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High-pressure studies on AOT reverse micellar aggregate by fluorescence probe method

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Abstract

The effect of pressure on the aqueous core of a reverse micellar aggregate was investigated by using fluorescence probe method. Steady-state and time-dependent fluorescence spectra of a water-soluble probe molecule, coumarin 343 (C343), which was dissolved in the water-pool of AOT/*n*-heptane reverse micelle, were measured at high pressures. On addition of water, the size of the water-pool was systematically changed. In the case of smaller water-pool ($w_0 < 5$), the fluorescence spectrum of C343 shows a marked red-shift with increasing pressure, while in the case of larger water-pool ($10 < w_0$), it is almost invariant. The pressure effect on the solvation dynamics is also highly dependent on the size of the water-pool.

Keywords: Pressure effect; Reverse micelle; AOT; Microemulsion; Fluorescence probe method; Time-dependent fluorescence Stokes shift; Solvation time

1. Introduction

Reverse micelles have attracted much interest not only due to models of biological membranes, but also enzyme-containing reverse micelles offering novel tools of biotechnology and drug delivery through solubilization of lipophilic drugs [1,2]. Moreover, they may provide a "microenvironment" in which a reaction may occur that does not occur in bulk water.

On addition of water, they form water droplets or microemulsions with the size of a nanometer, so-called "water-pool", which is surrounded by a layer of surfactant molecules dispersed in a non-polar or weakly polar organic solvent. In these self-associated molecular aggregates, the polar head-group of the amphiphilic surfactant molecule is directed toward the water-pool, while the non-polar hydrocarbon chain is directed toward bulk non-polar solvent. Of the many reverse micellar systems, AOT (aerosol-OT; sodium bis(2-ethylhexyl)sulfosuccinate) is the most well studied and well defined [1–5]. The size of the water-pool is characterized by the molar ratio of water to AOT, i.e. $w_0 = [H_2O]/[AOT]$. The radius of the water-pool (r_w) is a function of w_0, i.e. $r_w \approx 0.2w_0$ in nm [5]. Therefore, the size or radius of the water-pool can be systematically varied on addition of water.

The water molecules confined in nano-dimensional environment like the water-pool of reverse micelles may play an important and fundamental role in various natural and biological processes. The solvation dynamics of water molecules in self-associated molecular systems such as in the water-pool of reverse micelles [6–10], in the Stern layer of normal micelles [11–13], and in the cavity of cyclodextrins [14] have been studied by using the time-dependent fluorescence Stokes shift (TDFSS) for suitable fluorescent probe molecules. And it has been determined that the solvation dynamics of water molecules occurs in a time scale several orders of magnitude slower than that of bulk water molecules. Bulk water molecules exhibit the solvation dynamics in subpicosecond time scale [14,15]. Furthermore, in every such system, the solvation dynamics exhibits bimodal behavior, which has often been explained by dynamic exchange between bound and free water molecules [16,17]. These absolute time values, however, are too dispersive to deduce any systematic conclusion. Recent experimental and theoretical results have been reviewed by Nandi et al. [18] and Bhattacharyya and Bagchi [19].

Pressure effect on physico-chemical properties of normal micellar systems has long been investigated [20,21], and revealed various novel phenomena including the turn-over behavior of critical micelle concentration (CMC) [20–23]

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as well as the aggregation number against pressure [24,25]. For the purpose of understanding the stability and solvation behavior of micelles, the application of high pressure has been utilized as a useful approach, where the pressure effect on solvation structure is preferably small, yet the dynamical properties are markedly changed with a single probe molecule [26–28]. Pressure causes the time scale of diffusive dynamics to be slower, so that the fast dynamics at atmospheric pressure may be shifted to slower time scale and enable us to observe it at high pressures with a longer well-detectable time scale. Therefore, the high-pressure study may be useful for discriminating the diffusive process from non-diffusive (or inertial) relaxation process. Previously, we had investigated the pressure effect on the TDFSS of coumarin 153 probe in Triton X-100 normal micellar system and found that the solvation time of the water molecules confined in the Stern layer of micelles substantially increases with pressure [29]. To the authors' knowledge, there is no such investigation for reverse micelles.

