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# Solvation dynamics of coumarin 480 in neutral (TX-100), anionic (SDS), and cationic (CTAB) water-in-oil microemulsions

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## Abstract

The steady state spectra and time resolved studies indicate that the Coumarin 480 (C-480) molecules are located at the interfacial region in TritonX-100(TX-100)/cyclohexane/1-hexanol/water, sodium dodecyl sulfate(SDS)/1-hexanol/water, and cetyltrimethylammonium bromide(CTAB)/isooctane/1-hexanol/water microemulsions. The retardation of solvation dynamics of C-480 in these three microemulsions is observed. Moreover, the solvent relaxation times in these three microemulsions are independent of water loading. The close resemblance of solvation dynamics results among TX-100, SDS, and CTAB microemulsions imply that ionic solvation has no role in the slow solvation processes occurring in these microemulsions.

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## 1. Introduction

Recently, there is tremendous interest to study how the confined water molecules control structure, reactivity, molecular recognition, and dynamics in the biological macromolecules (protein surface and DNA) and in other restricted environments (reverse micelle, micelle, vesicle and cyclodextrin, etc.). Several groups have studied dynamics of such water molecules by various techniques, including solvation dynamics [1–7], dielectric relaxation [8], and NMR relaxation dispersion (NMRD) [9]. The advantage of solva-

tion dynamics over many other techniques is that it offers both spatial and temporal resolution. The most interesting feature of solvation dynamics measurement in confined environments [1,4–6] is the observation of an ultraslow component slower by several thousands folds of magnitude compared to bulk water [2,7]. Several theoretical models [10] and computer simulations [11–13] have been applied to explain the slow component of solvation dynamics.

Reverse micelles or water-in-oil (w/o) microemulsions are used as a model biological membrane to aid in understanding membrane chemistry [14]. Among the amphiphilic surfactant capable of forming w/o microemulsion, the anionic surfactant AOT (sodium dioctyl sulfosuccinate) has received

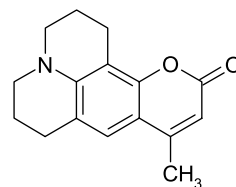
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particular attention because of its ability to solubilize relatively large amounts of water in a variety of hydrophobic organic solvents. The water is accommodated in the polar center of the aggregates in spherical pools, the size of which is controlled by the  $w_0$  ( $w_0 = [\text{water}]/[\text{AOT}]$ ) value. In case of AOT reverse micelle, the size of water pool ( $r_w$ ) is  $\sim 2w_0$ . Jain et al. [15] determined the existence of three types of water molecules in AOT reverse micelle using FT-IR measurement.

Microemulsions containing surfactant, co-surfactant (generally a short chain linear alcohol), oil, and water have important features. The reason for the significance of such quaternary w/o microemulsion is that the introduction of co-surfactant greatly extends the isotropic solution region. Most commonly available anionic surfactant, sodium dodecyl sulphate (SDS), formed w/o microemulsion in the presence of 1-hexanol and water. Rodenas and Pérez-Benito [16] determined the size and aggregation number of SDS microemulsion (w/o) in 1-hexanol by fluorescence quenching method. Among the quaternary w/o microemulsion containing non-ionic surfactants, in particular TritonX-100 (TX-100) has recently attracted considerable attention. Structural feature of the microemulsion (w/o) formed by TX-100, cyclohexane, 1-hexanol, and water has been well studied [17,18]. Cetyltrimethylammonium bromide (CTAB) is also formed by quaternary water-in-oil microemulsion in the presence of isooctane, 1-hexanol, and water [19]. Das et al. [19] first simultaneously estimated the water pool size and the interfacial thickness of CTAB/isooctane/1-hexanol/water microemulsion by combined use of chemical trapping and fluorescence quenching method. Atik and Thomas [20] determined the size of the water pool of structurally and compositionally similar w/o microemulsion (CTAB/dodecane/*n*-hexanol/water) by fluorescence quenching method.

