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2004 J. Phys.: Condens. Matter 16 S1207

(http://iopscience.iop.org/0953-8984/16/14/032)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) S1207–S1214 PII: S0953-8984(04)74961-9

Pressure effect on water solvation dynamics in micellar media

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Received 22 January 2004
Published 26 March 2004
Online at stacks.iop.org/JPhysCM/16/S1207
DOI: 10.1088/0953-8984/16/14/032

Abstract

Solvation dynamics of a fluorescent probe in micellar environment has been studied as a function of pressure using picosecond time-dependent fluorescence spectroscopy. Steady-state and time-dependent fluorescence spectra of coumarin 153 (C153) solubilized in two kinds of aqueous surfactant micellar solutions, i.e. *neutral* micelle; triton-X 100 (TX100) and *ionic* micelle; sodium dodecylsulfate (SDS) have been measured at high pressures. Both steady-state and time-dependent spectra exhibit opposite pressure dependence. For the steady-state spectra, with increasing pressure, the peak maximum shifts toward *blue* in the TX100 medium, while it shifts toward *red* in the SDS medium. The solvation time *decreases* for TX100, while it *increases* for SDS. The results suggest the different hydration structure surrounding micelles.

1. Introduction

Water plays an important role in natural and biological processes and its behaviour at the molecular level has long been of interest [1]. Numerous studies have been performed at atmospheric pressure about the unique dynamical properties of water confined in the interface or cavity of self-organized supramolecular assemblies like micelles [2]. In the molecular assemblies water molecules are confined geometrically in a small volume. The most interesting finding here is the observation of markedly slow and bimodal solvation dynamics.

Micelles are prototype of biological molecules, which are spherically shaped self-organized assemblies of amphiphilic surfactant molecules. Investigation of the pressure effect on various micellar properties has revealed various novel phenomena such as turnover behaviour of critical micelle concentration (CMC) [3] and aggregation number (n_{agg}) [4].

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0953-8984/04/141207+08$30.00

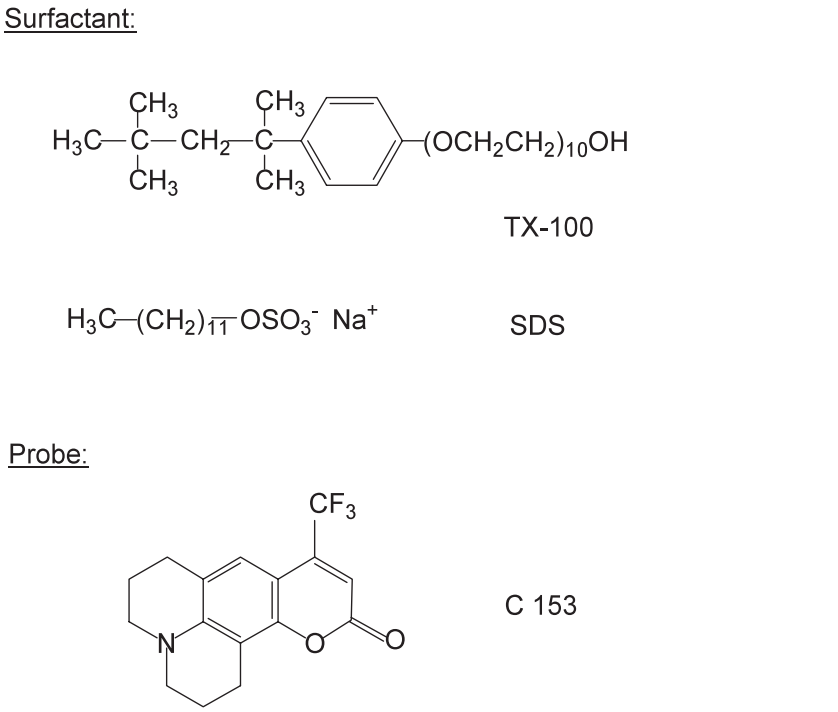

Figure 1. Structures of triton X-100 (TX100), sodium dodecylsulfate (SDS) and coumarin 153 (C153).

We report the result of pressure effects on the water solvation dynamics of a fluorescent probe, coumarin 153 (C153), inserted in a micellar hydration shell. We adopted triton X 100 (TX100) and sodium dodecylsulfate (SDS) surfactants which form representative *neutral* and *ionic* spherical micelles (cf figure 1).

