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Aggregation behavior of an amino acid-derived bolaamphiphile and a conventional surfactant mixed system

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ABSTRACT

The aggregation behavior of a mixed system consisting of a novel histidine-derived bolaamphiphile 1,12-dihistidine diaminododecane (H_2D) and the conventional surfactant dodecyltrimethylammonium bromide (DTAB) has been investigated. The microstructure of the H_2D/DTAB mixture has been identified by means of negative staining-TEM, dynamic light scattering (DLS), fluorescence spectra, FT-Raman spectroscopy, and differential scanning calorimetry (DSC). Rich morphologies are observed in the mixed system of H_2D and DTAB over a relatively wide proportion range. At $C_{DTAB}/C_{H2D} < 12:1$, vesicles are formed in the mixed system. At $C_{DTAB}/C_{H2D} > 12:1$, vesicles and tube-like aggregates coexist, and more tube-like aggregates appear with further increase of C_{DTAB}/C_{H2D}. The formation mechanisms of the aggregation with various morphologies at different C_{DTAB}/C_{H2D} ratios are further deduced.

1. Introduction

Bolaamphiphiles with two hydrophilic heads connected by one or two hydrophobic chains were synthesized about 30 years ago. Since then, bolaamphiphiles have drawn much attention for their many interesting properties [1–5]. Bolaamphiphiles give rise to aggregates such as micelles, monolayer membranes, multilayered sheets, and vesicles, which facilitate the practical application of bolaamphiphiles as biomembrane models, drug-delivery systems, and microreactors [6–9].

Amino acid-derived bolaamphiphile, in particular, seem to have the additional potential of being biologically and environmentally amiable [2,10,11]. Histidine is an extremely interesting molecule in addition to its important biological properties [12–15]. It has been used in supramolecular assemblies and crystal engineering of nonlinear optical crystalline materials because of the presence of intermolecular and intramolecular hydrogen bond [16,17]. Furthermore, imidazole has the properties of complexing coordination and conjugated acid–base. Thus, it is known as a biological catalyst and biological ligand [18–20]. In this work, a new bolaamphiphile, derived from the amino acid histidine, was synthesized. The compound 1,12-dihistidine diaminododecane (H_2D) has one saturated C_{12} alkyl chain and two histidine groups (Scheme 1).

Products containing mixed surfactants are often used for various practical purposes, since the mixed system can facilitate the appearance of a wide variety of mixed aggregates [21–26]. In general, the aggregate structures are related to the rearrangement of surfactants in the aggregates for a mixed surfactant system, which is different from the case with surfactants on their own.

In this work, the aggregation behavior of mixtures of the novel histidine-derived bolaamphiphile 1,12-dihistidine diaminododecane and the conventional surfactant dodecyltrimethylammonium bromide (DTAB) has been studied systematically. Rich morphologies are observed in the mixed system of H_2D and DTAB over a relatively wide proportion range. Here, to achieve the formation of microstructures with different morphologies, in addition to hydrophobic effects and hydrophilic interactions, hydrogen bonding between histidine groups and the stacking interactions of imidazole rings are very important factors in the self-assembly of amphiphile mixed systems. The study of these aggregates can contribute to fundamental research with the objectives of preparing "designer assemblies" and of their potential biological applications.

2. Experimental

2.1. Materials

1,12-Diaminododecane was CP grade with a purity of 98% obtained from Alfa Aesar Co. L-Histidine was obtained from Shanghai Biochemistry Reagent Co., China. Dodecyltrimethylammonium bromide was purchased from Sigma and used without further purification. Pyrene (99%) was obtained from Aldrich. All other reagents used were of analytical grade from Shanghai Chemical Reagent Company, and ultrapure Millipore water (18.2 MΩ) was used as solvent.

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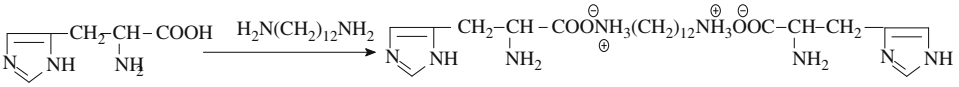

Scheme 1. Synthetic path for H_2D.

2.2. Synthesis of H_2D

H_2D was synthesized according to the following reaction scheme (Scheme 1) [27]. L-Histidine (1.552 g, 10 mmol) and a suspension of 1,12-diaminododecane (1.002 g, 5 mmol) in 50 mL of water were introduced into a flask equipped with a magnetic stirred bar. After reaction for 48 h, excess reactants were removed via centrifugation. The concentrated product was further vacuum-distilled until there was no water to evaporate. The final product H_2D was collected after anhydrous ethanol was used to extract the products and was removed by water bath at 60 °C. The yield of H_2D was about 52%. The structure was confirmed by IR and ^1H NMR spectra.