There are numerous studies related to solvation dynamics in AOT reverse micelles [21,22,25,26]. A very slow nanosecond component exists in most of these solvation dynamics measurements [21,22,25,26]. Though there are lots of solvation dynamics studies in AOT reverse micelle [21,22,25,26], but such studies in quaternary microemulsions are lagging behind. Very recently, Corbeil and Levin-



Structure of C-480

Scheme 1. Structure of C-480.

ger [23] have reported slow solvation dynamics in quaternary microemulsions of SDS and CTAB using Coumarin 343 (C-343) as a probe. Curiously, they have ignored the rather dramatic retardation of solvation dynamics in alkane/alkanol mixture itself. In this Letter, we would like to characterize TX-100/cyclohexane/1-hexanol/water, SDS/1-hexanol/water, and CTAB/isooctane/1-hexanol/water w/o microemulsions with the help of steady state and time resolved emission spectroscopy as well as like to measure the solvation dynamics in the above three microemulsions using Coumarin 480 (C-480, Scheme 1) as a probe. Unlike Corbeil and Levinger [23], here we have reported the slow solvation dynamics in alkane/1-hexanol mixture compared to pure 1-hexanol. Moreover, we would also like to verify the role of ionic solvation in the solvation dynamics in these microemulsions.

## 2. Experimental

C-480 (laser grade from Exciton) was used as received. SDS, TX-100, and CTAB were purchased from Aldrich and used without any purification. Cyclohexane and isooctane (spectroscopic grade, Spectrochem, India) were distilled before use. The 1-hexanol of spectroscopic grade (Spectrochem) was used as received. SDS microemulsion at different  $w_0$  was prepared by mixing an appropriate weight percentage of SDS, 1-hexanol, and water as referred by Rodenas and Pérez-Benito [16]. TX-100 microemulsion was prepared by adding 1-hexanol containing C-480 to a 0.2 M solution of TX-100 in cyclohexane in order to obtain a 3:2 (w/v) ratio of TX-100 to 1-hexanol [18]. Water was then added to vary  $w_0$ . The CTAB

microemulsions were prepared using the procedure given by Das et al. [19].

For absorption and fluorescence measurements, we have used Shimadzu absorption spectrophotometer (model no.: UV 1601) and Spex-fluorolog-3 spectrofluorimeter (model no.: FL3-11), respectively. The fluorescence spectra were corrected for wavelength sensitivity of the detection system and were obtained as a photon number intensity spectrum. The experimental setup for picosecond time correlated single photon counting (TCSPC) was described elsewhere [26]. The typical system response of our setup is  $\sim 75$  ps. The temperature was kept at  $298 \pm 1$  K for all measurements.

### 3. Results and discussion

#### 3.1. Steady state spectra

The previous work on SDS, CTAB, and TX-100 microemulsions suggests that like ternary microemulsions these are also spherical in nature and swell with increasing water content of the microemulsions [16–20]. Thus, only difference between these microemulsions and ternary systems is the presence of 1-hexanol at the interface in addition to the presence of headgroup, counterion, and ‘bound water’. In these microheterogeneous solutions, the probe molecule has the possibility to reside in a wide range of location. By comparing the steady state spectra of the probe molecule in various solutions and that of microemulsions, we can predict if it is partitioned to the interior of these microemulsions or not.

The absorption maxima of C-480 in pure solvents, mixture of solvents and microemulsions are listed in Table 1. The data in Table 1 indicate that no remarkable peak shifts are observed in all the three microemulsions compared to their bulk solvents. Representative absorption spectra of C-480 in TX-100 microemulsions are given in Fig. 1a. For all the three w/o microemulsions, a common feature in absorption spectra is that a tail is gradually growing at the red end side of the spectra with the formation of microemulsion. It indicates that probe molecules are approaching to the interior of the microemulsions. Moreover, the

Table 1

Steady state absorption and emission maxima of C-480 in TX-100, SDS and CTAB microemulsions, pure solvents and mixed solvents

Surfactant	$w^a$	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	$\lambda_{\text{em}}^{\text{max}}$ (nm)
(a) <i>Microemulsions</i>			
TX-100	0	380	449
TX-100	4	382	459
TX-100	12	382	465
SDS	9.8	390	466
SDS	37.4	391	469
CTAB	20	380	470
CTAB	40	380	472
(b) <i>Pure solvents and mixed solvents</i>			
Solvent		$\lambda_{\text{abs}}^{\text{max}}$ (nm)	$\lambda_{\text{em}}^{\text{max}}$ (nm)
1-hexanol		390	458
Water		395	490
Cyclohexane/1-hexanol (10:1, v/v)		380	443
Isooctane/1-hexanol (9:1, v/v)		379	447

<sup>a</sup>  $w = [\text{polar solvent}]/[\text{AOT}]$ .

absorption maximum of the C-480 in water is at 395 nm. Thus, it implies that the environment surrounding the probe molecules in these three microemulsions is not like that of bulk water.

