated inside niosome, a biologically stable, nontoxic to our body, multilamellar vesicle system, by using steady state and time-resolved fluorescence spectroscopy to explore the heterogeneity of such a system. Red edge excitation shifts (REES) of 7 nm for Coumarin-153 (C-153) and 11 nm for C-480 were observed with change in λ_{ex}. Average solvation dynamics is composed of two types of slow components and one fast component. There are two distinct restricted regions, one at the bilayer headgroup region and the other on the two extreme surfaces, which are responsible for the slow components. An unaltered fast component is reported for the segmental chain dynamics of poly(ethylene glycol) (PEG) located at the headgroup region of niosome. The trend in λ_{ex} dependence obtained for C-153 is found to be similar to that obtained for C-480. Such hindered solvation is attributed to the presence of a strong H-bonding environment of water molecules in the headgroup region, and movement of these highly bound water molecules along with a hydrated oxyethyelene moiety control the observed slow relaxation.



INTRODUCTION

Dynamics of solvent molecules and their effect on chemical reactions always remain an interesting field of importance in physical chemistry.[1−25] In fact, very often it is the action of the surrounding solvent that determines whether a reaction will occur or not. Nowadays, the dynamical properties of the solvation are easily monitored by ultrafast laser pulses, with pulse durations close to the typical vibrational period of molecular vibration. The first step in studying solvation dynamics involves construction of time-resolved emission spectra (TRES),[1] and it is monitored by the decay of the time correlation function $C(t)$ which is defined in terms of emission energies as

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \quad (1)$$

where $\nu(0)$, $\nu(t)$, and $\nu(\infty)$ are the observed frequencies at time zero, t, and infinity, respectively.

The water molecule plays a crucial role in controlling the structure, dynamics, and reactivity of natural systems.[25−28] In natural systems, water molecules are confined in self-organized molecular assemblies. Since micelles, reverse micelles, the lipid bilayer, etc. can serve as a model for biological systems, solvation dynamics in these self-organized molecular assemblies have been studied both theoretically and experimentally by various research groups.[13,14,16,17,29] Biological functions of many biomacromolecules and macromolecular bioassemblies largely depend on their hydration.[30,31] In our present work, we have studied a nonionic innocuous surfactant and a polymer which can form a bilayer, known as niosome, and undoubtedly the dynamics of water molecules will be different in different regions of such a vesicular system.

To probe different regions of the niosome, we take recourse to study excitation wavelength dependence. Several works have been reported that excitation wavelength variation study selects probes in different regions of a heterogeneous organized assembly.[24,32−52]Excitation at a blue end selects a probe residing in a less polar and hydrophobic ("buried") region, and on excitation at the red end probes located in a polar and exposed region are specifically selected. As a result, with an increase in the excitation wavelength the emission maximum exhibits a gradual red shift which is known as a red edge excitation shift (REES).[53−56] Recently an excitation wavelength dependence study has been applied to get a more clear picture of the heterogeneity of various bioassemblies.[13,22] Solvation dynamics in bulk water is very fast,[3,6,57] but many interfaces and organized assemblies display a slow component of solvation dynamics in the 100−1000 ps time scale.[4−10] Moreover, many simulation studies also predict that the water dynamics may vary markedly from one region to another in the case of various biologically important confined systems.[11,12,58−71] For this work, Tween80 with poly(ethylene glycol)

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[PEG6000] are selected to prepare highly stable niosomes.[72−82] Tween80 is a pharmaceutically acceptable, innocuous, nonionic biological surfactant,[82] and it was observed that PEG-based surfactants show high selectivity in disrupting the vesicular membrane.[83−85]

Niosomes are now widely studied as an alternative to liposomes, which exhibit certain disadvantages such as: they are expensive, their ingredients like phospholipids are chemically unstable because of their predisposition to oxidative degradation, they require special storage and handling, and purity of natural phospholipids is variable.[86,87] Niosomes represent a promising drug delivery module.[78−81,88] It was reported that PEG6000 acts as a stabilizing agent, when adsorbed on the niosome polar headgroup regions in molar ratio (Tween80/PEG6000/H_2O) 92.1:1.00:667.[72,73] In the present case, niosome has multilamellar vesicle structure, and it is expected that a thick oxyethylene−water shell will cover the headgroup as well as the bilayer region. For probing the heterogeneity of niosome, we have used two well-defined fluorescent dyes, Coumarin-153 and Coumarin-480. To the best of our knowledge, no such photophysical work inside niosome has been carried out, and we are very keen to observe the photophysical properties of a dye and to explore the heterogeneity of such a system using solvent relaxation kinetics with variation of excitation wavelength.

