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Effect of pressure on the critical micelle concentration of neutral surfactant using fluorescence probe method

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Abstract

We have investigated the pressure effect on the critical micelle concentration (cmc) of neutral surfactant micelle, Triton-X-100 (TX100), in aqueous solution by means of the fluorescence probe method. 2-*p*-Toluidinylnaphthalene-6-sulfonate (TNS) was used as a probe molecule, whose fluorescence yield remarkably increases in the micellar state. With increasing pressure, turnover behavior of cmc was observed at ca. 100 MPa. The fluorescence yield of TNS is sensitive to the local polarity and the local viscosity of the medium, which is associated with the formation of twisted intramolecular charge-transfer (TICT) state of TNS in the excited state. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Various attempts have been provided for studying the structure and dynamics of various micellar systems [1,2]. Of particular interest has been the fluorescence probe technique for understanding the local properties of the molecular aggregates. This technique is especially useful for studying the micropolarity and microviscosity of non-ionic surfactant micelles, for which the electrical conductivity method is not applicable.

It is well known that the fluorescence properties of 2-*p*-toluidinylnaphthalene-6-sulfonate (TNS) and its related molecules such as *N*-arylaminonaphthalenesulfonate (ANS) are markedly dependent on the polarity of the medium [3,4]. The sensitivity of the emission properties of such molecules has been considered to arise from an efficient nonradiative process, that is the formation of twisted intramolecular charge-transfer (TICT) state in the excited state in polar solvents [5]. The TICT process is so rapid in highly polar medium that the fluorescence quantum yield (ϕ_f) of the locally excited (LE) state becomes extremely low in aqueous solution. Whereas in the micellar environment, the reduced micropolarity and the increased microviscosity may cause the rate of the TICT process to decrease. As the result, the TNS molecule bound to micellar aggregates exhibits an appreciably high fluorescence yield [4,6]. Making use of this fact, we adopted the TNS molecule as a fluorescence probe in order to follow the micelle formation at high pressures. The concentration above which micellar aggregates are formed is referred to as "critical micelle concentration (cmc)".

The primary effect of pressure on the micellar system is the variation of cmc [1,7–9], which is closely connected to the changes of partial molar volume of micelle formation, aggregation number, and water penetration into micelles. The pressure dependence of cmc for ionic micelles such as sodium dodecylsulfate (SDS) has been studied so far by the electrical conductivity method [10] and the fluorescence probe method as well [7]. Turnover behavior of cmc has been observed with increasing pressure.

In this paper we are concerned with the pressure effect on the cmc of a representative neutral micelle formed in Triton-X-100 (TX100) [11], where the TNS molecule is used as a fluorescence probe molecule for detecting the cmc value.

2. Experimental

The surfactant TX100 and the probe molecule TNS were obtained commercially (Nakarai Tesque) and they were used as received. Water employed as solvent was chromatographic grade. They showed no impurity emission in the spectral region of interest at the present sensitivity level. To

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obtain the absolute value of the emission quantum yield of TNS, the instrumental sensitivity at each wavelength was calibrated using quinine sulfate–0.1 N sulfuric acid solution as a reference standard [12].

The measurements of steady-state emission spectra were performed for the solutions with the TNS concentration of $\sim 10^{-5}$ M and the TX100 concentration over 0.17×10^{-3}–0.33×10^{-3} M at 295 K as a function of pressure up to 450 MPa. These concentrations assure less than one TNS molecule per micelle on an average. A high pressure optical cell equipped with four sapphire windows and equipments of high pressure generation have been described elsewhere [13,14].

3. Results and discussion

3.1. Determination of cmc

Fig. 1 shows typical fluorescence spectra for TNS in TX100 aqueous solution above and below cmc. Below cmc where the surfactant is molecularly dispersed, it shows a broad and weak emission with the maximum around 470 nm (21.3×10^{3} cm^{-1}), which is almost identical to the free TNS emission in aqueous solution. Whereas, above cmc where the probe molecule is predominantly solubilized in micelle, it shows a relatively strong emission with the maximum at 440 nm (22.7×10^{3} cm^{-1}), which is considered as the TNS emission interacting with micelles. In the micellar state, the fluorescence yield appreciably increases with pressure. Pressure dependence of the relative fluorescence yield (Φ_p/Φ_0) well above the cmc is shown in Fig. 2. This indicates the decrease in micropolarity around the probe, which may be caused by the squeezing of the water molecules out of micelles at high pressures. Whereas, below the cmc where the TX100 molecules are in single dispersed state it was too weak to detect the yield change with pressure.