In the present paper, we report the results of high-pressure studies of the aqueous core of the AOT reverse micelle in *n*-heptane solution. The fluorescence probe method is used to solve the question of how the pressure affects the solvation dynamics of water confined in the water-pool of AOT reverse micelles with different w_0 values. Here we adopted a water-soluble laser dye, coumarin 343 (C343), as a useful fluorescent probe.

2. Experimental

Coumarin 343 (C343) (laser dye, Exciton C519), *n*-heptane (spectroscopic grade, Nacalai tesque), and distilled water (Nacalai tesque) were used as received. AOT (Aldrich) was purified according to the literature procedure [30]. The purified AOT was dried and kept in vacuo for 24 h before use. The concentration of AOT is 0.1 M. The typical concentration of probe C343 is 5×10^{-5} M, which is much lower than the micelle concentration. Size of the water-pool was changed from $w_0 = 5$ to 70 on the addition of water.

Steady-state and time-resolved emission spectra were measured at high pressures of up to 500 MPa. The high-pressure cell equipped with four sapphire windows and the pressure generating system used for the present measurements have been described previously [31]. Sample solution was provided in a quartz inner cell. All the steady-state and time-resolved fluorescence measurements at high pressures were performed at room temperature (293 K). The excitation wavelengths for steady-state and time-resolved measurements are 425 and 405 nm, respectively, where there is no absorption in Triton X-100. The steady-state fluorescence spectra at atmospheric pressure were measured using a Shimadzu (model RF-5300PC) spectrofluorophotometer.

High-pressure steady-state spectra were recorded on a spectrometer which was originally constructed for high-pressure measurements [32]. Time-resolved emission data at high pressures were collected on a laser system by using time-correlated single photon counting (TCSPC) technique. The TCSPC laser system and the method of data analysis have been described elsewhere [33]. Second harmonic radiation of a mode-locked Ti:sapphire laser (Spectra-Physics, Tsunami Model 3950) was used as the excitation light source. It is pumped by a continuous wave argon ion laser and has a repetition rate of 82 MHz. The pulse repetition rate is decreased to 26.8 MHz by using an electro-optic light modulator (Con Optic, Model 1305). The instrument response function (IRF), which was determined by using the scattering of the solution at the excitation wavelength in the high-pressure cell, had a full width half maximum (FWHM) of ∼50 ps, giving a time-resolution better than 30 ps after signal deconvolution.

3. Results and discussion

3.1. Steady-state fluorescence spectra at high pressures

In Fig. 1(a) are shown the fluorescence spectra of C343 in various organic solvents without AOT at atmospheric pressure (0.1 MPa). A gradual red-shift is observed with increasing solvent polarity. In Fig. 1(b) are shown the fluorescence spectra of C343 in the AOT reverse micelle dissolved in *n*-heptane. On addition of water, the w_0 value can be changed from 0 to 70. The fluorescence peak maxima (λ_{max}) of C343 in the AOT reverse micelle in *n*-heptane solution were plotted as a function of w_0, which is shown in Fig. 2. With increasing w_0, λ_{max} shifts toward red. An especially large red-shift is observed up to ca. $w_0 = 10$. While at the w_0 value greater than approximately 20, the change rate becomes smaller. The red-shift implies that the environment around the probe becomes more polar. Comparing with Fig. 1(a), we find that for the dry micelle ($w_0 = 0$), the peak location is identical to the location of methanol, i.e. $\lambda_{max} =$ 456 nm. And then it increases up to 488–490 nm at $w_0 =$ 15–20, which is almost equal to the location of bulk water. This may considered as indicating the fact that by increasing the size of water-pool, the amount of non-bounded water increases and the probe gradually shifts toward the more water-containing position. Furthermore, the present result about the peak shift with w_0 may also demonstrate the previous finding that the state of the water-pool less than $w_0 = 10$ can be discriminated from that of the larger one [4]. Stable microemulsions are formed not until $w_0 >$ 10–20 [34].