2. EXPERIMENTAL SECTION

Coumarin-153 and Coumarin-480 were obtained from Exciton (laser grade) and used as received. PEG6000 and Tween-80 were obtained from Aldrich chemical. The chemical structures of the Coumarin-153, PEG6000, and Tween-80 are shown in Scheme 1 in the Supporting Information. We have prepared niosome as described by a sonication method.[72,73] Briefly, Tween80, PEG6000, and water were vortex mixed at a certain molar fraction to prepare the lamellar liquid crystal, and then niosome was obtained by sonicating the diluted solution (2% PEG + 98% water) with the lamellar liquid crystal for 30−85 min. Size measurement of niosome was performed by dynamic light scattering measurements, and it was used to follow the preparation process of niosome. The concentration of Coumarin dyes in the experiment was kept at 2×10^{-6} (M). The absorption and fluorescence spectra were measured using a Shimadzu (model no: UV-2450) spectrophotometer and a Jobin Yvon Fluoromax-3 spectrofluorimeter. The fluorescence spectra were corrected for the spectral sensitivity of the instrument. For steady state experiments and time-resolved experiments, all samples were excited at three different wavelengths 375, 408, and 440 nm, respectively. The experimental setup for picosecond time-correlated single-photon counting (TCSPC) has been described elsewhere.[89] Briefly, the samples were excited at three different wavelengths using a picosecond laser diode (IBH, Nanoled), and the signals were collected at the magic angle (54.7°) using a Hamamatsu microchannel plate photomultiplier tube (3809U). The instrument response function of our setup is 110 ps. The same setup was used for anisotropy measurements. The analysis of the data was done using IBH DAS, version 6, and decay analysis software. The same software was also used to analyze the anisotropy data.

3. RESULTS AND DISCUSSIONS

3.1. Steady State Studies. Absorption spectra of C-153 inside niosome, tween80, PEG solution, and water were obtained at 423, 421, 427, and 434 nm, respectively. Fluorescence spectra of C-153 in niosome, tween80, PEG solution, and water were obtained at 526, 532, 545, and 547 nm at λ_{ex} = 410 nm, respectively (Figure 1b). C-153 shows 7 nm REES, indicating the heterogeneous nature of the system. C-153 may be residing at many plausible locations such as on the headgroup region near the water pool (outer and inner) or in the hydrocarbon chain of tween80 or in the bulk water pool. Now we are trying to explore the location of the probe by elaborating all our results one by one. First, a negligible shift in absorption spectra of C-153 in between the tween80 micelle and niosome and a 4 nm red shift in PEG solution compared to niosome indicate that the chromophore moiety is transferred into a less polar region inside niosome compared to that in polymer solution. Absorption at 423 nm inside niosome proves that C-153 is located in a region where it is perturbed by the presence of PEG, and the absorption of C-153 in niosome matches with the absorption in methanol (424 nm). It is already known that PEG is adsorbed on the headgroup region. Again, the polarity of the headgroup is less than the bulk water pool but greater than the hydrophobic alkyl chain just like methanol. One inference that can be drawn is that the probe is located in a region of methanol-like polarity, probably around the headgroup region. Second, fluorescence results also indicate that C-153 goes into a region whose polarity is very much less than that of the PEG solution as well as that experienced in the micellar solution. Now emission maxima of C-153 in methanol and in *n*-heptane are 532 and 450 nm, respectively. The matching of absorption and emission maxima of C-153 inside the niosome with the values of that in methanol suggests that C-153 is located in a region that is less polar than water but more polar than *n*-heptane, i.e., the interfacial headgroup region. For further confirmation, we have taken another dye C-480 inside niosome and carried out all the above experiments. It exhibits almost the same trend with change in excitation wavelength which proves the existence of heterogeneity in the present system. Emission maxima of C-480 inside niosome shift from 472 to 483 nm when the λ_{ex} value is changed from 375 to 440 nm (Figure1a). For simple and clear representation regarding the main aspects of this article (excitation wavelength dependence inside niosome and heterogeneity of our system) and also to avoid overcrowding of data in this manuscript, some of the data obtained using C-480 are given in the Supporting Information. Additionally, the full width at half maxima (fwhm) value is also a parameter to measure