2. Experimental section

C153 (laser dye, Lamda Physik), TX100 (spectroscopic grade, Nacalai Tesque), SDS (99%, Nacalai Tesque) and distilled water (Nacalai Tesque) were used as received. For the TX100 solution, concentrations of TX100 and C153 are 5.0×10^{-3} and 2.3×10^{-6} M. For the SDS solution, those of SDS and C153 are 4.0×10^{-2} and 3.8×10^{-6} M. These concentrations are about 20 and 5 times higher than CMC[4].

The high-pressure optical cell and the pressure generating system have been described previously [5]. All the steady state and time-dependent fluorescence were measured at 290 K and the pressures up to 500 MPa. The excitation wavelengths for steady-state and time-dependent measurements are 405 and 400 nm, respectively. All time-resolved emission data were collected with a time resolution of 50 ps using time-correlated single-photon counting (TCSPC) method. The instrument response is 50 ps (fwhm), which reduces to less than 20 ps after deconvolution.

[4] CMC is 0.26×10^{-3} M for TX100 and 8.0×10^{-3} M for SDS. The concentration ratio of C153 to each surfactant fulfils the condition that one micelle contains less than one C153 molecule. The average number of probe C153 molecule is ∼0.1 for both systems, where n_{agg} of TX100 and SDS micelles is supposed 250 and 100, respectively.

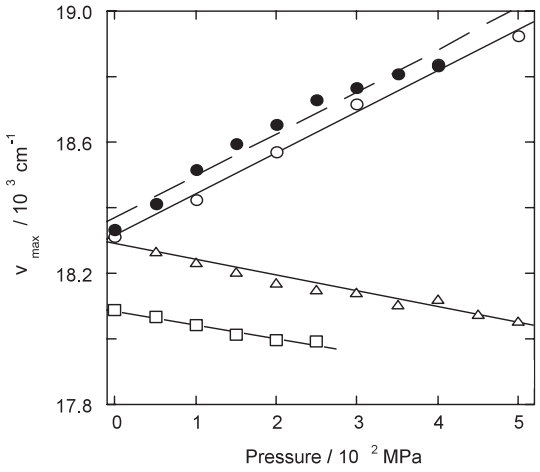

Figure 2. Pressure dependence of the fluorescence peak maximum (ν_{max}) of C153 in TX100/H_2O (●), TX100/D_2O (○), SDS/H_2O (□) and 1-butanol (△).

By following the previous procedure [6], time-dependent fluorescence spectra are reconstructed from observed decay curves, which provide the solvation response function;

$$C(t) = \{\nu(t) - \nu(\infty)\}/\{\nu(0) - \nu(\infty)\} \tag{1}$$

where $\nu(t)$, $\nu(0)$ and $\nu(\infty)$ denote the fluorescence maxima observed at times t, zero and infinity. It is this response function which has been used to compare with the theoretical prediction of solvation dynamics.

3. Results

3.1. Steady-state spectra

As shown in figure 2, the fluorescence peak maximum (ν_{max}) of C153 in aqueous TX100 micelle solution shifts linearly toward *blue* with increasing pressure. In contrast, ν_{max} of C153 in aqueous SDS micelle solution shifts linearly toward *red* with increasing pressure. The pressure peak shift of C153 in 1-butanol was also determined for comparison, since ν_{max} in 1-butanol at 0.1 MPa (18 320 cm^{-1}) is almost equal to that in the TX100 micelle medium. The dielectric constant of 1-butanol is 17.51 D. 1-butanol solution shows the red-shift. An analogous red-shift has also been reported in a series of *n*-alcohols [7].

3.2. Time-dependent spectra

$C(t)$ of C153 in TX100 micelle at different pressures are constructed from time-dependent fluorescence spectra. Every decay curve exhibits bimodal behaviour. Two time components are determined at each pressure by fitting each $C(t)$ curve to a double exponential function;

$$C(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) \tag{2}$$

where τ_1 and τ_2 are the fast and slow time components. The pre-exponential factors (a_1, a_2) are related by $a_1 + a_2 = 1$. The average time values, $\langle\tau\rangle = a_1\tau_1 + a_2\tau_2$, were plotted against pressure in figure 3. We find that $\langle\tau\rangle$ shows quite different behaviour between neutral TX100 and ionic SDS micelle media. In SDS micelle, not only the pressure red-shift of ν_{max}, but also the pressure dependence on $\langle\tau\rangle$ in SDS micelle behaves just like those in alcohol solvents.