Representative emission spectra for TX-100 microemulsions are shown in Fig. 1b. The emission peaks for pure solvents, mixture of solvents and microemulsions are listed in Table 1. The red shifts in emission spectra for all the three microemulsions compared to bulk solvents confirm that C-480 molecules reside inside the microemulsions and it also suggests that the probe molecules experience a different polarity at this position. The emission maxima of C-480 in all the three microemulsions indicate that the probe molecules inside the microemulsions experience a polarity very close to that of ethanol [27]. In this context, it should be mentioned that the emission maximum of the probe in bulk water is 490 nm. Moreover, both the absorption and emission spectra are not very sensitive to water loading. Considering the above discussion, we speculate that the probe molecules must reside at the interface of the microemulsions. For that reason, the probe molecules are experiencing alcohol like polarity in the interior of the microemulsions. In all the three microemulsions (w/o), excitation spectra monitored at two different wavelengths (blue end and red end side of the

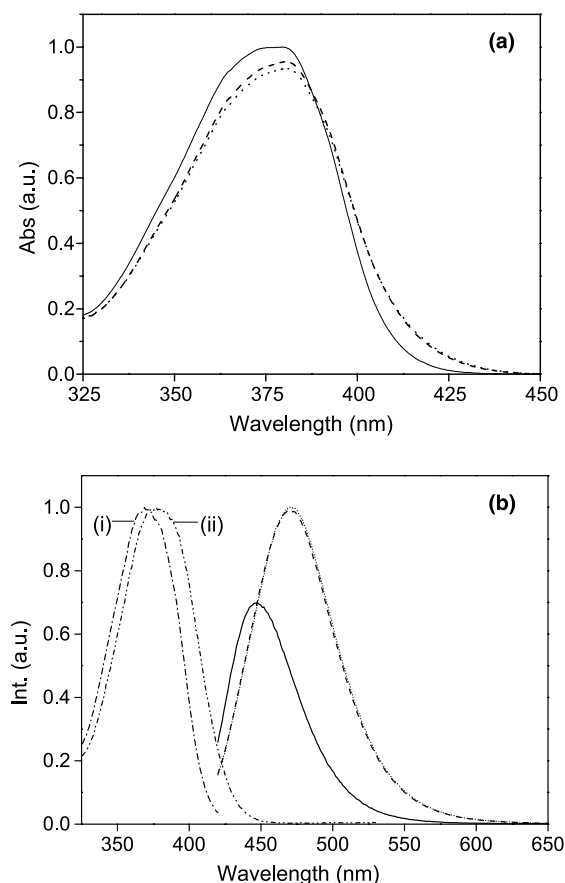


Fig. 1. (a) Absorption spectra of C-480 in CTAB/isooctane/1-hexanol/water microemulsions. Solid lines for isooctane/1-hexanol (9:1, v/v) mixture, dash lines for  $w_0 = 20$ , and dot lines for  $w_0 = 40$ . (b) Emission and excitation spectra of C-480 in CTAB/isooctane/1-hexanol/water microemulsions. Solid lines, dash lines, and dot lines for emission spectra of C-480 in isooctane/1-hexanol (9:1, v/v) mixture,  $w_0 = 20$  and  $w_0 = 40$ , respectively. Dash dot lines for excitation spectra of C-480 in CTAB microemulsion ( $w_0 = 12$ ) monitored at (i) 430 nm and (ii) 540 nm.

emission spectra) are different, indicating that probe molecules are partitioned into two different environments (Fig. 1b).