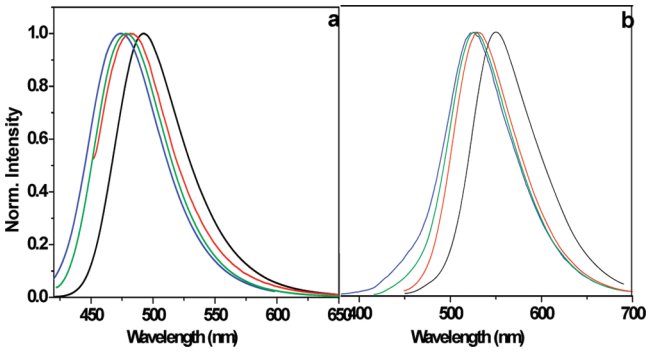


Figure 1. (a) Emission spectra of C-480 inside niosome excited at 375 nm (blue line), 410 nm (green line), and 440 nm (red line) and in pure water (black line). (b) Emission spectra of C-153 inside niosome excited at 375 nm (blue line), 410 nm (green line), and 440 nm (red line) and in pure water (black line).

Table 1. Decay Parameters of Anisotropy of C-153 Inside Niosome at Different λ_{ex}[a]

system	λ_{ex} (nm)	r_0	a_{1r}	a_{2r}	τ_{1r} (ps)	τ_{2r} (ps)	τ_r (ps)
niosome	375	0.36	65%	35%	859	4580	2160
niosome	410	0.35	68%	32%	615	2460	1206
niosome	440	0.32	72%	28%	413	1690	913
water	375−440	0.38	100%	–	100	–	100

[a] Error limit = ±5%.

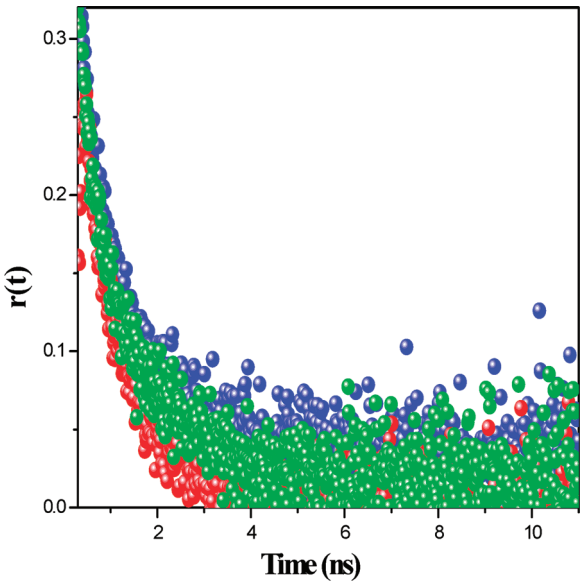


Figure 2. Anisotropy decay plot of C-153 inside niosome excited at at 375 nm (blue), 410 nm (green), and 440 nm (red).

the heterogeneity of any system. The larger the value of fwhm, the greater the heterogeneous character of the system. It is observed that fwhm gradually decreases on increasing the λ_{ex} value to longer side for both the dyes (Tables 1a and 1b in Supporting Information).