Fig. 3 shows the fluorescence spectra of C343 in AOT reverse micelles at different pressures for $w_0 = 5$, and the pressure dependence on λ_{max} for $w_0 = 5$, 20 and 50 was plotted in Fig. 4. In the case of $w_0 = 5$, it shows a blue-shift with increasing pressure, while in the case of $w_0 = 20$ and 50, it is almost invariant. The blue-shift for $w_0 = 5$ indicates that the environment of C343 transfers to a less polar environment as the pressure increases. This may be caused by

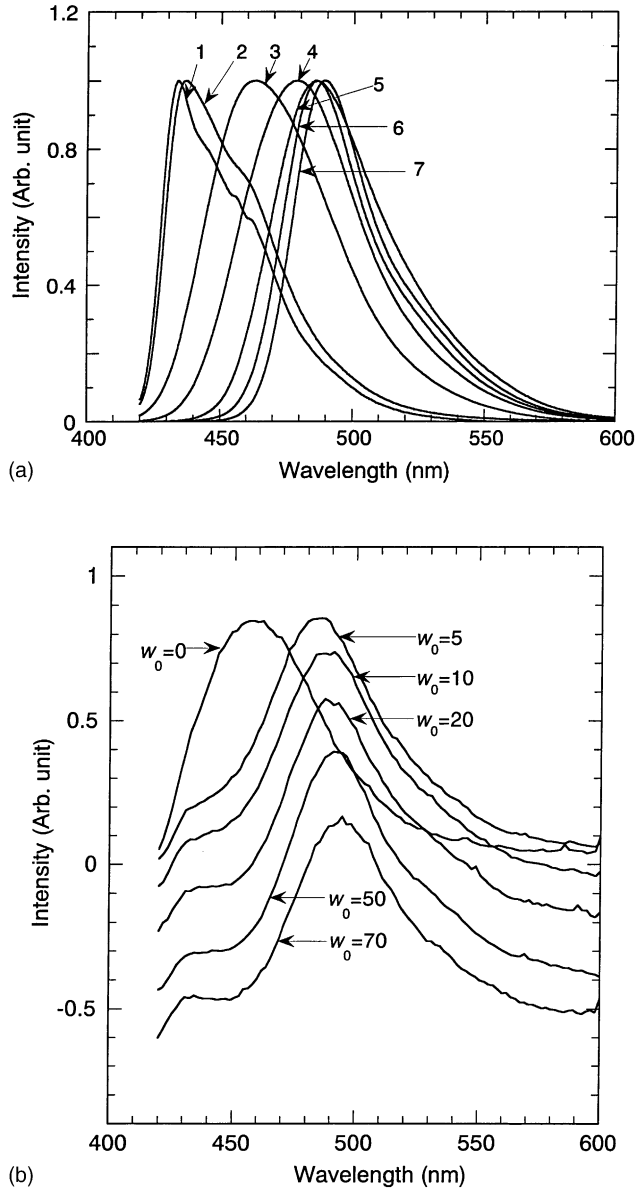

Fig. 1. (a) Fluorescence spectra of C343 in (1) *n*-hexane, (2) *n*-heptane, (3) ethanol, (4) methanol, (5) water, (6) acetone, and (7) acetonitrile at 0.1 MPa. Intensity was normalized at each maximum wavelength; (b) fluorescence spectra of C343 in AOT/*n*-heptane for $w_0 = 0$, 5, 10, 20, 50, and 70 at 0.1 MPa. Intensity was normalized and shifted downward in the increasing order of w_0.

either squeezing of water molecules out of the water-pool or moving of the probe molecule toward the non-polar hydrocarbon core of the surfactant. While in the case of more water molecules in a larger water-pool, as for the case of $w_0 = 20$ and 50, the spectrum is less sensitive to the compression. Namely, pressure has almost no effect on the central part of the large microemulsion.