### 3.2. Time-resolved studies

#### 3.2.1. Time-resolved fluorescence anisotropy

Though absorption, emission, and excitation spectra give a qualitative idea about the location of the probe, it can be determined more accurately by time resolved fluorescence anisotropy. Time

resolved fluorescence anisotropy,  $r(t)$ , was calculated using the following equation:

$$r(t) = \frac{I_{\parallel}(t) - GI_{\perp}(t)}{I_{\parallel}(t) + 2GI_{\perp}(t)}, \quad (1)$$

where  $G$  is the correction factor for detector sensitivity to the polarization direction of the emission,  $I_{\parallel}(t)$  and  $I_{\perp}(t)$  are fluorescence decays polarized parallel and perpendicular to the polarization of the excitation light, respectively. Fig. 2 shows representative anisotropy decay of C-480 in TX-100 microemulsion (w/o). The results are given in Table 2. The very high value of rotational relaxation time (540 ps) of C-480 in 1-hexanol is due to high viscosity of 1-hexanol. C-480 in isooctane exhibits a rotational relaxation time of 100 ps, whereas the same in isooctane/1-hexanol (9:1, v/v) mixture occurs in 150 ps. The increase in rotational relaxation time in isooctane/1-hexanol (9:1, v/v) mixture compared to isooctane may arise due to the slight increase in viscosity upon addition of 1-hexanol or it may arise due to hydrogen bonding of the probe with 1-hexanol in the isooctane/1-hexanol (9:1, v/v) mixture. The similar explanation is also applicable to cyclohexane/1-hexanol (10:1, v/v) mixture for the increase in rotational relaxation time compared to cyclohexane. The results in Table 2 indicate that the rotational motion of the probe in all these three different microemulsions (w/o) occurs at much slower rate

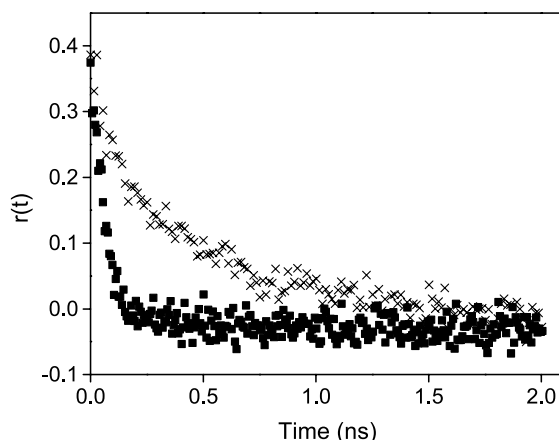


Fig. 2. Decays of fluorescence anisotropy ( $r(t)$ ) of C-480 in pure cyclohexane (■) and TX-100/cyclohexane/1-hexanol/water microemulsion at  $w = 4$  (×).

Table 2

Rotational relaxation time of C-480 in TX-100, SDS and CTAB microemulsions, pure solvents and mixed solvents

Surfactant	$w_0$	$r_0$	$a_{1r}$	$\tau_{1r}$ (ps)	$a_{2r}$	$\tau_{2r}$ (ps)
(a) <i>Microemulsions</i>						
TX-100	4	0.38	0.16	120	0.22	700
TX-100	12	0.38	0.15	70	0.23	730
SDS	9.8	0.40	0.15	70	0.25	720
SDS	37.4	0.38	0.16	120	0.22	680
CTAB	20	0.39	0.31	140	0.08	660
CTAB	40	0.39	0.31	170	0.08	650
(b) <i>Pure solvents and mixed solvents</i>						
Solvent		$r_0$	$a_r$	$\tau_r$ (ps)		
Cyclohexane		0.40	0.40	70		
Isooctane		0.40	0.40	100		
1-hexanol		0.37	0.37	540		
Cyclohexane/1-hexanol (10:1, v/v)		0.40	0.40	210		
Isooctane/1-hexanol (9:1, v/v)		0.39	0.39	150		
Water		0.40	0.40	125		

compared to their bulk solvents, inferring that the probe molecules are associated with the interior of the microemulsions. Moreover, the fluorescence depolarization in a particular microemulsion is not affected by the addition of water, confirming that the probe molecule resides at the interface of the microemulsion. We cannot also rule out the possibility of residing some probe molecules in the bulk solvent, as C-480 is a neutral probe. The excitation spectra also support this conjecture. The bimodal decay in these microemulsions can be explained with the help of two-step model and wobbling-in-a cone model [24]. Heitz and Bright [28] also applied this model to describe the biexponential decay in AOT reverse micelle. The two-step model describes that observed longer rotational relaxation time ( $\tau_{2r}$ ) is a convolution of the relaxation time corresponding to the overall rotational motion of the micelle ( $\tau_m$ ) and lateral

