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# Steady-state and time-resolved spectroscopic investigations on the existence of stable methanol/AOT/n-heptane reverse micelles

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ABSTRACT

In this work, we have reported our study on the controversial issue whether methanol molecules can be effectively encapsulated by surfactant AOT to form true reverse micelles. We compared the different photophysical properties of coumarin 153 (C153) in methanol/AOT/n-heptane reverse micelles and methanol/n-heptane binary mixture by means of steady-state absorption, fluorescence and time-resolved fluorescence spectroscopies. In the reverse micelles, the fluorescence emission spectra of C153 were dependent on the excitation wavelength, while in binary mixtures, the excitation wavelength dependence was not observed. The biexponential decay curves of C153 in reverse micelles give a further confirmation for the two different environments where C153 molecules reside in. In other words, C153 molecules can exist both inside the core of the reverse micelles and outside of it. These results proved that the methanol can be effectively encapsulated by AOT in n-heptane solvents to form stable methanol/AOT/n-heptane reverse micelles.

## 1. Introduction

Reverse micelles (RMs) are nanopools of polar solvents sequestered from a continuous nonpolar phase by a surfactant layer, with polar head groups of surfactants pointing inward to polar solvents and hydrocarbon tails pointing toward nonpolar organic solvents (Fig. 1a) [1,2]. Over the past decades, RMs have been widely investigated for their utility as microreactors for heterogeneous chemistry, the templates for nanoparticle synthesis, and a tenable model for confined water in biological systems [3–5]. RMs can be divided into two catalogues: aqueous reverse micelles and non-aqueous reverse micelles according to their different form [6]. Till now, many efforts have been done to investigate aqueous RMs, for example, varied techniques have been applied to learn about the changes occur in the nanopools of water on the RMs interior [2,7]. In recent years, growing interest has been attracted to the RMs containing the non-aqueous polar solvents such as glycerol [8], ethylene glycol [9,10], formamide [11–13], dimethyl formamide [14], methanol [1,11,15–21], and so on. One of the most important reasons is that many chemical reactions taking place on a microreactor scale tend to appear in non-aqueous solvents. Water may not be the suitable candidate for creating a nanoscale restricted geometry supposing the materials synthesized in these reverse micellar systems were not soluble in aqueous medium.

There have been many investigations regarding the methanol/AOT/hydrocarbon reverse micelles [1,11,15–21]. For example, Sarkar and co-workers have reported their efforts on solvation dynamics of several coumarin probes in methanol-based reverse micelles. In their study, the $\omega$ dependence of solvation time is observed in methanol/AOT/n-heptane system for all the probes coumarin 153, coumarin 152, coumarin 152 A, coumarin 490, and coumarin 480 [11,17–20]. Moreover, they have probed the structure of methanol and AOT in RMs by Fourier transform infrared (FTIR) spectroscopy and DLS measurements [6]. Their work certainly proves the existence of stable methanol/AOT/n-heptane reverse micelles, and the size of the reverse micelles changes little with the increasing $\omega$ value. Venables et al. reported the measurement of the O-H librational band in nanoscopic pools of methanol confined within methanol/AOT/isooctane reverse micelles [21]. In the RMs the O–H librational band shifts to lower frequency with increasing $\omega$, while in methanol/isooctane binary mixtures the band did not shift. They concluded that methanol resides in reverse micelles [21]. Recently, Lu et al. investigated the formation of methanol-containing AOT RMs in n-heptane solvents using IR125 as a probe [1]. Their results revealed by photophysics of IR125

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*Abbreviations:* C153, coumarin 153; RMs, reverse micelles; DLS, dynamic light scattering; C343, coumarin 343; FTIR, Fourier transform infrared; AOT, sodium bis(2-ethylhexyl)sulfosuccinate; M, mol/L; $\lambda_{em}$, maximum emission wavelength; $\lambda_{abs}$, maximum absorption wavelength; TCSPC, time-correlated single photon counting; $\Phi_f$, fluorescence quantum yield.

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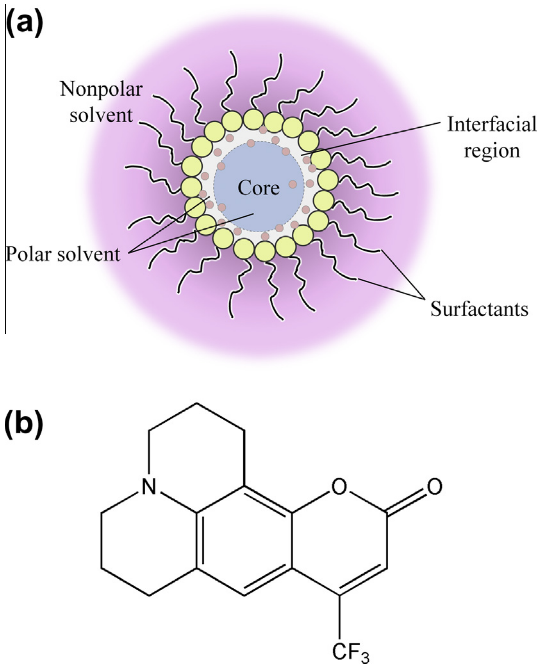

**Fig. 1.** (a) Reverse micelle structure. (b) Structure of coumarin 153.

proved that methanol can be effectively encapsulated by AOT in n-heptane solvents to form stable methanol/AOT/n-heptane RMs [1].