Here the sizes of the probe molecule and the water-pool are worth noting. The long axis of coumarin molecule is approximately 1 nm [35], while r_w values of the AOT water-pool are estimated to be 1, 4, and 10 nm for $w_0 = 5$,

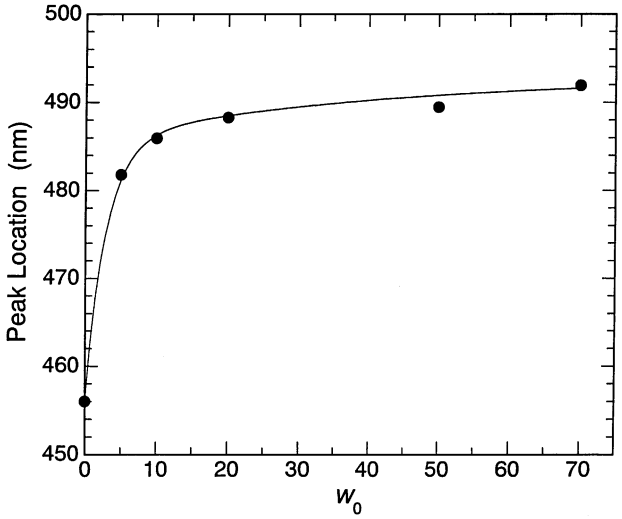

Fig. 2. Fluorescence peak location of C343 in AOT/*n*-heptane reverse micelle at 0.1 MPa as a function of w_0.

20, and 50, respectively [5]. We find that in the case of $w_0 = 5$, the radius of the water-pool is approximately equal to the long axis of the probe. Therefore, the information obtained by the coumarin probe for the smaller AOT water-pool may reflect the property of micellar interface.

3.2. Time-resolved fluorescence spectra at high pressures

In the absence of water (i.e. $w_0 = 0$) (or dry micelle), fluorescence decays of C343 in 0.1 M AOT in *n*-heptane

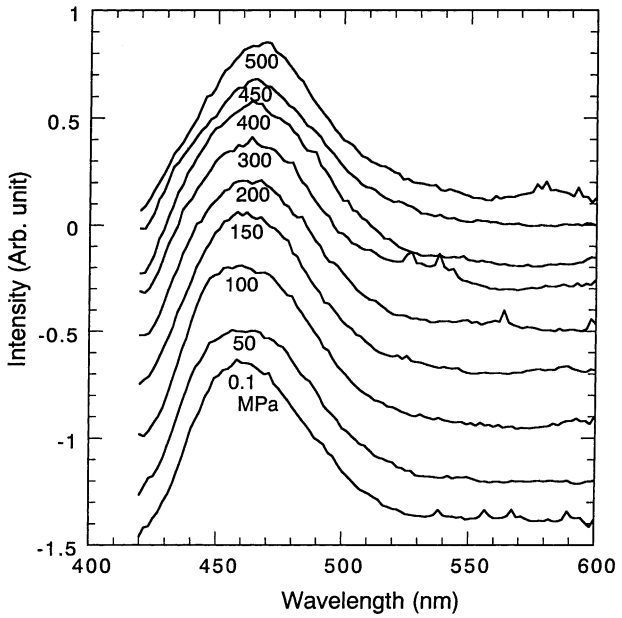

Fig. 3. Fluorescence spectra of C343 in AOT/*n*-heptane reverse micelle system with $w_0 = 5$ at the pressures of 0.1, 50, 100, 150, 200, 300, 400, 450, and 500 MPa from the bottom. Intensity was normalized and shifted upward with the increasing order of pressure.