The fluorescence intensity rapidly increases above the cmc of TX100. To determine the cmc's at high pressures by making use of this behavior, we attempted to measure the fluorescence yield (ϕ_f) at each pressure. We plotted the results both (i) as a function of TX100 concentration at constant pressure and (ii) as a function of pressure at constant TX100 concentration. Representative plots are shown in Fig. 3. Both plots exhibited fairly sharp breaks at cmc. As the result, we defined the cmc value from the intersection of two straight lines joining the points well

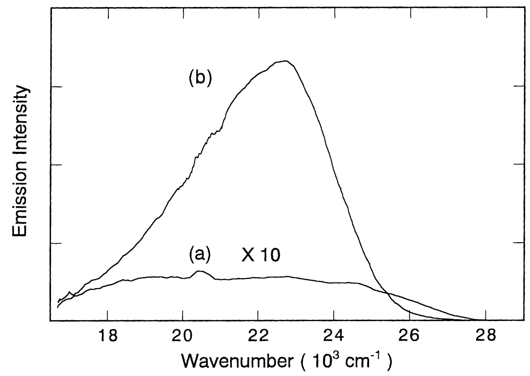

Fig. 1. Fluorescence spectra of TNS (a) in the singly dispersed state (173×10^{-3} M) and (b) in the micellar state (0.327×10^{-3} M).

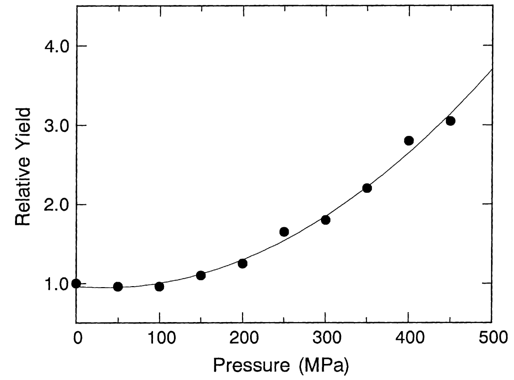

Fig. 2. Relative fluorescence yield (Φ_P/Φ_0) as a function of pressure at 0.8×10^{-3} M.

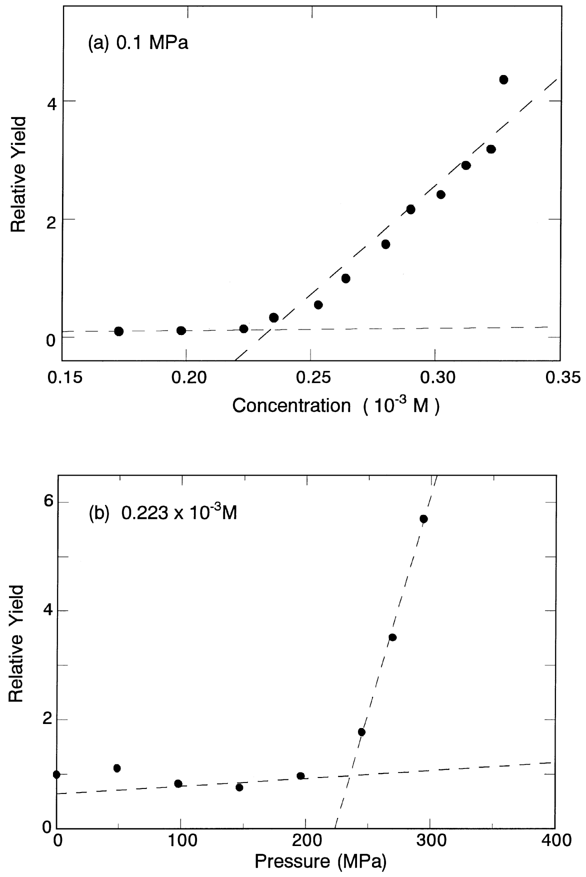

Fig. 3. (a) Plot of relative fluorescence yield as a function of TX100 concentration at constant pressure (0.1 MPa). (b) Plot of relative fluorescence yield as a function of pressure at constant TX100 concentration (0.223×10^{-3} M).

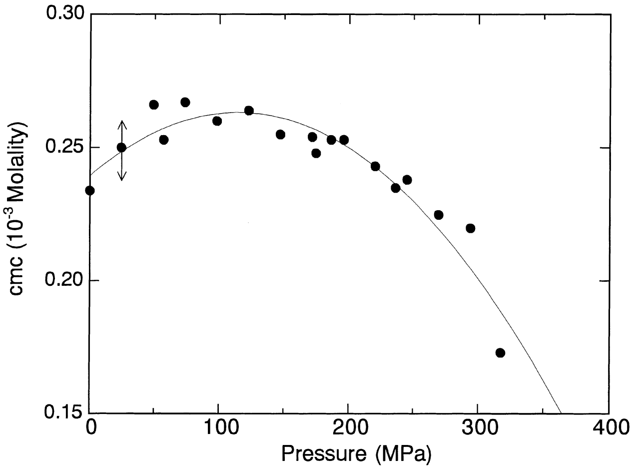

Fig. 4. Plot of cmc as a function of pressure. The arrow represents an error bar.

below and well above the cmc, as depicted in Fig. 3. The cmc value thus determined at atmospheric pressure (0.1 MPa) is 2.4×10^{-4} M. This is in excellent agreement with the previous literature data [15]. The atmospheric cmc value previously reported ranges over 2.4×10^{-4}–2.68×10^{-4} M depending on the wavelengths used for analysis [15].