3.2. Time-Resolved Studies. *3.2.1. Time-Resolved Anisotropy Results.* To get an intimate idea regarding the location of the probe, i.e., microenvironment around the dyes inside niosome, we have performed a time-resolved fluorescence anisotropy study. The time-resolved fluorescence anisotropy $r(t)$ is obtained by using the following equation

$$r(t) = \frac{I_{\parallel}(t) - GI_{\perp}(t)}{I_{\parallel}(t) + 2GI_{\perp}(t)} \quad (2)$$

where G is the correction factor for detector sensitivity to the polarization direction of the emission. The value of G in our case is 0.6. $I_{||}(t)$ and $I_{\perp}(t)$ are fluorescence decays polarized parallel and perpendicular to the polarization of the excitation light, respectively. All the anisotropy decays are biexponential in nature, and all results are fitted by using the following equation

$$\tau_r = \tau_{1r}a_{1r} + \tau_{2r}a_{2r} \quad (3)$$

where τ_{1r} and τ_{2r} are the first and second components of the decay time of the C-153; a_{1r} and a_{2r} are the corresponding relative magnitude of these components, respectively; and τ_r is the average rotational relaxation time. All the anisotropy decays

Table 2. Decay Parameters of $C(t)$ of C-153 in Niosome at Different Excitation Wavelengths[a]

			$C(t)$						
system	λ_{ex} (nm)	missing component	τ_1	a_1	τ_2	a_2	τ_3	a_3	τ_{av} (ps)
niosome	375	30%	1194	0.68	10680	0.18	195	0.13	2650
niosome	410	38%	1001	0.64	7579	0.13	198	0.23	1672
niosome	440	54%	680	0.56	2770	0.10	196	0.29	750

[a] Error limit = ±5%.

of C-153 inside niosome are found to be biexponential in nature, and anisotropy results are largely dependent on the excitation wavelength. All the anisotropy results are given in Table 1, and fitted decays are shown in Figure 2. For C-480, the anisotropy results show a trend similar to that of C-153 (Table 3 and Figure 1 given in Supporting Information). Our anisotropy data support the wobbling in cone model,[90] and we obtained a biexponential nature of the decay where the slow component arises due to the overall rotational motion of the cone containing the probe and the fast component is due to the wobbling in cone dynamics of the probe itself. Such a type of motion has already been reported in various confined media.[90−97]

3.2.2. Time-Resolved Excitation Wavelength-Dependent Solvation Dynamics Studies. All the time-resolved emission spectra (TRES) (Figures 3a and 3b in Supporting Information) [λ_{ex} = 375 nm] were constructed by following the procedure of Fleming and Maroncelli.[1] The TRES at a given time t, $S(\lambda; t)$, is obtained from the fitted decays, $D(t; \lambda)$, by relative normalization to the steady-state spectrum $S_0(\lambda)$ as follows

$$S(\lambda; t) = D(t; \lambda)\frac{S_0(\lambda)}{\int_0^{\infty} D(t; \lambda)\mathrm{d}t} \quad (4)$$

Each TRES was fitted by log-normal line shape function which is defined as

$$g(\nu) = g_0 \exp\left[-\ln 2\left(\frac{\ln[1 + 2b(\nu - \nu_p)/\Delta]}{b}\right)^2\right] \quad (5)$$

where g_0, b, ν, and Δ are the peak height, asymmetric parameter, peak frequency, and width parameter, respectively. The peak frequency obtained from this log-normal fitting of TRES was then used to construct the decay of solvent correlation function ($C(t)$) as described in eq 1. The solvent correlation function $C(t)$ was fitted to a third exponential decay function

$$C(t) = \sum_{i=1}^{3} a_i e^{-t/\tau_i} \quad (6)$$

where τ_i are the relaxation time constants and a_i are the corresponding relative amplitudes. The solvent relaxation times thus obtained from the solvent correlation function ($C(t)$) are summarized in Table 2. The representative decays of $C(t)$ are shown in Figure 3. From Table 2 we obtained an average solvation time of C-153 consisting of a fast component around 195 ps (13% in amplitude) and two slow components around 1194 ps (68%) and 10 680 ps (18%) when excited at 375 nm. On longer wavelength excitation, the fast component remained almost unaltered, while the slow components markedly