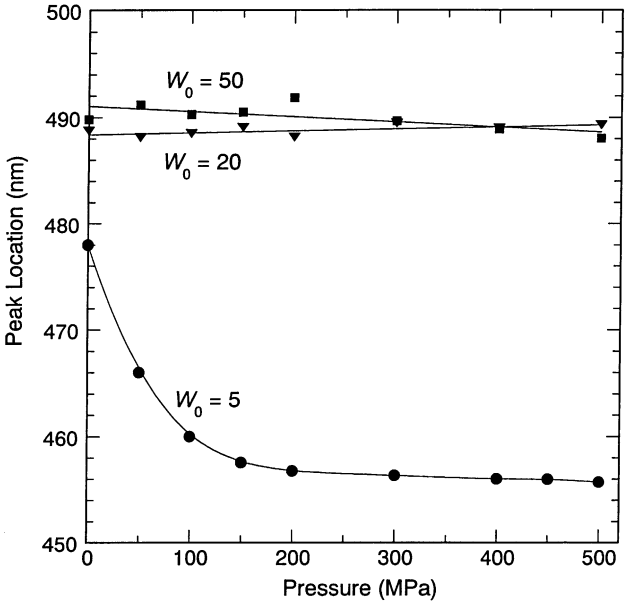

Fig. 4. Plot of fluorescence peak shift as a function of pressure for $w_0 = 5$, 20 and 50.

are independent of the wavelength detected. On addition of water ($w_0 > 5$), however, the fluorescence decays of C343 in AOT reverse micelle in *n*-heptane significantly depend on the detection wavelength. The decay at the red end exhibits a distinct growth, while at the blue end the decay is exponential. Such wavelength-dependent behavior of the fluorescence decay implies that the fluorescence of C343 exhibits the "time-dependent Stokes shift" (TDFSS) in the water-pool of AOT reverse micelles. This suggests that the environment surrounding the C343 probe should be polar enough to exhibit a solvation phenomenon.

If the probe molecules reside in the non-polar hydrocarbon core of micelles, the TDFSS cannot be observed at all. This will be the case for the dry micelle. Conversely, if they are in bulk pure water phase, the solvation dynamics should be too fast to be observed in our present setup having a time-resolution of ~20 ps. It is worth noting that the solvation time of coumarin dye in pure bulk water should fall at around 310 fs [14]. Therefore, we can conclude that the present observation of TDFSS provides convincing evidence that the probe molecule is located within the water-pool of the AOT reverse micelles, where the motion of water molecules should be markedly restricted to show a much larger solvation time.

The TDFSS of C343 inserted in the water-pool (or microemulsions) of AOT reverse micellar aggregates was studied as a function of w_0 and at high pressures. Fluorescence decay data sets were collected at every 10 nm to span the entire steady-state spectrum at different pressures for different w_0 values. The individual wavelength-dependent fluorescence decay curves were fitted to the sum of three exponentials using nonlinear least-squares regression algorithm. The fits were considered acceptable since the χ^2-statistics [36] were close to unity and the residuals did not show a clearly non-random pattern. The instrument response function (IRF) was deconvoluted from the decay data. Time-dependent fluorescence spectra of C343 in AOT reverse micelles in *n*-heptane solution were reconstructed. The reconstructed spectral data points at time t were well fitted to a log-normal line shape function [37]. To obtain the best estimate of the time-dependent fluorescence ($\tilde{\nu}(t)$), the peak frequency was employed.

The time-dependent properties of the emission spectrum are generally quantified in terms of spectral response function ($C(t)$), which is defined by

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

where $\tilde{\nu}(t)$, $\tilde{\nu}(0)$, and $\tilde{\nu}(\infty)$ denote the fluorescence maxima observed at times t, zero, and infinity, respectively. It is this response function which has been used directly comparable to the theoretical prediction of solvation dynamics, since experimentally determined $C(t)$ is related to the response function of solvation energy relaxation under proper conditions [38,39]. The formation of the excited state of a probe molecule occurs more rapidly than the nuclear rearrangement of solvent molecules, so that the excited-state probe finds itself initially (at $t = 0$) in a solvent configuration characteristic of the ground state. With increasing time, the solvent restructures in response to the charge distribution of the excited-state probe molecules. Namely, $C(t)$ provides a measure of the solvation relaxation process. The spectral reconstruction method leading to the response function $C(t)$ has been described in detail by Maroncelli and Fleming [40,41]. The experimental $\tilde{\nu}(t)$ versus t datasets were well reproduced by