However, some other researchers suggested that whether methanol contained reverse micelles can exist stably is still uncertain. Riter et al. reported the AOT microemulsions that contain methanol as the polar phase for the first time using dynamic light scattering (DLS) and spectroscopy of coumarin 343 (C343) [15]. They found that the RMs maintained a small size even as $\omega$ ($\omega$ = [methanol]/[AOT], it is the ratio of molar concentration of methanol to AOT) was increased [15]. Levinger et al. suggested that one of the most important properties is that the size of the RMs depends upon the amount of polar solvent [22,23]. Considering the methanol contained nanoparticles did not support the swelling law, they suggested that the methanol does not reside encapsulated inside a RMs structure [23]. Shirota has studied the solvation dynamics of methanol and acetonitrile in RMs by the photophysics of C343 [16]. The solvation dynamics of methanol in RMs becomes faster with a larger ratio of polar solvent to surfactant ($\omega$) of micelles. However, the $\omega$ dependence of the solvation dynamics of acetonitrile in RMs is not observed. They ascribed this difference to the presence of the intermolecular hydrogen-bonding network in methanol/AOT/heptane system [16]. However, Levinger and co-workers proposed that C343 is probably stabilized from the methanol or acetonitrile dissolved in the hydrocarbon solvent, which is the similar situation with the preferential solvation observed for C343 in acetonitrile/benzene mixtures [23,24]. Recently, Garciá-Flores et al. demonstrated that when both methanol and water are present in solution, AOT micelles definitively favor the solubilization of water over methanol [25]. Accordingly, Levinger and co-workers suggested that although methanol in AOT/hydrocarbons forms clear solutions, these mixtures do not present true reverse micelles [23].

Since there are some controversial reports on the existence of methanol-based AOT reverse micelles, it will be significant to make great efforts on this issue. Rather than RMs, some researchers indicate that the systems including AOT/alkane and methanol are better defined as a bicontinuous medium without a polar core and interfacial structure [23], which is similar to the binary mixture of methanol/alkane. Therefore, it will be a valid method to explore dynamic and photophysical properties of probe molecules in methanol/AOT/alkane microemulsions and methanol/alkane binary mixture, and then make comparison of the two systems to verify whether the RMs can form or not. The solvation dynamics of coumarin 153 (Fig. 1b) in reverse micelles and alcohol/alkane binary mixture have been reported by Hazra et al. [18] and Cichos et al. [26] In this work we have compared the photophysical properties of coumarin 153 in methanol/AOT/n-heptane reverse micelles and methanol/n-heptane binary mixture by means of steady-state absorption, fluorescence and time-resolved fluorescence spectroscopies. The spectral behaviors of coumarin 153 proved that the methanol can be effectively encapsulated by AOT in n-heptane solvents to form stable reverse micelles.

## 2. Experimental section

The coumarin 153 (C153) was purchased from Exciton. AOT (sodium bis(2-ethylhexyl)sulfosuccinate) was purchased from Aladdin Reagent and used without further purification. Methanol and n-heptane of high-performance liquid chromatography grade were purchased from Tianjin Kemiou Chemical Reagent and used as supplied. The methanol/AOT/n-heptane reverse micelles solutions are formed by dissolving a certain amount of solid AOT in n-heptane with the concentration of AOT maintained at 0.09 M (mol/L) in all samples [27]. Then, methanol solvent is added to the solutions to obtain the appropriate value of $\omega$, where $\omega$ = [methanol]/[AOT]. In our measurements, the $\omega$ value is varied from 0 to 20. We defined these RMs systems with $\omega$ = 0, 0.5, 1, 2, 4, 6, 10, 14, 20 as P0, P0.5, P1, P2, P4, P6, P10, P14, P20, respectively. The solutions are then thoroughly shaken and sonicated for 5 min to obtain a transparent, homogenous and thermodynamically stable solution [27].

The methanol/n-heptane binary mixtures are prepared by adding methanol solvent to n-heptane solvent via volumetric method. The mole fraction of methanol $w$ is 0.013, 0.026, 0.052, 0.078, 0.13, 0.182, and 0.26, respectively. We defined these binary mixture systems P1', P2', P4', P6', P10', P14', and P20' respectively. It is noteworthy that we set the methanol content in P1' the same with P1 in order to make comparison of photophysics of C153 in these two environments conveniently. The only difference between P1 and P1' is that there is a measured amount of AOT in P1 while in P1' there is not. The same situation happens in other samples P2, P2'; P4, P4', etc. In all cases concentration of C153 is kept as $4 \times 10^{-5}$ M.

The UV–vis absorption spectra were obtained using an HP 8453 spectrophotometer. The steady-state fluorescence and time-resolved fluorescence decays were recorded on a Horiba Jobin Yvon FluoroMax-4 spectrofluorometer. The time-resolved fluorescence decays were recorded using the time-correlated single photon counting (TCSPC) method. The data were fitted to multiexponential functions after deconvolution of the instrument response function using DAS6 v6.4 data analysis software provided by Horiba Instruments.

## 3. Results and discussion

### 3.1. Steady-state absorption spectra

The representative absorption spectra of C153 in methanol/AOT/n-heptane systems are shown in Fig. 2. C153 has an absorption peak at 424 nm in methanol. In n-heptane it has two absorption peaks at 392 nm and around 410 nm, though the peak at 392 nm has maximum absorbance. When 0.09 M AOT and