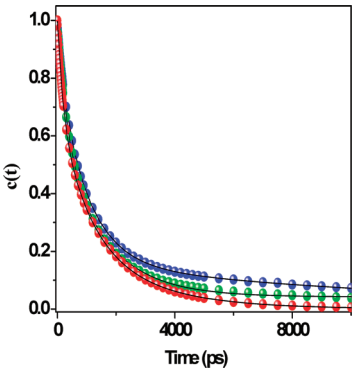
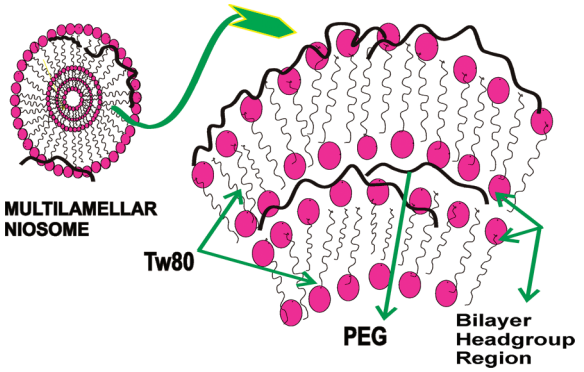


Figure 3. Decay plot of solvent correlation function ($C(t)$) of C-153 inside niosome excited at 375 nm (blue line), 410 nm (green line), and 440 nm (red line).

decreased. Excitation at 410 and 440 nm caused both the slow components to gradually decrease. Similarly, for C-480 we have also obtained an unaltered fast component (~45 ps) and two slow components (Table 2 in Supporting Information) which change with a change in excitation wavelength. We got different solvation times for different dyes C-153 and C-480. This was expected from the standpoint of their structural diversity (Scheme 1). Solute-dependent solvation dynamics was also observed by Maroncelli[98] and proposed that a difference in the nature of their hydrogen-bonding interactions with the solvent is the reason for different time regimes. Unfortunately, we cannot detect the solvation dynamics of C-480 at λ_{ex} = 440 nm. This is due to a very negligible absorbance value of C-480 at this wavelength and low signal-to-noise ratio of our experimental setup which rendered it impossible to detect any rise component of C-480 at λ_{ex} = 440 nm. In spite of this limitation, we have obtained a trend for two excitation wavelengths as obtained for C-153, which helped us to generalize our results. Such unaltered fast solvation has already been reported by several authors.[24,49,99−102] The amount of solvation dynamics missed can be calculated by the Fee−Maroncelli procedure[103] (Table 2) where the emission frequency at time zero $\nu^{p}_{em}(0)$ is determined by using the absorption frequency ν^{p}_{abs} of C-153 in a polar environment (here niosome) as $\nu^{p}_{em}(0) = \nu^{p}_{abs} - (\nu^{np}_{abs} - \nu^{np}_{em})$ and ν^{np}_{abs} and ν^{np}_{em} are the steady state frequencies of absorption and emission of C-153 in nonpolar medium (cyclohexane). Missing components for C-480 inside niosome excited at 375 and 410 nm are given in Table 2 in the Supporting Information which also shows the similar trend as done by C-153.

Prior to discussion about the reason behind such slow dynamics, we have to take a close look at the structural features of our system. Niosome has a multilamellar vesicle structure, and it is composed of nonionic polyoxyethylene surfactant and a long-chain polymer. It is expected that a thick oxyethylene−water shell covers the headgroup as well as the bilayer headgroup region of niosome which was again compacted by the presence of a long oxyethylene chain of the polymer moiety. In many studies it was reported that the poly(oxyethylene) group can show icelike structure which is very constrained and contained a highly dense water network.[104,105] Niosome in the present study is three layered in structure with a thickness of 8−22 nm[72,73] which implies that there is an extended region of interest where the slow water dynamics is possible due to the presence of a highly structured water−oxyethylene network.

