



Determination of critical micelle concentration of dendritic surfactant synthesized via a selective ring-opening addition reaction



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ABSTRACT

An azetidine-2,4-dione was applied to synthesize dendrons with four carbons in the end ([G-0.5]-C4 and [G-1]-C4) via a selective ring-opening addition reaction, which was subsequently extended to obtain a dendritic surfactant ([G-1]-C4 surfactant) by acidification. The dendrons were characterized by Fourier transform infrared (FT-IR), ¹H nuclear magnetic resonance (¹H NMR), elemental analyzer (EA), and fast atom bombardment mass spectrometry (FAB MS). The dendritic surfactant, with a cationic head and branched hydrophobic C4 tails, was dissolved in 2 wt.% dimethyl sulfoxide (DMSO) aqueous solution for the determination of critical micelle concentration (CMC) by fluorescence and electrical conductivity measurements. The resulted CMC values were very close within measurements, ca. 0.013–0.05 mM. Transmission electron microscopy (TEM) and zeta potential measurement also provided an evidence of micelle formation and shape. Moreover, anionic dyes were adsorbed onto the micelles successfully to confirm the positive charge of [G-1]-C4 surfactant.

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1. Introduction

Researches on dendrimers have received great attention due to their regularly-ordered and highly-branched structures. The molecular size, shape, and nature of dendrimers can be precisely controlled, and they could consist of multiple functional groups at the periphery via proper design. Accordingly, dendrimers are found useful in many fields such as nanoscale applications [1,2], liquid–crystalline systems [3,4], catalysis [5,6], self-assembly systems [7–10], electro-optical materials [11–13], drug delivery [14,15], and silicate-intercalated nanocomposites [16,17].

A bifunctional compound, 4-isocyanate-4'-(3,3-dimethyl-2,4-dioxo-acetidino) diphenyl methane (IDD), was adopted for the synthesis of dendrons in a previous study of ours [17]. This compound has special reactivities of both isocyanate and azetidine-2,4-dione groups toward amines. The isocyanate group is more reactive than azetidine-2,4-dione group, and it reacts quickly with amine, hydroxyl, and other reactive hydrogens. Although the azetidine-2,4-dione group

is less reactive, it is only selective to react with primary aliphatic amines to form malonamide linkages [18]. Based on the above special reactivities, alcohol of various carbon-chain lengths could be used in the first step and followed by triamine (ring-opening reaction) and IDD reactions in turn to prepare a series of dendrons. In that previous work [17], 1-decanol and diethyltriamine (DETA) were employed to obtain dendrons with terminal C10 groups. The resultant dendrons were subsequently acidified to form long-carbon-chain dendritic surfactants, and hence applied to the intercalation of montmorillonite clays [17].

To extend the preparation and investigation of this type of dendritic surfactants, an alcohol with a shorter carbon chain, 1-butanol, is chosen in the current study for the synthesis of dendrons with terminal C4 groups. By adding strong acid to interact with the secondary amine group at the focal point of the dendron, the related dendritic surfactant with terminal C4 groups could be obtained. It is interesting to study the solution features of surfactant such as critical micelle concentration (CMC) for further exploration of its application [19]. As the surfactant concentration in aqueous solution increases, the hydrophobic segments aggregate easily to form micelles. Micelles are hydrophobic inside and hydrophilic outside in water. Accordingly, it can solubilize nonpolar materials in the hydrophobic region. In this paper, pyrene and 2-anilinonaphthalene (2-AN) are selected as the fluorescence probes to determine the CMC of the prepared dendritic surfactant because both of them are nonpolar and strongly sensitive to the polarity of their surroundings [20,21]. In order to compare

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the results, electrical conductivity is also used for CMC determination based on the ionic feature of the prepared dendritic surfactant. In addition, other measurements such as transmission electron microscopy (TEM), zeta potential, and anionic dye adsorption are conducted to further confirm the formation and charge property of dendritic surfactant micelles.