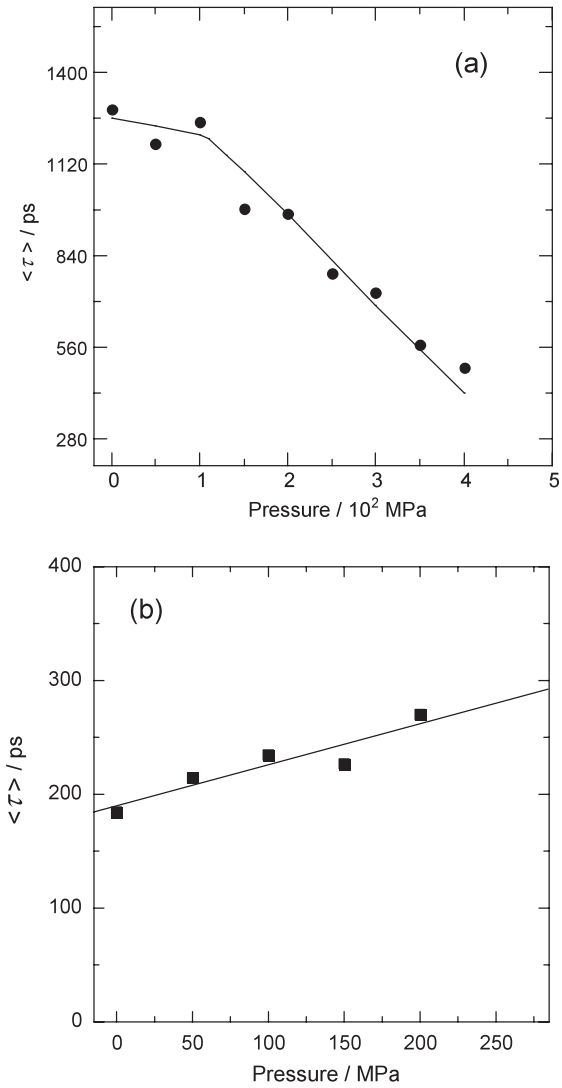

Figure 3. Pressure dependence of the average solvation time $\langle\tau\rangle$ in (a) TX100 and (b) SDS micelle media. The data points are the averaged values over several measurements.

4. Discussions

4.1. Location of probe

For the purpose of discussing the solvation dynamics in a micellar environment, it is important to figure out the location of the probe within a micelle. At first we discuss this problem on the basis of steady-state fluorescence spectra. If it resides in the core region of micelles, the intensity of ν_{max} should be much greater. The structure of the hydrophobic group for a TX100 surfactant molecule is analogous to 2-methylbutane except for the benzene ring. The fluorescence intensity of C153 in TX100 micelle medium at ν_{max} of C153 in 2-methylbutane (21 740 cm^{-1}) is surprisingly weak. On the other hand, such a hydrophobic molecule is insoluble in bulk water. In addition, if it stays in the bulk water phase, ν_{max} should be located at a much lower wavenumber than the observed one.

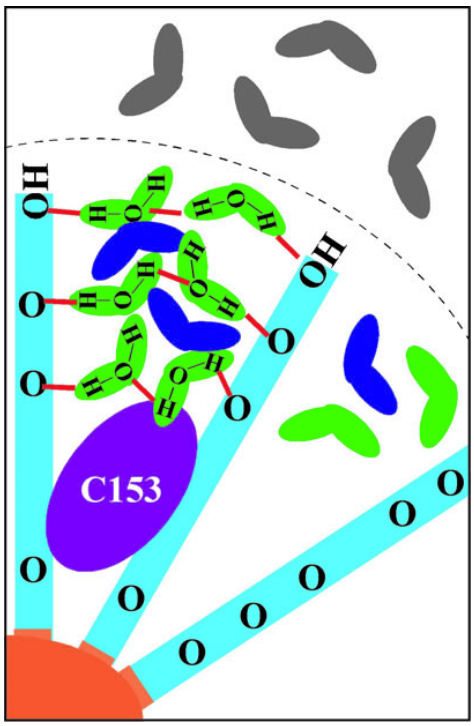

Figure 4. Schematic illustration representing the Stern layer of a TX100 micelle and the location of the C153 probe molecule.

(This figure is in colour only in the electronic version)

Furthermore, based on the time-dependent fluorescence spectra, if the probe stays in the bulk water phase, the solvation is too fast to be detected with our present time resolution. The solvation in bulk water is completed within 1 ps [8]. Conversely, if it stays in the nonpolar hydrocarbon-core region of a micelle, TDFSS is not observed at all. In completely nonpolar solvents such as 2-methylbutane, TDFSS cannot be detected.

In conclusion, the C153 probe is located within the Stern layer which surrounds a micelle. Figure 4 shows the schematic illustration representing the proposed location of a probe molecule dissolved in the TX100 micelle.