Scheme 1. Two-Dimensional Representation of Niosome



These icelike structured water molecules bound to a fairly concentrated polyoxyethylene group in the headgroup region of niosome are responsible for slow dynamics. Solvation time using the present probe in niosome is 1000 times slower than that in pure water, in which solvation is completed within 1 ps.[106] In our present system, we also got two slow components of 10 and ~1 ns along with a fast component using C-153 and C-480 as the solvation probes. There are many reports concerning the ultraslow solvation dynamics inside an organized system.[32,48,107−109] Solvent relaxation in such complex bioassemblies may depend on several factors, namely, strength of the hydrogen bonds, the surfactant or polymer orientational relaxation time, and their dipole moment, etc. In our case, we have two types of slow components which directed our attention again to the structural heterogeneity inside niosome. We have already observed that the probe molecules are preferentially located in the headgroup region inside niosome. The bilayer headgroup part is special because it is enriched with a larger number of headgroups compared to the two extreme surfaces. (Shown in Scheme 1.) Although PEG can be present in all headgroup like regions, the two extreme surfaces have less hardness (rigidity) regarding the change in mobility between bulk water and niosome. The presence of the hydrophilic PEG moiety makes these two extremes a soft boundary which has polarity close to the bulk water molecules compared to that of the bilayer headgroup part. Now it is possible to aver that two types of restricted water dynamics are operating inside niosome. A thick layer of H-bonded water is present around both the headgroups of tween80 and PEG6000. We have noticed that the relative amplitude of the ultraslow component is lowered by almost 50%, while the decrement is 18% for the other slow component with change in λ_{ex}. All the above observations are in accordance with the results obtained for C-480, and they enable us to make some conclusive inference about the nature of the ultraslow component which is showing very sharp dependency on λ_{ex}. Bound water molecules in the vicinity of the region commonly shared by the surfactant headgroup and PEG are undoubtedly responsible for such ultraslow dynamics. Actually, the sandwich-like location of PEG may create a clustering of water molecules which can form multiple H bonds between themselves, giving higher stability due to such close packing. However, at the two extremes, the PEG molecule is more open (rigidity is less); such clustering is absent; and the density of multiple H-bonded water molecules is decreased. So firmness of water layer in the vicinity of PEG at surfaces is low which makes it more labile compared to that in the sandwich-like region. The other slow component is assumed to be raised from the comparatively

less rigid extreme surfaces. Such fast movement of water molecules compared to the sandwich-like part implies that water molecules are freer in this region and that its λ_{ex} dependency is also less.

Slow solvation dynamics having a component near or greater than 10 ns have already been discussed by taking aid of the dynamic exchange model[10] as described by Nandi and Bagchi.[24,42,44] According to this model, the slow component of the solvation dynamics originates from the interconversion of the bound and free water molecules. Our bilayer system which contains a long-chain polymer and highly concentrated oxyethylene chains is too complex to be studied using solvation dynamics by considering such a microscopic scenario. Actually, a more reasonable explanation could be that completely hydrated oxyethylene chains (considerably large amount) are present near the vicinity of the dye buried inside niosome, and collective relaxation of this dye environment is responsible for such ultraslow dynamics.

Such a slow component (~10 ns) inside bilayer assemblies has already been reported by Hof et al. by considering slow movement of geometrically strained and fully hydrated polyoxyethylene chains.[32] Since our system is very large compared to our experimental fluorophore, a broad distribution of them inside the bilayer headgroup region (8−22 nm) cannot be negligible, and these hydrated dyes are more labile compared to the that of long oxyethylene chains. So another plausible reason for such ultraslow components may be the self-diffusion of dyes (long lifetime) along the radial direction of the niosome as described in previous studies.[44,110] Now we can summarize that λ_{ex} variation has proved to be a very useful tool for probing the heterogeneity of a complex organized assembly by tracking the water molecules along with hydrated surfactant or polymer moiety present in all restricted regions and also those located far away from the center of the niosome.

CONCLUSION

To the best of our knowledge this is the first photophysical work inside niosome, and we have demonstrated that such a system is a good candidate for showing appreciable heterogeneity by using steady state and time-resolved excitation wavelength techniques. We have justified our results using two different dyes inside our niosome system. Two types of restricted regions were found in such complex multilamellar assembly. One is at the bilayer headgroup region indicated by the presence of an ultraslow component (~10 ns), and the other is at the two extreme surfaces of the niosome indicated by a slow component (~1 ns) of solvation dynamics. Both the slow components became faster as we increased the excitation wavelength, showing a considerable amount of λ_{ex} dependency. The unaltered fast components responsible for segmental chain motion of PEG6000 are obtained, and it remains unchanged with change in excitation wavelength. Such hindered motion of water molecules was corroborated by restricted rotational relaxation, and it got faster with variation of excitation wavelength.

ASSOCIATED CONTENT

Supporting Information. Tables and figures of C-480 inside niosome and the structures of all the dyes and surfactants. The materials are available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: nilmoni@chem.iitkgp.ernet.in. Fax: 91-3222-255303.

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