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Pyrenesulfonate Solubilized in an Aerosol OT (AOT) Reversed Micelle. Location and Distribution

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Pyrenesulfonate (PSA^-) solubilized in an AOT reversed micelle was found to exist both in the water pool and in the surfactant phase by analyzing decay profiles of laser-induced transient species. Relative abundance in the two phases strongly depends on the molar ratio of $[H_2O]/[AOT]$.

The AOT reversed micelle contains a water pool, the size of which can be controlled by changing the molar ratio of $[H_2O]/[AOT]$ (= Wo).[1] The micelle is well known to solubilize a variety of molecules. In the case of pyrene derivatives such as (11-(1-pyrenyl)undecyl)trimethylammonium, known as one of the tentative fluorescing probes, the cationic head is anchored at the micellar surface while the pyrenyl moiety is located in the hydrophobic phase of the surfactants.[2] On the other hand, solubilization of pyrenesulfonate (PSA^-) having no alkyl chain seems to be more complicated by its delicate balance between hydrophilic and hydrophobic interactions. At least two different phases, water pool and surfactant phases, are considered for solubilization of PSA^-. Those PSA^-s are denoted as (PSA^-)wp and (PSA^-)sp, respectively. Recently we have reported that the transient absorption spectra observed after laser irradiation give some information about location and distribution of PSA^- in the AOT reversed micelles.[3] In this work we analyze decay profiles of the transient species as a function of Wo. Based on this analysis coupled with the observation of excimer fluorescence, we estimate relative abundances of (PSA^-)wp and provide an evidence that more than two PSA^- molecules exist in the large water pool.

The apparatus for measurements of laser-induced transient absorption spectra has previously been reported.[3,4] The fluorescence spectra were observed by using nitrogen laser as an excitation light under the condition where two-photon processes are negligible. The AOT/H_2O/isooctane reversed micellar solution containing sodium salt of PSA^- was deaerated by repeated freeze-pump-thaw cycles. PSA^- dissolved in the external organic phase was

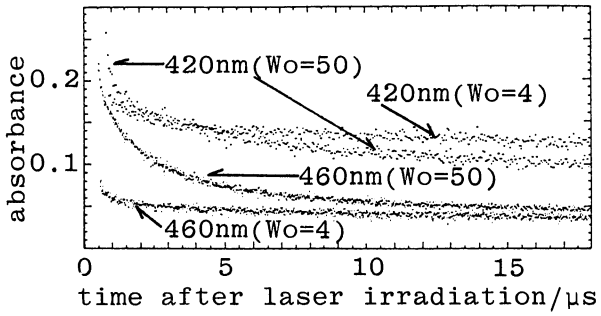

Fig. 1. Decay profiles of triplet (420 nm) and $PSA^{\pm}$ (460 nm).

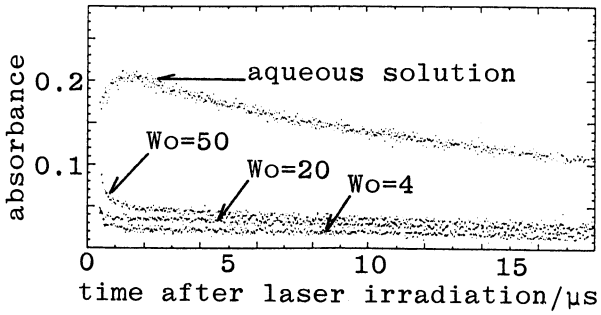

Fig. 2. Decay profiles of PSA^{2-} (490 nm) as a function of Wo.

considered to be negligibly small since no fluorescence was detected for the supernatant part of saturated PSA^- isooctane solution.

In the recent paper,[3] we found that four transient species are formed after irradiation of PSA^- with 351 nm (XeF) laser and give the following absorption maxima in aqueous solution : triplet (420, 525 nm), $PSA^{\pm}$ (460 nm), PSA^{2-} (490 nm) and $(e^-)aq$ ($\simeq$ 700 nm). $PSA^{\pm}$ is a zwitter ion formed by two-photon ionization of pyrenyl chromophore and its intensity and lifetime are little affected by oxygen gas. $(e^-)aq$ is a solvated electron in association with the formation of $PSA^{\pm}$. PSA^{2-} is a dinegative ion formed according to the following scheme : $PSA^- + 2h\nu \rightarrow PSA^{\pm} + (e^-)aq$, $(e^-)aq + PSA^- \rightarrow PSA^{2-}$. This dinegative ion almost disappears under oxygen atmosphere.

The intensities and decay profiles of these transient species strongly depend on Wo as shown in Figs. 1 and 2. The decay profiles at 420 nm for the reversed micelle with Wo = 50 was reproducible by using sum of three exponential functions, leading to three different lifetimes (τ_{420}) of $\simeq$ 200 μs, 9 - 10 μs and $\leq$ 1 μs. Two major transients with longer lifetimes were attributable to the triplets : there exist at least two types of triplet with different lifetimes of 9 - 10 μs and $\simeq$ 200 μs. The shorter one was nearly equal to the lifetime of the triplet observed in aqueous solution (10.0 ± 0.5 μs). The contribution of this triplet decreases with decrease of Wo. Therefore, the transient with $\tau_{420} \simeq$ 10 μs is attributable to the triplet of $(PSA^-)wp$. The other triplet with $\tau_{420} \simeq$ 200 μs, most dominant species observed for smaller reversed micelles (Wo = 4, see Fig. 1) are likely to be originated from $(PSA^-)sp$. The long lifetime of this triplet may be caused by weak immobilization of PSA^- on the polar surface of AOT. Those assignments can be supported by the quenching experiments with oxygen gas or paramagnetic transition metal ions such as Co^{2+}. The transient species having the shortest lifetime ($\tau_{420} \leq$ 1 μs) have not yet been clearly assigned since a reliable decay profile was not obtained in such a short range of time because of the overlap of strong fluorescence.