4.2. Pressure peak shift

Steady-state fluorescence spectra of C153 in a series of homogeneous solvents at 0.1 MPa exhibit red-shift with increasing solvent polarity [9]. Dielectric constant of alcohols as well as water increases with pressure. So the pressure red-shift for ν_{max} of C153 in the SDS micelle medium indicates the increasing polarity around the probe, which is identical to the behaviour in bulk water solvent.

The pressure blue-shift of ν_{max} in the TX100 micelle medium, on the other hand, indicates that the application of pressure causes the environment of the C153 probe to shift toward a less polar state. This fact is generated from either (a) the movement of the probe toward the core region of the TX100 micelle or (b) the squeezing of water molecules out of the hydration shell of micelles, which is called the 'Stern layer'. In either case the water molecule around the probe in the Stern layer decreases in number.

The thickness of the Stern layer has been determined by light scattering studies as 0.6–0.9 nm for SDS micelle [10] and 2.0 nm for TX100 micelle [11]. Moreover, n_{agg}, which is the average number of surfactant molecules in a micellar unit, is ∼60 for the SDS micelle [12] and ∼250 for the TX100 micelle [13] at 0.1 MPa. Taking these data into account, we conclude that the pressure blue-shift for the TX100 micelle is caused by the different hydration structure from SDS surrounding micelles. The headgroup of the TX100 molecule ($-(OCH_2CH_2)_{10}OH$), which contains ten oxygen atoms and a hydroxyl group capable of H-bond formation with water molecules, is much larger than that of the SDS molecule (SO_4^-). Namely the headgroup size of SDS is significantly smaller than that of TX100. As for the SDS micelle, because of its smaller size and smaller thickness, the property of the Stern layer is not fully discriminated from bulk solvent. So the solvation dynamics significantly reflects the dynamics of bulk water. The pressure red-shift is caused by the polarity increase in bulk water.

4.3. Bimodal solvation

According to dielectric relaxation [14], bimodal behaviour of $C(t)$ is responsible for *free* and *bound* water molecules, which are in equilibrium. The *free* water molecules are those which are not H-bonded with any other molecule in the hydration zone of micelles. The *bound* water molecules are those which are immobilized by one to two H-bonds with the headgroup of a micelle. In many studies of solvation dynamics at 0.1 MPa, the two time components have been assigned as *free* and *bound* water molecules. Although it has been proposed that τ_1 is responsible for a bound water or a H-bond between a water molecule and a headgroup, while the origin of τ_2 remains obscure.

Possible dynamics contributing to the solvation are (1) the reorientation of a bulk water molecule, (2) that of a *free* water molecule, (3) that of a *bound* water molecule, (4) the rotation, libration, or torsion of a surfactant headgroup, and (5) the exchange dynamics of surfactant molecules between the micelle and monomer phases. It is the two slowest ones among them which are detected. Here, (5) is ruled out since its timescale of 10^{-3}–10^{-5} s is too slow to be detected [15]. As a result, the physical processes corresponding to τ_1 and τ_2 are responsible for (3) and (4), respectively.

According to MD simulation studies [16], a large contribution to the slow solvation dynamics in micellar media comes from headgroup relaxation. Large amplitude motion of a polymer chain with a timescale of 100 ns [17] is ruled out. But small amplitude motions like libration or segmental rotation within a micelle headgroup are possible in the present timescale. In conclusion τ_2 is responsible for the reorientational motion of a surfactant headgroup, while τ_1 of the bound water.

4.4. Pressure effect on solvation time

For the case of *n*-alcohol solvents, the increase in solvation time is due to the increase in solvent viscosity with pressure. Furthermore, in a series of *n*-alcohol solvents at 0.1 MPa, the less polar is the solvent, the slower becomes the solvation time [7]. Just as in the same way as *n*-alcohols, $\langle\tau\rangle$ in SDS micelle increases with pressure. This fact suggests a more viscous and more polar environment at high pressures, which reflects just the feature of bulk phase.

For the solvation time in *neutral* TX100 micelle medium, however, the result is opposite to that in *ionic* SDS micelle medium. The decrease in $\langle\tau\rangle$ for TX100 micelle medium is considered as exclusively originating from the dynamic feature within the Stern layer where the dynamics is completely shielded from bulk water. The Stern layer of TX100 is composed of a highly developed H-bond network structure.