diffusion of the fluorophore ( $\tau_D$ ) along the micellar headgroup region [24]. The wobbling-in-a cone model serves to quantify the restricted internal motion of the probe ( $\tau_c$ ) in terms of a cone angle ( $\theta_0$ ) and wobbling diffusion coefficient ( $D_w$ ) [24]. The  $\tau_m$ ,  $\tau_D$ ,  $\tau_c$ ,  $\theta_0$ , and  $D_w$  are calculated from the relevant equations defined by Quitevis et al. [24] and tabulated in Table 3.

### 3.2.2. Solvation dynamics

The time resolved emission spectra (TRES) have been constructed following the procedure given by Fleming and Maroncelli [29]. In all the three w/o microemulsions and in above mentioned bulk solvents, we have observed a shift in the TRES. The relative shifts ( $\Delta\nu$ ) in the TRES for different w/o microemulsions and in bulk solvents are shown in Table 4. Representative TRES at  $w_0 = 20$  of CTAB microemulsion is shown in

Table 3

Analytical reorientation parameters of C-480 in TX-100, SDS and CTAB microemulsions

Surfactant	$w_0$	$\tau_c$ (ps)	$\tau_m$ (ns)	$\tau_D$ (ns)	$D_w \times 10^8$ (S <sup>-1</sup> )	$\theta_0$
TX-100	4	145	1.43	1.372	6.98	33.78°
TX-100	12	77	7.03	0.815	12.13	32.45°
SDS	9.8	77	13.10	0.761	11.41	31.48°
SDS	37.4	146	34.58	0.694	6.93	33.78°
CTAB	20	178	12.66	0.696	14.81	54.50°
CTAB	40	230	81.70	0.655	11.46	54.50°

Table 4

Decay characteristics of  $C(t)$  of C-480 in TX-100, SDS and CTAB microemulsions, pure solvent and mixed solvents

Surfactant	$\Delta\nu^a$ (cm <sup>-1</sup> )	$w_0$	$a_1$	$\tau_1$ (ns)	$a_2$	$\tau_2$ (ns)	$\langle\tau_s\rangle^b$ (ns)
(a) <i>Microemulsions</i>							
TX-100	1220	4	0.61	0.570	0.39	18.20	7.44
TX-100	1144	12	0.61	0.600	0.39	16.00	6.60
SDS	1073	9.8	0.70	0.297	0.30	18.50	5.75
SDS	972	37.4	0.70	0.326	0.30	16.50	5.17
CTAB	1410	20	0.56	0.360	0.44	15.60	7.06
CTAB	1330	40	0.56	0.350	0.44	14.20	6.44
(b) <i>Pure solvent and mixed solvents</i>							
Solvent	$\Delta\nu^a$ (cm <sup>-1</sup> )		$a_1$	$\tau_1$ (ns)	$a_2$	$\tau_2$ (ns)	$\langle\tau_s\rangle^b$ (ns)
1-hexanol	970		1.00	0.184	0	0	0.184
Cyclohexane/ 1-hexanol (10:1,v/v)	930		0.65	0.790	0.35	9.58	3.86
Isooctane/ 1-hexanol (9:1,v/v)	910		0.81	0.625	0.19	11.14	2.62

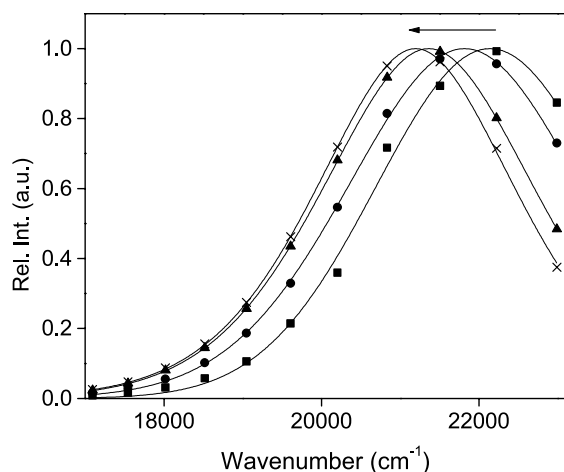
<sup>a</sup>  $\Delta\nu = \nu_0 - \nu_\infty$ .<sup>b</sup>  $\langle\tau_s\rangle = a_1\tau_1 + a_2\tau_2$ .