2. Experimental

2.1. Materials

Methylene di-*p*-phenyl diisocyanate (MDI), triethylamine (TEA), isobutryl chloride, 1-butanol, DETA, and 2-AN were purchased from Sigma-Aldrich and Acros without purification. Pyrene was supplied by TCI. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone prior to use. Dimethyl sulfoxide (DMSO), hexane, ethyl acetate, and other solvents were analytical grade and used as received. Tinopal® CBS-X (M.W.=518.6), Erythrosine (M.W.=897.86), Methylene blue (M.W.=319.85), and Methyl violet 2B (M.W.=393.95) were bought from BASF, ICN, and Sigma-Aldrich.

2.2. Synthesis and characterization of dendrons

2.2.1. Equipment

Fourier transform infrared (FT-IR) spectra were recorded on a Horiba FT-720 spectrophotometer. The dried sample (1 wt.%) was mixed in KBr pellet. ^1H nuclear magnetic resonance (^1H NMR) spectra of the dendrons were obtained from a Varian Gemini-300 FT-NMR spectrometer with DMSO- d_6 . Fast atom bombardment mass spectrometry (FAB MS) analysis was conducted by a JEOL JMS SX/SX 102A mass spectrometer. FAB MS was equipped with the standard FAB source and the upper limit of measurable molecular weight was 2000. Elemental analyzer (EA) was taken on Elementar Vario EL III.

2.2.2. Synthesis of IDD

Synthesis of IDD was performed by the following procedures which have been described elsewhere [17,18,22,23]. TEA (37 g, 0.37 mol) in xylene (100 mL) was added to a solution of MDI (100 g, 0.4 mol) and isobutryl chloride (32 g, 0.3 mol) in xylene (250 mL). The mixture was stirred and refluxed for 4 h, then cooled to room temperature. The resulting solution was filtered to remove the quaternary ammonium salt and concentrated to 50 mL. The product was then crystallized from cyclohexane to obtain IDD (20.4 g, 21.3%) as a white powder. (Found: C, 70.76; H, 5.01; N, 8.41%. $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_3$ requires C, 71.24; H, 5.03; N, 8.74%); FT-IR spectrum ($\nu_{\text{max}}/\text{cm}^{-1}$): 2268 (N=C=O), 1853 (C=O), 1745 (C=O). ^1H NMR δ_{H} (200 MHz; CDCl_3 ; Me_4Si) 1.4 (6H, CH_3), 1.31(2H, Ph- CH_2 -Ph), 6.91–7.70 (8H, Ph-H). m/z (FAB) (M^+ , 320).

2.2.3. Synthesis of [G-0.5]-C4 dendron

IDD (4.75 g, 14.82 mmol) was dissolved in dry THF (20 mL), and 1-butanol (1 g, 13.49 mmol) was subsequently added to the solution. The mixture was stirred and reacted at 65 °C in a nitrogen atmosphere for 2 h. The solvent was evaporated and the product was purified by silica gel chromatography with hexane/ethyl acetate (2:1) to get [G-0.5]-C4 (4.99 g, 93%) as yellow powder. (Found: C, 69.66; H, 6.25; N, 7.46%. $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_4$ requires C, 70.0; H, 6.6; N, 7.1%); FT-IR spectrum ($\nu_{\text{max}}/\text{cm}^{-1}$): 3319 (NH), 1857 (C=O), 1743 (C=O), 1701 [(NH)C=O(O)]. ^1H NMR δ_{H} (300 MHz; DMSO- d_6) 0.9 (3H, CH_3), 1.4 (6H, CH_3), 1.58 (2H, CH_2), 3.86 (2H, Ph- CH_2 -Ph), 4.05 (2H, CH_2), 7.07–7.63 (8H, Ph-H). m/z (FAB) (M^+ , 394).