3.2. Pressure dependence of cmc

Fig. 4 shows the pressure dependence of the cmc's of TX100 at 295 K. They were calculated in molality units by assuming that the compressibility of the dilute solutions used equated to that of pure water [16]. We find that in low pressure region it increases with pressure, while in high pressure region it turns to decrease. Namely, the cmc undergoes a maximum, just as has been observed for ionic surfactant micelles, such as cationic sodium dodecylsulfate (SDS) [10,17], anionic decyltrimethylammonium bromide (DeTAB) and their related ionic micelles [18,19]. The pressure at which the cmc of TX100 attains a maximum was determined as 100–110 MPa, which is almost identical to those of SDS and DeTAB. The pressure effect on the cmc for SDS, which has been studied by electrical conductivity method [10] as well as fluorescence probe method [7], shows a turnover maximum at around 100 MPa.

When we consider the true equilibrium between the two species; [single dispersed state]$\rightleftarrows$[micellar state], the change of the partial molar volume (ΔV^0) involved in the formation of micelles from single molecularly dispersed state in their standard state can be described for the case of non-ionic micelles by the following relation [18],

$$\Delta V^0 = RT\left(\frac{\partial \ln[\text{cmc}]}{\partial P}\right)_T \tag{1}$$

where ΔV^0 represents the difference between the partial volume of micellar state (V_m) and singly dispersed state (Vs). According to Eq. (1), we calculated the ΔV^0 values as a function of pressure. The result is shown in Fig. 5. We found that for the micellar formation of TX100, ΔV^0 varies linearly from $+4.6$ cm^3/mol at atmospheric pressure (0.1 MPa) to -7.0 cm^3/mol at 300 MPa, the change of sign occurring at ca. 100 Mpa. In the case of ionic micelles, however, appreciably larger ΔV^0 value at atmospheric pressure has been reported [19]. In this figure, we compare with the result of a cationic micelle, sodium decylsulfate (SDeS) [19], whose ΔV^0 value at atmospheric pressure is 8.2–8.4 cm^3/mol and asymptotically approaches to non-ionic ones with pressure.

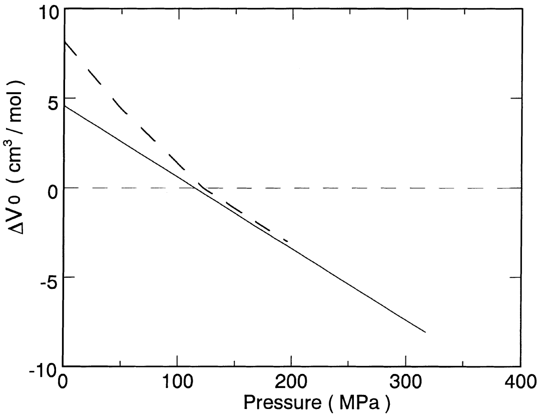

Fig. 5. Change of ΔV^0 with pressure for TX100 (solid line) and SDeS (dashed line).

The positive ΔV^0 value at atmospheric pressure can be explained as follows: the paraffin chains of TX100 possess a hydrophobic character. When hydrophobic molecules in hydrophobic environment are put into water solvent, a decrease in volume should be observed, since the hydrophobic molecules may enter into the open structure of water. Upon micellization, when the hydrocarbon-water contact is eliminated, the chains are more free to expand due to decreased hydrophobic interaction, so that ΔV^0 takes positive. Furthermore, in the case of ionic molecule, the volume contraction due to electrostriction provides a smaller V_s value, as compared with the non-ionic case, resulting a larger ΔV^0 value.

According to the solubility studies of alkylbenzene in water, the volume contraction due to the hydrophobic interaction has been estimated as 4∼9 cm^3/mol, which decreases with increasing pressure [20].

The micelles having a fairly open structure should have a higher compressibility as compared with the molecularly dispersed state in solution. Namely, V_m decreases more steeply than V_s. Thus, the decrease in ΔV^0 change of its sign with increasing pressure could reasonably be accepted.

4. Concluding remarks

In this paper we have determined the pressure dependence of cmc for non-ionic surfactant, TX100, by the fluorescence probe method, using the TICT-state formation of TNS in polar medium as a probe. This method was found satisfactory, since two linear branches are obtained with slopes sufficiently different to afford an accurate estimate of the cmc as the point of intersection. The cmc vs pressure curve passes through a maximum at ca. 100 MPa. This is similar in shape with ionic systems previously studied [7,20], but different in ΔV^0 value in low pressure region, which is due to the decreased solvation and the smaller V_s value in non-ionic dispersed state.

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