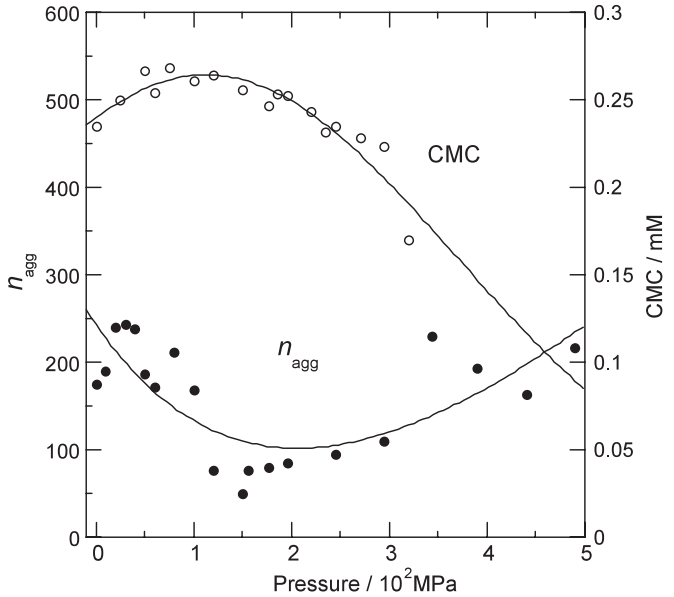

Figure 5. Pressure dependence of CMC and n_{agg} in the TX100 micelle medium.

When we discuss the pressure effect on $\langle\tau\rangle$ for the TX100 micelle, consideration of the pressure effect on n_{agg} is inevitable. For both TX100 and SDS micelles, n_{agg} exhibits turnover behaviour against pressure having a minimum at 80–100 MPa [4], which is closely related to the turnover behaviour of CMC (see figure 5). Based on the variation of n_{agg} and CMC with pressure, the micelle conformation changes as well. In the pressure range up to 100 MPa, where $\langle\tau\rangle$ shows a slight decrease for TX100, the decrease in n_{agg} indicates the micelle becoming smaller. In such a case the number of the H-bond bridges between headgroups should increase since water molecules are more likely to enter in between the headgroups. This fact causes $\langle\tau\rangle$ to increase since the headgroup motion is restricted. Conversely, the application of pressure weakens the H-bond strength. This effect causes $\langle\tau\rangle$ to decrease with pressure. As a result the pressure dependence of $\langle\tau\rangle$ in the pressure range up to $\sim$100 MPa is a consequence of the balance between the two oppositely acting pressure effects, i.e. the formation of H-bond bridges and the weakening effect of the H-bond.

In the pressure range above 100 MPa, on the other hand, $\langle\tau\rangle$ for the TX100 micelle decreases with pressure. This is not only due to the weakening effect of the H-bond but also to the decreased formation of the bridge structure. At the large value of n_{agg} for TX100 micelles, i.e. at high pressures, the bridge structure of the H-bond is formed only at the limited tip portion of the headgroups. This is the case for the SDS micelle. It is this reason that $\langle\tau\rangle$ of TX100 gets closer to that of SDS at high pressures. The viscosity of bulk water increases with pressure. This pressure effect should lead to the slower relaxation dynamics responsible for headgroups. At higher pressures the solvation time of C153 in SDS micelle media increases with pressure.

5. Concluding remarks

Based on the peak location of the steady-state emission and the timescale of TDFSS at 0.1 MPa, we conclude that the C153 probe molecule is situated within the Stern layer of both micelles. With increasing the pressure, ν_{max} shifts toward *blue* in the TX100 micelle, while it shifts

toward *red* in the SDS micelle. The blue-shift indicates a less polar environment. Therefore, the blue-shift for TX100 suggests the squeezing of water molecules out of the Stern layer or the movement of the probe molecule toward the hydrocarbon core of micelles. The red-shift for the SDS micelle, on the other hand, is just corresponding to the behaviour of alcohol solvents, which is interpreted by the increase in bulk solvent polarity with pressure.

In the TDFSS measurements for TX100 and SDS micelle media at high pressures, every decay curve of $C(t)$ was well-fitted to a double exponential function. With increasing pressure, $\langle\tau\rangle$ for TX100 decreases, whereas for SDS it increases.

Such opposite pressure effects on $\langle\tau\rangle$ as well as $\nu_{\max}$ between neutral and ionic micelles can be explained by the different Stern-layer structure. The thick and well-organized hydration shell composed of a H-bond network in the neutral TX100 micelle completely shields the bulk water. This reduces to a markedly different environment from bulk water, where the dynamics of H-bonded headgroup dynamics plays an important role. Whereas the solvation dynamics in the ionic SDS micelle substantially reflects the bulk water dynamics.

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