$$\tilde{\nu}(t) = \tilde{\nu}(\infty) + \Delta\tilde{\nu}\sum_{i}^{2} a_i \exp\left(-\frac{t}{\tau_i}\right) \quad (2)$$

where $a_1 + a_2 = 1$. The value of $\tilde{\nu}(\infty)$ was determined as the wave number obtained from the asymptotic base-line of the biexponentially fitted curve. It should be noted that when the time scale of electronic deactivation is comparable to that of the solvation relaxation, which is the present case, the correct value of $\tilde{\nu}(\infty)$ cannot be obtained from the steady-state spectrum.

Reconstructed solvent response functions ($C(t)$) for different w_0 at different pressures are shown in Fig. 5. At first, we find from this figure that the solvation dynamics of C343 in the water-pool of AOT reverse micelle exhibits bimodal behavior. Such bimodal behavior has been observed previously [6–9] and the possible cause has been discussed in the framework of Bagchi model [16,17]. Namely, the fast and slow components, τ_1 and τ_2, have been explained to be responsible respectively for the relaxation of confined water in the water-pool and the relaxation of the head group of surfactant molecule which is hydrogen-bonded with water molecules.

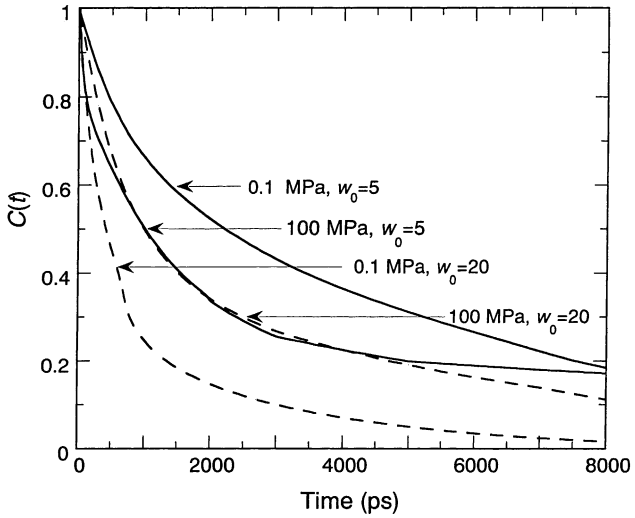

Fig. 5. Decay of solvent response function, $C(t)$ for C343 in AOT/*n*-heptane reverse micelle.

The decay parameters of $C(t)$ thus obtained are summarized in Table 1. It is clearly seen that the solvation times are slower than that of pure bulk water by more than two orders, as has been observed previously. The absolute time values at 0.1 MPa, however, are not always in good agreement with the previous values by Bhattacharyya and coworkers [6–8] and Hazra and Sarkar [9], which will be due to the difference in the probe molecules. Comparing the time data between $w_0 = 5$ and 20 at 0.1 MPa, one sees in the table that the solvation time decreases when w_0 is increased.

It has been observed by means of FT-IR spectroscopy [34] that the aqueous core of the water-pool is composed of three different states of water, i.e. free water, bound water and trapped water. Here the free water is the bulk state composed of hydrogen-bonded-associated chains of water molecules. The bound water is the hydrogen-bonded state between the water and the micellar interface. The trapped water refers to the monomeric water or matrix-isolated dimers, where the amount of trapped water is reported as quite small [34,42]. The decrease in solvation time by increasing the w_0 value is considered to be due to the increase in the contribution of free water molecules within the water-pool of reverse micelles.