2.2.4. Synthesis of [G-1]-C4 dendron

DETA (0.4 g, 3.88 mmol) was added to a solution of [G-0.5]-C4 (3.13 g, 7.94 mmol) in dry THF (12 mL). The solution was stirred and reacted at 70 °C under nitrogen for 2 h. The solvent was evaporated

and the product was purified by recrystallization from an excess of acetone to get [G-1]-C4 (2.62 g, 76%) as yellow powder. (Found: C, 66.14; H, 7.21; N, 10.64%. $\text{C}_{50}\text{H}_{65}\text{N}_7\text{O}_8$ requires C, 67.32; H, 7.34; N, 10.99%); FT-IR spectrum ($\nu_{\text{max}}/\text{cm}^{-1}$): 3324 (NH), 1700 [(NH)C=O(O)], 1649 [C=O(NH)]. ^1H NMR δ_{H} (300 MHz; DMSO- d_6) 0.89 (6H, CH_3), 1.36 (12H, CH_3), 1.56 (8H, CH_2), 2.55 (4H, CH_2), 3.11 (4H, CH_2), 3.78 (4H, Ph- CH_2 -Ph), 4.05 (4H, CH_2), 7.07–7.59 (8H, Ph-H). m/z (FAB) (M^+ , 892).

2.3. Preparation and characterization of dendritic surfactant

2.3.1. Preparation of [G-1]-C4 surfactant

[G-1]-C4 (3.91 g, 4.38 mmol) was dissolved in dry THF (20 mL) and stirred at 70 °C. HCl (37% in water, 0.434 g, 4.4 mmol) was added to the [G-1]-C4 solution. The resulting solution was filtered and dried under vacuum to get the acidified [G-1]-C4 surfactant.

2.3.2. CMC determination

For CMC measurements, the [G-1]-C4 surfactant samples were prepared from 0.0001 to 1 mM in 2 wt.% DMSO aqueous solution. For the fluorescence measurements, pyrene and 2-AN were adopted as nonpolar probes. In the case of pyrene as fluorescence probe, 0.1 mL of 6.0×10^{-6} M pyrene in acetone was evaporated in a vial. Then, 1 mL of surfactant sample was added into the vial and kept at room temperature for 24 h. Consequently, the surfactant sample with a constant pyrene concentration of 6.0×10^{-7} M was prepared [24]. The excitation was induced at 335 nm and the emission was recorded in the range of 350–500 nm on a Hitachi F-2500 fluorescence spectrophotometer [24]. Five characteristic peaks were observed in the pyrene emission spectrum and the intensity ratio of the first to the third peak (I_1/I_3) was evaluated [20,21,24].

In the case of 2-An as fluorescence probe, 0.1 mL of 10^{-4} M 2-AN in ethanol was evaporated in a vial. Next, 1 mL of surfactant sample was added into the vial and kept at room temperature for 24 h for preparing the surfactant sample with a constant 2-AN concentration of 10^{-5} M. The excitation wavelength of 2-AN was 294 nm and the emission was in the range 310–550 nm [25].

The electrical conductivity of dendritic surfactant solution was detected at 25.0 ± 0.5 °C by a conductivity meter (Eutech Cyberscan CON 11) and repeated three times to get an average. The uncertainty within the measurements was less than $\pm 0.2\%$ in the $\mu\text{S cm}^{-1}$ scale.

2.3.3. Micelle morphology and dye adsorption

The micelle morphology of dendritic surfactant was observed by TEM (JEOL JEM-1400), and its zeta potential was measured by Malvern Zeta-sizer Nano-ZS instrument.

As for batch dye adsorption experiment, four kinds of dyes were adopted: Tinopal® CBS-X, Erythrosine, Methylene blue, and Methyl violet 2B. Tinopal CBS-X and Erythrosine are negatively charged in water whereas Methylene blue and Methyl violet 2B are positively charged. In this experiment, 10 mL of 10 ppm dye in water was mixed with 50 mg of [G-1]-C4 surfactant in a container at room temperature to reach equilibrium for 2 h. UV-vis spectrophotometer (Shimadzu UV-1601) was used to detect the dye concentration in water. The adsorption percentage was determined by $(1 - \text{dye concentration remained after adsorption}/\text{initial concentration}) \times 100\%$.

3. Results and discussion

3.1. Characterization of dendrons

The schematic drawing of synthesis of dendrons and dendritic surfactant is depicted in Fig. 1. In the first step, IDD and 1-butanol were reacted at 65 °C to create [G-0.5]-C4. As shown in Fig. 2, the FT-IR peak at 2268 cm^{-1} (N=C=O isocyanate) disappeared while the peak at 3319 cm^{-1} (NH) and 1701 cm^{-1} (C=O stretching of urethane)

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