2.3. Sample preparation

Samples were prepared by mixing the appropriate amount of individual surfactant solutions and carefully homogenizing afterward. For every sample, the H_2D concentration was kept constant (0.4 mM), whereas the composition of the DTAB was varied by changing the molar fraction of DTAB, defined as $X_{DTAB} = n_{DTAB}/(n_{DTAB} + n_{H2D})$.

2.4. Negative-staining TEM

A drop of the sample solution (~10 μL) was placed on a carbon-coated Formvar 200 mesh copper grid. The sample was allowed to stand for 5 min, and then any excess solution was removed by filter paper. The samples were then negatively stained with 1% (w/v) phosphortungstic acid and allowed to dry. The samples were last visualized under a Philips Tecnai-12 transmission electron microscope operating at 120 kV and each experiment was repeated two or more times.

2.5. FT-Raman

The spectroscopic measurements were investigated by Renishaw Raman Microscope. The excitation was 532 nm, and the exposure time was 10 s.

2.6. Differential scanning calorimetry (DSC)

Calorimetric experiments were performed with Netzsch DSC-204 F1. DSC thermograms of the H_2D/DTAB mixed system were obtained from 10 to 100 °C at a scan rate of 1.5 °C/min.

2.7. Dynamic light-scattering (DLS)

Dynamic light-scattering measurements were made at 25.0 ± 0.1 °C and at a scattering angle of 90° to the incident beam, using an ALV 5022 laser light-scattering instrument equipped with a 22 mW He–Ne laser at 632 nm (JDS model 1145P) in combination with an ALV-5000 digital correlator covering a sampling time range of 1.0 μs to 1000 ms. Experiment duration was in the range of 5–10 min, and each experiment was repeated two or more times.

2.8. Microcalorimetry

Heat of dilution was measured using a VP-ITC titration microcalorimeter from MicroCal Inc. (Northampton, MA) at (25 ± 0.1) °C. Experiments were made titrating concentrated H_2D into water. Solutions were prepared in phosphate buffer and were degassed before use. The reference cell was filled with deionized water. H_2D solution was titrated into the sample cell as a sequence of 50 injections of 5×10^{-6} dm^3 aliquots. The duration of each injection was 10 s, and the time delay (to allow equilibration) between successive injections was 240 s. The contents of the sample cell were stirred throughout the experiment at 307 rpm to ensure thorough mixing. Raw data were obtained as a plot of heating rate (μcal s^{-1}) against time (min). These raw data were then integrated to obtain a plot of observed enthalpy change per mole of injected H_2D (ΔH_{obs}, kcal mol^{-1}) against H_2D concentration (mM).

2.9. Steady-state fluorescence

Steady-state fluorescence experiments were performed with a RF-5301 luminescence spectrometer (Japan Shimadzu Company) equipped with a thermostated water-circulating bath. Pyrene was used as the probe to determine the microenvironmental polarity of H_2D/DTAB aggregates by observing its fluorescence fine structure. The emission spectra were measured in the range of wavelength 350–600 nm with the excitation wavelength at 338 nm. The pyrene concentration was 1.0×10^{-6} M.

3. Results and discussion

3.1. Aggregation behavior of H_2D

The aggregation behavior of the solution of H_2D alone is determined by conductivity, isothermal titration microcalorimetry, and DLS measurements. The titration of the concentrated H_2D into water leads to the observation of an inflection in the ITC isotherm plot of molar enthalpy change against H_2D concentration (Fig. 1A). The position of this inflection (3.3×10^{-5} M) corresponds to the critical micellization concentration (cmc) of H_2D. Electrical conductivity plot against H_2D concentration is shown in Fig. S1 (Supplementary Material). The breakpoint in the curve (3.0×10^{-5} M) corresponds to the cmc of H_2D, which is consistent with the ITC results. The size distributions of H_2D micelle by DLS are shown in Fig. 1B. At 4×10^{-4} M H_2D (above cmc of H_2D), only one hydrodynamic radius distribution exists, and no other apparent hydrodynamic radius distributions indicating aggregates with a larger size are observed. The distribution centering at 1.78 nm corresponds to H_2D micelles.

3.2. Aggregation behavior of the H_2D/DTAB mixed system

According to our above results and some earlier studies, no large structures were expected to form from the individual H_2D and DTAB molecules except micelles [28,29]. To obtain aggregates with richer morphologies, the formation of microstructures in the mixed system of H_2D/DTAB was investigated at the fixed H_2D concentration of 4.0×10^{-4} M by varying the mixed molar ratios of C_{DTAB}/C_{H2D}. Notably, the DTAB concentration is below the critical