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Adsorption, aggregation and wetting behaviors of biodegradable surfactant: Perfluoropolyether quaternary ammonium salt

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ABSTRACT

A novel cationic fluorinated surfactant, (PFP-AI), was synthesized via amidation and quaterisation successively with perfluorinated acyl fluride (PFPF) as starting material. Their structure was analyzed by FT-IR, ^{1}H NMR and ^{19}F NMR. The TG indicated the PFP-AI possess thermal stability with initiation decomposition temperatures about 217 °C. The physicochemical properties of PFP-AI were studied systematically by equilibrium surface tension, dynamic surface tension, dynamic light scatting measurement (DLS) and transmission electron microscopy (TEM). The results revealed the PFP-AI exhibited high surface activity (γ_{cmc} = 16.4 mN/m) and could aggregate into vesicles at the concentration of 4.15 mmol/L. Furthermore, contact angle measurements demonstrated that PFP-AI exhibited efficient wettability on the hydrophobic surface.

Introduction

Fluorinated surfactant is a kind of surfactant with special function [1]. When the hydrogen atoms in the hydrophobic group of hydrocarbon surfactant are partially or completely substituted by fluorine atoms, such surfactants are called fluorinated surfactant [2]. Compared with conventional surfactant, fluorinated surfactant possess some unique physic-chemical properties: [3,4] lower surface tension, high thermally and chemical resistant, great wetting [5,6], oil repellent and water proof, and biologically inert. With its specific performance properties, the fluorinated surfactants are widely applied in different industries from mineral flotation [7] to biomedicine [8–10]. Owing to their excellent hydrophobic and oleophobic properties [11], fluorinated surfactants are generally applicable as water-proof and oil-repellent finishes for textiles [12,13]. The most common fluorinated surfactant is the perfluoroalkyl derivatives [14,15], such as perfluorooctane sulfonates (PFOS) [16] and perfluorooctanoic acids (PFOA) [17]. However, this long chain perfluoroalkyl group ($\geq$C$_7$) is too stable to be biodegraded within several years in the environment. And the PFOS/PFOA has been attributed to persistent organic pollutions (POPs), due to its persistence in environment and accumulation along the food chain [18], which is poisonous [17] to humans [19]. Besides the fluorinated surfactants with perfluoroalkyl carbon chains, especially the linear structure, has poor flexibility [20], relatively high Krafft point [21], and poor solubility [22].

Therefore, it is necessary to develop new type of fluorinated surfactants to replace PFOA/PFOS. The recent trend of PFOS/PFOA alternatives mainly changes the structure of fluorocarbon chain, including surfactants from short fluorocarbon chain or perfluoropolyether. Bodduri [23] synthesized a perfluorobutyl-substituted alkyl disulfonate derivative, which surface tension was 26.0 mN/m. Perfluoropolyethers [24], as a class of biodegradable fluorocarbons, are increasingly important. With oxygen heteroatoms inserted into the fluorocarbon chain, the fluorinated surfactant molecules become more elastic [25], biodegradability and low Krafft point. As a kind of environmental friendly, more biodegradability and safer [26] surfactants, it is more necessary to research perfluoropolyethers surfactants. However, perfluoropolyethers surfactants have been seldom reported.

In this work, a perfluoropolyethers quaternary ammonium salt was synthesized via a two-step reaction: [27] amidation and quaternization. Fourier transforms infrared spectroscopy (FT-IR), ^{1}H NMR and ^{19}F NMR spectra, surface tension analysis, contact angle (CA), dynamic light scatting measurement (DLS) and electron microscopy (TEM) methods were performed to investigate the structures and properties of this surfactant. The purpose of this study is to find out a novel and efficient green surfactant.

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Experimental

Materials

N,N′-Dimethyl-1,3-propyldiamine was obtained from Aladdin. 2,5-Bis(trifluoromethyl)-3,6-dioxaundecafluorononanoyl fluoride (PFPF) was supplied by Lisheng Reagent Biochemistry Technology Co., Ltd. (Guangdong, P.R. China). Diethyl ether, acetone and acetonitrile were all purchased from Tianjin Shentai Chemical Reagent Co., (Tianjin, P.R. China). Triethylamine was obtained from Tianjin Kemel Chemical Reagent Co., Ltd. (Tianjin, P.R. China). Methyl iodide and pyrene (99%) were purchased from Alfa Aesar. Water we used in all experiments was deionized water (18.2 MΩ).