At the higher water content of $w_0 = 20$, on the other hand, the contribution of the fast component increases, which is relevant to the increase of the free water content. The bound water molecules should be tightly bounded with the polar head group of surfactant molecules, so that the mobility of their environment may be relatively slower than the central water molecules in the water-pool, which are not affected by the surfactant head-group.

The most significant finding of the present work is the fact that the pressure dependence on the solvation dynamics is reversed between $w_0 = 5$ and 20. Namely, in the case of $w_0 = 5$, the solvation time decreases and the fraction of the fast component slightly increases with increasing pressure. In the case of $w_0 = 20$, conversely, the solvation time increases and the fraction of the fast component decreases with increasing pressure. A possible explanation for this result is as follows: For the small water-pool ($w_0 = 5$), the main species responsible for the solvation dynamics is responsible for the hydrated head groups of the surfactant. With increasing pressure, the hydrogen bonding between water and head group will be distorted or weakened, which has been evidenced by NMR measurements [43]. As a result, for $w_0 = 5$, the solvation time becomes faster with pressure. For the large water-pool ($w_0 = 20$), on the other hand, the main contribution responsible for the solvation dynamics is free water. With increasing pressure, the diffusion of the free water will be retarded. As a consequence, the solvation time becomes slower with pressure.

Finally, we can see in the table that the amount of total dynamic spectral shift ($\Delta\tilde{\nu}$) decreases with increasing pressure, especially for $w_0 = 5$. The decrease in $\Delta\tilde{\nu}$ is related to the blue-shift of the spectrum with pressure. This fact has been discussed in detail in the previous paper (see Fig. 7 in [29]).

Table 1
Spectral shift ($\Delta\tilde{\nu}$), solvation times (τ_1, τ_2), average solvation times ($\langle\tau_s\rangle$), and amplitudes (a_1, a_2) of C343 in AOT microemulsion at high pressures

Pressure (MPa)	$(\Delta\tilde{\nu})^a$ (cm^{-1})	τ_1 (ps)	a_1	τ_2 (ps)	a_2	$\langle\tau_s\rangle^b$ (ps)
$w_0 = 5$						
0.1	1960	661	0.29	6020	0.71	4470
100	1080	360	0.36	3410	0.64	2310
$w_0 = 20$						
0.1	1260	382	0.71	2810	0.29	1090
100	1180	693	0.57	6110	0.43	3020

[a] $\Delta\tilde{\nu} = \tilde{\nu}(0) - \tilde{\nu}(\infty)$.
[b] $\langle\tau\rangle = a_1\tau_1 + a_2\tau_2$.

4. Concluding remarks

In this work, we have observed new unexpected results of the pressure effect on the static and dynamic properties of the water-pool of AOT reverse micelles in *n*-heptane. The results are highly dependent on the size of the water-pool (or w_0).

Previously, we had studied the solvation dynamics in the water-pool of AOT/*n*-propane reverse micelle in near critical condition (at 10 MPa) [44], and found that the solvation time is independent of pressure. However, when we are concerned with the pressure range up to 500 MPa, the static and dynamic properties of the water-pool of AOT are clearly dependent on pressure.

It should be stressed that the pressure effect on the solvation dynamics is dependent on the size of the water-pool, which reflects the existence of different states of water molecules within the water-pool of the AOT reverse micelle.

The pressure effect on the relaxation time of $C(t)$ for small water-pool ($w_0 = 5$) is mainly responsible for the solvation behavior at micellar interface, where water molecules are hydrogen-bonded with head groups of surfactant molecules. The interfacial water molecules in reverse micelles, in all respects, are similar to the water molecules present in the Stern layer of normal micelles and also in the hydrated core of protein surfaces and biological membrane. The present high-pressure solvation behavior at the micellar interface is considered to be closely related to the pressure turn-over behavior of CMC and aggregation number of normal micelles, which we studied previously [22,23], since the stability of micelles should be associated with the property at the hydrated interface of hydrophilic head groups in amphiphilic molecules. It should be noted that we observed the pressure turn-over behavior of solvation dynamics for a normal micelle [45].

Acknowledgements

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