Fig. 3. Time-resolved emission spectra of C-480 in CTAB/isooctane/1-hexanol/water microemulsion for  $w_0 = 20$  at (i) 0 (■), (ii) 200 (●), (iii) 1000 (▲), and (iv) 5000 (×) ps.

Fig. 3. The solvation dynamics is quantitatively calculated from the decay of the solvent correlation function,  $C(t)$  as

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)}, \quad (2)$$

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

properties of the solvent correlation function ( $C(t)$ ) are listed in Table 4 and shown in Fig. 4.

In order to get a clear idea of solvation of C-480 in these three microemulsions, it is necessary to measure solvation dynamics in their corresponding bulk solvents. The measured solvation time of C-480 in 1-hexanol is 184 ps with a single-exponential in nature. The measured solvation time isooctane/1-hexanol (9:1, v/v) mixture is 2.62 ns with a time constant of 625 ps (81%) and 11.14 ns (19%). In cyclohexane/1-hexanol mixture (10:1, v/v), the average solvation time is 3.86 ns with a time constant of 790 ps (65%) and 9.58 ns (35%). In a mixture of solvents of different polarity, a process of preferential solvation described as dielectric enrichment occurs in the solvation shell of dipolar solute molecules [30]. This may be a possible cause for such a slow dynamics of C-480 in isooctane/1-hexanol (9:1, v/v) and cyclohexane/1-hexanol (10:1, v/v) systems compared to pure 1-hexanol.

In SDS microemulsion, the average solvation time varies from 5.75 to 5.17 ns as  $w_0$  is going from 9.8 to 37.4. Thus, the observed slow dynamics is not due to the bulk 1-hexanol, rather it reflects the dynamics of the interior of microemulsion. Rodeñas and Pérez-Benito [16] determined the size of the water pools of SDS microemulsions by fluo-

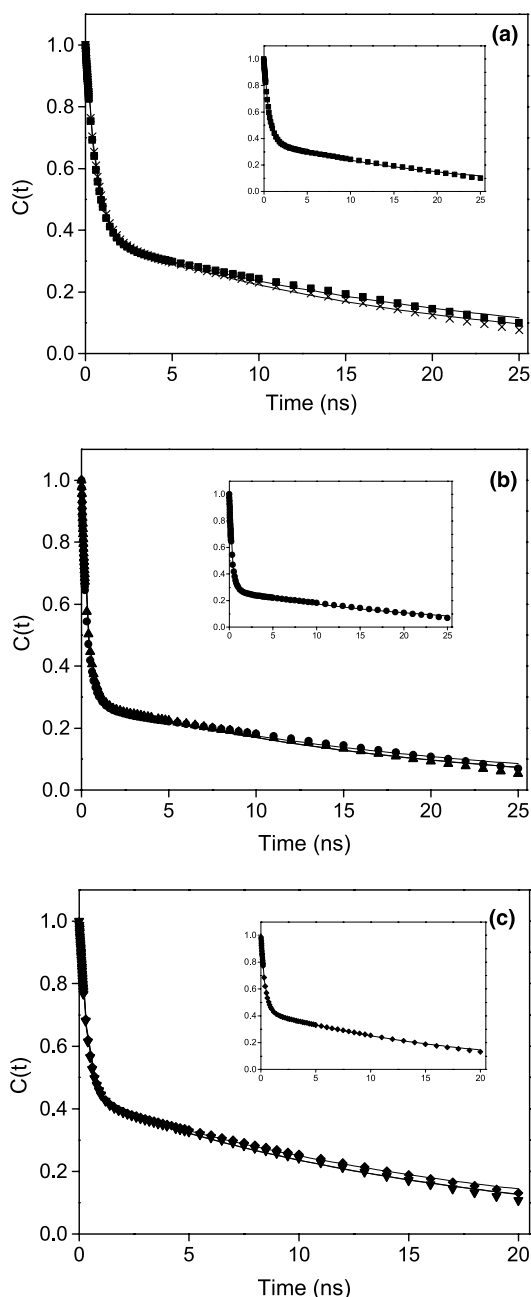


Fig. 4. Decay of the solvent correlation function ( $C(t)$ ) of C-480 (a): (i) at  $w_0 = 4$  (■), (ii) at  $w_0 = 12$  (×) of TX-100/cyclohexane/1-hexanol/water microemulsions, (b): (i) at  $w_0 = 9.8$  (●), (ii) at  $w_0 = 37.4$  (▲) of SDS/1-hexanol/water microemulsions, and (c): (i) at  $w_0 = 20$  (◆), (ii) at  $w_0 = 40$  (▼) of CTAB/isooctane/1-hexanol/water microemulsions. Insets are given for better clarification.