Synthesis of perfluoropolyethers quaternary ammonium salt

The reactive intermediate based on 2,5-bis(trifluoromethyl)-3,6-dioxaundecafluorononanoyl fluoride (PFPF, 19.9 g, 40 mmol) and N,N′-dimethyl-1,3-propyldiamine (4.50 g, 44 mmol) were prepared with triethylamine (4.45 g, 44 mmol) as an acid binding agent, ether as solvent. The PFPF was added dropwisely into the round-bottom flask and vigorously stirred for 2 h at 0 °C under the protection of nitrogen, and then the solution was heated to 43 °C for 4 h. This amidation reaction produces a tertiary amine intermediate. Then the reaction solution was evaporated to remove the solvent, washed five times with deionized water, dried over anhydrous sodium sulfate, filtered, and dried under high vacuum. The intermediate was reacted subsequently with methyl iodide (5.68 g, 40 mmol) in acetonitrile at 40 °C to obtain the corresponding quaternary ammonium salts (PFP-AI). Crude compound PFP-AI was precipitated with acetone to get faint yellow solid (24.3 g, 85.2% yield). The melting point of the PFP-AI was 126 °C by micro melting point apparatus, which indicated the product in high purity.

Characterization

Fourier transform infrared spectroscopy (FT-IR) was confirmed by a Bruker Vertex-70 spectrometer. The PFPF was cast directly onto a KBr plate, while the product of quaternary ammonium salts (PFP-AI) was mixed with KBr powder for measurement. The ^{1}H NMR and ^{19}F NMR experiments were determined by a Varian INOVA-400 Hz spectrometer at 25 °C using CD_3COCD_3 as the lock solvent and CF_3CO_2H as the reference.

The thermal stability analysis of final product PFP-AI was characterized by thermogravimetric analysis (model HTG-3, Beijing Henven Scientific Instrument Factory, Beijing, China). The sample was heated from 20 °C to 500 °C with a heating rate of 10 °C/min in a nitrogen atmosphere at a flow rate of 50 mL/min. The purity was identified by melting point using X-5 (Guyi Yuhua Instrument and Meter Co., Ltd., Guyi, China)

Measurements

Equilibrium surface tension measurements

The equilibrium surface tension was determined by the De-Nuöy ring method using a KRUSS K12 (Krüss Company, Germany) Processor Tensiometer at (25.0 ± 0.1)°C. Before the measurements, the prepared solutions were stored for 24 h to keep equilibrium. The surface tension was measured three times in each concentration.

Dynamic surface tension measurements

The experiment data of dynamic surface tension (DST) was obtained by the maximum bubble pressure method using a Krüss BP100 bubble-pressure tensionmeter (Krüss Company, Germany, accuracy ± 0.01 mN/m) at (25.0 ± 0.1)°C.

Electrical conductivity measurements

The electrical conductivity was observed by a conductivity analyzer (model DDS-11A, Shanghai Leici-Chuangyi Instrument and Meter Co., Ltd., Shanghai, China). Before the measurements, each sample was put thermostatic water bath to control the temperature

Contact angle measurements

The compound PFP-AI's hydrophile was test with contact angle using Krüss DSA 25 instrument (Krüss Company, Germany). The wettability of the solution on Polytetrafluoroethylene (PTFE) film and paraffin film were tested. The temperature and environmental humidity were kept constant at (25.0 ± 0.1)°C, (50 ± 5)%, respectively.

Dynamic light scattering (DLS)

To investigate the effective diameter and size distribution of the PFP-AI aggregates in aqueous solution, dynamic light scattering (DLS) was performed with a Zeta Plus Paricle Size Analyzer instrument (Brookhaven, USA). The scattering angle was set to 90° for experiment. Sample solutions were pre-equilibrated for 5 h at (25.0 ± 0.1)°C.

Transmission electron microscopy (TEM)

The TEM was employed to observe the structures of the surfactant aggregates using negative staining techniques. The TEM investigation was performed with a JEM-1011 transmission electron microscope (Jeol Company, Japan) at an acceleration voltage of 100 kV. A drop of sample solution was covered on a carbon-coated copper grid and negatively stained with 2 wt% phosphotungstic acid. The aggregates were measured after stored in 25 °C for 2 and 90 days respectively.

Results and discussion

Synthesis and characterization of PFP-AI

The preparation of perfluoropolyethers quaternary ammonium salt was performed according to the two-step reaction as shown in Fig. 1. The chemical structures of reactant and product were identified by Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance spectroscopy (NMR).

Fig. 2 is the FT-IR spectra of products (PFP-AI) and raw materials (PFPF). From the infrared spectrum, it can be seen that the sharp and strong peak at 1236 cm^{-1} and around 1150 cm^{-1} are attributed to stretching vibrations of C—F and C—O—C, respectively. The

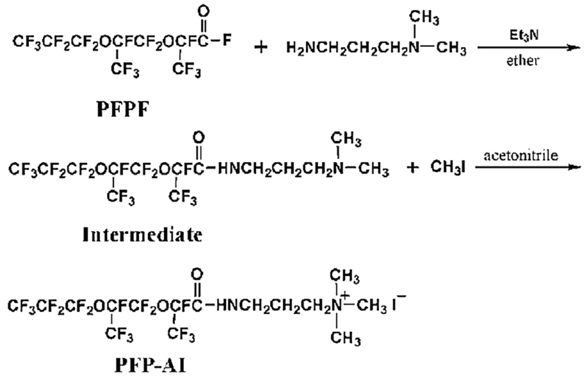

Fig. 1. Preparation of PFP-AI surfactant.

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