



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Dansyl-labeled anionic amphiphile with a hexadecanoic carbon chain: Synthesis and detection for shape transitions in organized molecular assemblies



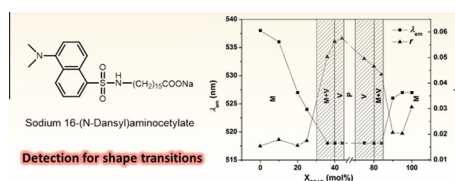
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HIGHLIGHTS

- A dansyl-labeled anionic amphiphile with a hexadecanoic carbon chain was synthesized.
- The synthesized amphiphile can be used to differentiate micelle and vesicle.
- The fluorescence anisotropy can detect the micellar growth efficiently.
- The synthesized amphiphile is a better fluorescence probe than pyrene and DPH.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 18 September 2014

Received in revised form 22 November 2014

Accepted 25 November 2014

Available online 25 December 2014

Keywords:

Fluorescence probe

Dansyl

Aggregates transition

Micellar growth

ABSTRACT

The probing properties of a new fluorophore-labeled anionic surfactant, sodium 16-(N-dansyl)aminocetate (16-DAN-ACA) were investigated systematically in molecular assemblies, especially in the transitions between micelles and vesicles. 16-DAN-ACA can efficiently differentiate the two different aggregate types in mixed cationic and anionic surfactant systems. The fluorescence anisotropy of 16-DAN-ACA was found to be sensitive for directly detecting the micellar growth in micelles containing oppositely charged surfactants; both cationic cetyltrimethylammonium bromide (CTAB) systems and anionic sodium dodecyl sulfate (SDS) systems were studied. The results indicated that the 16-DAN-ACA is a good fluorescent probe for differentiating the different aggregates, and even more can be used to detect the micellar growth.

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Introduction

Recently, different organized molecular assemblies have attracted more attention, such as spherical and rod-like/worm-like micelles, vesicles and lamellar phases, due to their special properties and applications [1–11]. Therefore, identifying how to characterize the transitions of different aggregates is becoming more and more important. Because of their ability of providing the straightforward images and detailed size information about the aggregates, electron microscopy and light scattering become two of

the most popular characterizing strategies. However, in most cases, these techniques can only give limited information about the aggregates at the molecular level. New techniques need to be developed and used to solve the new problems.

Fluorescence spectroscopy is well-known to provide more detailed information at the molecular level. For example, fluorescence probes are highly sensitive to their local environment such as micropolarity, and they have multiple useful photophysical parameters like fluorescence intensity, lifetime and anisotropy, excimer/exciple formation, etc. Therefore, fluorescence probe techniques have been extensively employed to investigate the formation and transition of aggregates [11–15]. In order to ideally probe organized molecular assemblies, the desired fluorophores

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should have attractive features like being sensitive to its molecular packing. Pyrene [16] and 1,6-diphenyl-1,3,5-hexatriene (DPH) [17,18] are two commonly used fluorescence probes due to their high efficiency in the measurement of micropolarity and microviscosity, respectively. However, the location of the kind of fluorescence probe in various aggregates is removable and unknown. Therefore, the variation of their related fluorescence parameters is usually the combined contribution from both the transition of aggregates and the change of the location of probes. This problem may be expected to be solved using fluorophore-labeled amphiphile. This kind of fluorescence probe, when used as part of the surfactant, can take part in the formation of aggregates so as to provide more reliable information. In fact, some fluorophore-labeled amphiphiles have been used to detect the related physical properties of various aggregates [19–29]. However, most of these studies focused on micelle [19–23] or membrane [24–28] systems.

In our previous work, a fluorescent group, dansyl, which shows representative character of intramolecular charge transfer (ICT), has been attached to the tail of an anion surfactant (12-aminolauric acid) to form a surfactant-fluorescence probe sodium 12-(*N*-dansyl)aminododecanate (12-DAN-ADA) [30,31]. We found that 12-DAN-ADA can efficiently differentiate two different kinds of aggregates (micelles and vesicles) in the mixed cationic and anionic surfactant systems, as well as in the double-chain cationic surfactant systems based on the polarity- and viscosity-dependence of the dansyl group. Further studies demonstrated that 12-DAN-ADA is a more efficient probe of transitions between micelles and vesicles than those commonly used fluorescence probes, such as pyrene and DPH [30].

In order to investigate the effect of the solubility of the surfactant-fluorescence probes on the efficiency of probing the transitions between micelles and vesicles, in the present work, we extended the alkyl chain of 12-DAN-ADA to prepare another surfactant-fluorescence probe with longer hydrophobic chain, sodium 16-(*N*-dansyl)aminocetate (16-DAN-ACA), and measured its corresponding fluorescence parameters in the transitions of micelles and vesicles. Although, the chemical structures of 12-DAN-ADA and 16-DAN-ACA are very similar, the procedure for obtaining the 16-DAN-ACA is laborious. As expected, the corresponding fluorescence parameters (fluorescence anisotropy and emission maximum) of 16-DAN-ACA can also reflect efficiently the transitions between micelles and vesicles. All the results demonstrated that the solubility of the surfactant-fluorescence probes did have an effect on the efficiency of probing the transitions between micelles and vesicles.