rescence quenching method and reported that the size of the water pools ( $r_w$ ) at  $w_0 = 9.8$  and  $37.4$  are  $14.1 \text{ \AA}$  and  $19 \text{ \AA}$ , respectively. So, the solvent relaxation time in SDS microemulsion is practically unaffected with increase in water content or size of the microemulsion. At low water content ( $w_0 = 20$ ) of CTAB microemulsion, the average solvation time is  $7.06 \text{ ns}$  with a time constant of  $360 \text{ ps}$  (56%) and  $15.60 \text{ ns}$  (44%). At  $w_0 = 40$ , the time constants of fast and slow components are  $350 \text{ ps}$  (56%) and  $14.20 \text{ ns}$  (44%) leading to average solvation time of  $6.44 \text{ ns}$ . Hence, the observed dynamics is not the dynamics of 1-hexanol in isooctane/1-hexanol (9:1, v/v) mixture; rather it implies the dynamics inside the microemulsion. The size of the water pool ( $r_w$ ) of the isooctane/CTAB/1-hexanol/water at  $w_0 = 22.8$  is  $29.1 \text{ \AA}$  as reported by Das et al. [19]. Whereas at  $w_0 = 40.6$ , the size of the water pool ( $r_w$ ) of a structurally and compositionally similar reverse micelle (dodecane/CTAB/1-hexanol/water) is  $54 \text{ \AA}$  [20]. The slight decrease of solvation time with the increase in  $w_0$  is due to the increase in size of the water pool of the microemulsion. Though the effect of size and water loading to the solvation dynamics is not so severe in this case also. Thus, for both SDS and CTAB microemulsions solvent relaxation is practically insensitive to water loading, inferring that the probe molecules are located at the micellar interface regardless of surfactant. Consequently, the observed slow dynamics in these two microemulsions reflect the collective motion at the interface, which includes constrained motion of 1-hexanol, water bound to the surfactant or to the interface, the ionic headgroup of SDS or CTAB. The  $\text{Na}^+$  ion of SDS and  $\text{Br}^-$  ion of CTAB may be responsible for such slow dynamics in these two microemulsions, because ionic solvation is very slow [23,31]. Later we will discuss this point. Moreover, rotational motion of the probe may contribute to solvation process.

In order to avoid any ambiguity, we have measured solvation of C-480 in cyclohexane/1-hexanol mixture (10:1, v/v) and the average solvation time is  $3.86 \text{ ns}$  with a time constant of  $790 \text{ ps}$  (65%) and  $9.58 \text{ ns}$  (35%). The measured dynamics in TX-100 microemulsion at  $w_0 = 4$  and  $w_0 = 12$  are  $7.44$  and  $6.60 \text{ ns}$ , respectively, with biexponential in nature. So, the observed dynamics



is not due to the 1-hexanol in cyclohexane/1-hexanol mixture (10:1, v/v), but it reflects the dynamics inside the microemulsion. Structural feature of the TX-100 microemulsion indicates that a hydrodynamic radius increases with the increase in  $w_0$  of the microemulsion [18]. Thus, here also solvation dynamics is practically  $w_0$  independent. The slow solvation dynamics may be ascribed to the motion of the water molecules ('bound' water) attached to the polyoxyethylene group of TX-100 at the interface. The constrained dynamics of 1-hexanol at the interface may also contribute to the slow dynamics. However, in the present case we cannot rule out totally the effect of polyoxyethylene chain of TX-100, because the chain dynamics of polymers occurs in the time scale of 100 ns [32]. If, we assume a dielectric relaxation time ( $\tau_D$ ) of 100 ns for the polyoxyethylene chain of TX-100 and  $\epsilon_0/\epsilon_\infty \sim 6-8$  ( $\epsilon_0$  is assumed to be in between 30 and 40 and  $\epsilon_\infty$  assumed to be that of ordinary bulk water, i.e., 5), then according to continuum theory, the  $\tau_L$  is  $\sim 16$  ns. Moreover, rotational motion of the probe may also contribute to solvation process.