Figure 1 also shows that the intensity as well as the decay profile observed at 460 nm strongly depends on Wo. The lifetime of the major transient in the large reversed micelles, for example, Wo = 50 or 40, is about 1.6 μs, which is equal to the lifetime of $PSA^{\pm}$ observed in aqueous solution (1.60 ± 0.05 μs). Both lifetime and intensity of this transient species were little changed by the presence of O_2 or Co^{2+}. Thus this species is attributable to the $(PSA^{\pm})wp$. With decrease of Wo the absorbance at 460 nm is markedly reduced. The transient species with $\tau_{460} \simeq 1.6$ μs almost disappeared but instead a long lifetime species with $\tau_{460} \simeq 200$ μs became dominant for the reversed micelle with Wo = 4. This transient species is probably attributable to the triplet of $(PSA^{-})sp$ since the lifetime was remarkably shortened by oxygen gas.

The absorbances at 420 nm and 460 nm due to the triplet with $\tau_{420} \simeq 10$ μs and $PSA^{\pm}$ with $\tau_{460} \simeq 1.6$ μs, respectively, are considered to reflect relative abundance of $(PSA^{-})wp$. By assuming that the molar extinction coefficients of these species are equal to those in aqueous solution we obtained the following relative abundances of $(PSA^{-})wp$ as a function of Wo : 40 - 50% (Wo = 50), 30 - 35% (Wo = 40), ≃ 20% (Wo = 30), ≃ 15% (Wo = 20), and a few % (Wo = 4, 8), where the concentration of PSA^{-} ($[PSA^{-}]$) was kept constant (1×10^{-4} mol/l). The detailed result will be reported elsewhere.

As shown in Fig. 2, the absorbances at 490 nm observed in the reversed micellar solutions are extremely reduced in comparison with that observed in aqueous solution. Such a weak absorption at 490 nm seems to be originated not from $PSA^{\pm}$ but from the triplet or PSA^{2-} because of the strong oxygen effect on their decay profiles. The observed absorbance at 490 nm for the reversed micelle with Wo = 50 is significantly larger than that for the micelle with Wo = 4 in the whole range of time. This behavior is different from the Wo dependence of the decay profile of the triplet at 420 nm as shown in Fig. 1. Furthermore, the decay profiles at 490 nm for the large micelles were found to change depending on $[PSA^{-}]$: relative contribution of the transient species with a short lifetime (≃ 1 μs) increases with increase of $[PSA^{-}]$. Thus the PSA^{2-} species significantly contributes to the absorbance at 490 nm for the large micelles.

Now, how can we explain the formation process of PSA^{2-} in the reversed micellar solution ? It requires for the formation of PSA^{2-} that a solvated electron can attach to an unexcited PSA^{-} molecule during its lifetime. A photoelectron ejected from a molecule dissolved in nonpolar organic phase is known to be effectively captured by the water pool in a few hundreds femtoseconds.[5] The captured electron keeps alive in a relatively long period (≤ 150 ns).[3] Therefore, it is very likely that this electron may attach to an unexcited PSA^{-} molecule coexisting in the same water pool. In

other words, it suggests that some of the reversed micelles can solubilize more than two PSA^- molecules. If there exist two PSA^- molecules in the same water pool we can expect an effective detection of excimer fluorescence from these PSA^- molecules. As shown in Fig. 3 the excimer fluorescence of PSA^- in aqueous solution was observed at ≃ 500 nm as reported previously.[6] No excimer fluorescence was observed for the micellar solutions with Wo = 4 and 8. The fluorescence spectra is in agreement with that of the monomer observed in dilute aqueous solution of PSA^-. However, for the reversed micelle with Wo = 50, fluorescence intensity at 500 nm reaches ≃ 80% of the intensity observed in aqueous solution with the same concentration of PSA^-. This increase provides an evidence of the excimer formation in the large reversed micelles. Thus the observations of this excimer fluorescence and the transient absorption attributable to PSA^{2-} suggest that the large reversed micelle contains more than two PSA^- molecules in the same water pool.

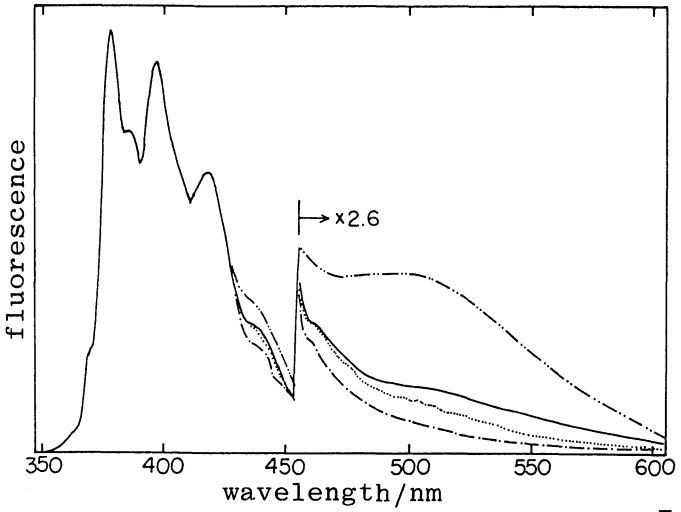

Fig. 3. Fluorescence spectra of PSA^- in aqueous solution (——; 1 x 10^{-4} mol /l, —··—; 5 x 10^{-4} mol/l) and in reversed micellar solution (----- ; Wo = 50, —·—; Wo = 4).

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