Experimental section

Chemicals

5-Cyclohexadecen-1-one (>97.0%) was purchased from TCI. Dansyl chloride (99%), pyrene (98%), 1,6-diphenyl-1,3,5-hexatriene (DPH, 98%), and sodium dodecyl sulfate (SDS, 99%) were purchased from Acros. Triton X-100 was from E. Merck Co. (Darmstadt). Branched-chain sodium dodecylbenzenesulfonate (SDBS), hydroxylamine hydrochloride (NH₂OH·HCl), and Pd–C catalyst were obtained from Beijing Chemical Co. All the above reagents were used as received. Deionized water was treated with KMnO₄ over 24 h and distilled before use.

Dodecyltrimethylammonium bromide (DTAB), dodecyltriethylammonium bromide (DEAB), and cetyltrimethylammonium bromide (CTAB) were synthesized from *n*-alkyl bromide and corresponding trialkylamine [32]. The three products were recrystallized five times from acetone, acetone/diethyl ether, and acetone/ethanol, respectively. The purity of all the synthesized cationic surfactants was examined, and no surface tension mini-

mum was found in the surface tension curve. All other reagents were of analytical grade at least.

General instruments

¹H NMR spectra were recorded on a Mercury Plus 300 M (USA) or a ARX-400 M (Swiss) instrument, and chemical shifts are reported in parts per million relative to TMS in proton spectra. Elemental analyses of C, H, and N were conducted on an Elementar Vario EL elemental analyzer (Germany). MS results were conducted on a ZAB-HS magnetic mass spectrometer (Micromass, UK).

Fluorescence measurements

All of the fluorescence measurements were performed on a time-correlated single-photon-counting FLS 920 fluorescence spectrometer (Edinburgh) at room temperature (23–25 °C) except where noted in the text. Samples were excited at 337 nm. The stock solutions (1.0 × 10^{−4} M) of 16-DAN-ACA were prepared in ethanol. A certain amount of stock solution was added to a tube and heated slightly to remove some solvent. Then the final concentration of the probes was adjusted by adding an appropriate amount of the analyte solutions. A FLS 920 fluorescence spectrometer equipped with filter polarizers that use the L-format configuration using a 1-cm quartz cuvette was used for fluorescence depolarization measurements. An average of three fluorescence anisotropy values was recorded.

Synthesis and characterization of 16-DAN-ACA

The synthetic route of 16-DAN-ACA was shown in Scheme 1, in which 16-aminohexadecanoic acid (compound 6) was synthesized by adopting a modified literature method [33].

Synthesis of cyclohexadecanone (compound 2)

5-Cyclohexadecen-1-one (compound 1, 5 g, 21.2 mmol) was dissolved in ethanol (45 mL). Pd–C catalyst (1%, w%) was added to the solution of compound 1 while stirring vigorously at room temperature under a H₂ atmosphere. Stirring was continued for a total of 1.5 h. The resulting solution was filtered and the solvent was removed to give compound 2 as a white solid. ¹H NMR (CDCl₃/Me₄Si, 400 MHz) δ (ppm): 1.29 (s, 22H, $-(CH_2)_{11}-$), 1.62 (m, 4H, $-CH_2CH_2COCH_2CH_2-$), 2.40 (t, 4H, $-CH_2COCH_2-$).

Synthesis of cyclohexadecanone oxime (compound 3)

Compound 2 (5.8 g, 24.4 mmol) was dissolved in methanol (140 mL). NH₂OH·HCl (3.5 g, 50.4 mmol) and NaHCO₃ (3.5 g, 41.7 mmol) were added to the stirred methanol solution. The mixture was stirred and refluxed for 5 h. After that, the mixture was brought to room temperature and stirred overnight. The methanol phase was added in water (30 mL) and extracted with CHCl₃ (3 × 80 mL). The CHCl₃ phase was dried by anhydrous sodium sulfate overnight and filtered. The filtrate was evaporated under reduced pressure and the residue was dried in vacuum to give compound 3 as a white solid. ¹H NMR (CDCl₃/Me₄Si, 400 MHz) δ (ppm): 1.30 (s, 22H, $-(CH_2)_{11}-$), 1.51 (m, 4H, $-CH_2CH_2CNOHCH_2CH_2-$), 2.18 (t, 2H, $-CH_2CNOH$), 2.36 (t, 2H, $-CH_2CNOH$).

Synthesis of cyclohexadecanone-oxime *p*-toluenesulfonate (compound 4)

Compound 3 (5.9 g, 23.3 mmol) was dissolved in the mixture of CH₂Cl₂ (240 mL) and pyridine (40 mL). TsCl (7.6 g, 39.9 mmol), dissolved in CH₂Cl₂ (1200 mL), was added drop-wise to the above solution while stirring vigorously at 0 °C. After addition was completed, the mixture was brought to room temperature and stirred overnight. The CH₂Cl₂ layer was extracted with hydrochloric acid

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