The solvation dynamics of C-480 at the interface of all the three microemulsions retarded drastically compared to the same in bulk water because the relaxation time of ordinary water is 310 fs using C-480 [33]. The bimodal nature of solvation dynamics in these three microemulsions may be explained with the help of Bagchi's dynamic exchange model [10], which was already applied to proteins and other microemulsions [4,5]. According to this model a dynamic exchange between 'bound' and 'free' water molecule is responsible for bimodal decay of solvation dynamics in these microemulsions. The most interesting feature in these three microemulsions is that the solvent reorganization is not very sensitive to water loading or size of the water pool. This observation is different from what we have seen in AOT microemulsions [21,22,25,26]. In previous solvation dynamics studies on AOT microemulsions, the dye molecules migrated to the water pool of the microemulsions as the hydrodynamics radii or water content of the microemulsions increased [21,22,25,26]. As a result of this, solvation dynamics gradually becomes faster with the increase

in water content of AOT microemulsions. But we do not observe a trend like AOT microemulsions in the solvation response as the water content and size of the water pool of these three microemulsions are increased. It supports the interpretation that the probe molecule resides at the interfacial region of the microemulsions. Very recently, Corbeil and Levinger [23] have also indicated that the probe molecule (C-343) is located at the micellar interface of SDS and CTAB quaternary microemulsions. They have also observed that the solvation dynamics in these microemulsions is insensitive to water loading [23]. Thus, our solvation dynamics results in these three microemulsions are in very close resemblance to that of Corbeil and Levinger [23]. Though we have observed a slow dynamics in these microemulsions, but a major portion of solvation dynamics which occur below  $\sim 75$  ps is not detected by us due to limited time resolution of our setup. The solvation dynamics of C-480 in all three microemulsions are very similar, though we have used three different types of surfactants, namely, cationic (CTAB), anionic (SDS), and neutral (TX-100). This may arise due to the use of neutral probe (C-480) for solvation dynamics measurements. The nature of these three microemulsions differs from that of AOT microemulsion with respect to the headgroup as well as the presence of 1-hexanol at the interface. Thus, it is conceivable that the presence of 1-hexanol at the interface of these microemulsions leads to significantly different behavior from that of AOT microemulsions. We have assumed that ionic solvation may take part for slow solvation dynamics in SDS and CTAB microemulsions. Since the observed dynamics of C-480 in SDS and CTAB microemulsions is very similar to that in TX-100 microemulsion containing neutral surfactant; it appears that the role of ionic solvation in the measured solvation dynamics in the interior of the microemulsions is negligible. Mandal et al. [34] also concluded that ionic solvation has no role in the solvation dynamics observed in the water pool of the TX-100 microemulsion in mixed solvents. The average solvation time of water in TX-100, CTAB, and SDS micelles using the same probe are 1.45, 0.474, and 0.689 ns, respectively [35]. It confirms that the dynamics inside these

microemulsions are more restricted than the same in micelles.

#### 4. Conclusion

The steady state spectra of C-480 in SDS, CTAB, and TX-100 microemulsions suggest that the probe molecules reside at the interface of these microemulsions. The rotational motion of the probe implies that the probe molecule experiences a restricted environment in the interior of the microemulsions. Moreover, the fluorescence depolarization in a particular microemulsion is not affected by the addition of water, confirming that the probe molecule resides at the interface of the microemulsion. The solvation dynamics of C-480 at the interface of all the three microemulsions retarded drastically compared to the same in bulk water or in bulk solvent. Unlike AOT microemulsions, the solvation dynamics of C-480 in three microemulsions is not very sensitive to water loading or size of the water pool. This different behavior of solvation dynamics between AOT microemulsions and these three microemulsions can be explained with the help of the different location of the probe in the microemulsions. The very similar results of solvation dynamics in SDS, CTAB, and TX-100 confirms that ionic solvation has no role in the solvation processes in these microemulsions.

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