Journal of Industrial and Engineering Chemistry 42 (2016) 63–68

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Micellization and aggregation properties of sodium perfluoropolyether carboxylate in aqueous solution

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ARTICLE INFO

Article history:
Received 26 May 2016
Received in revised form 18 July 2016
Accepted 22 July 2016
Available online 29 July 2016

Keywords:
Surfactant
Sodium perfluoropolyether carboxylate
Micellization
Aggregation
Properties

ABSTRACT

Sodium perfluoropolyether carboxylate (PFPE-Na) was synthesized via hydrolyzing the corresponding hexafluoropropylene oxide oligomer (PFPF). The structure of PFPE-Na was characterized by FT-IR and ^{19}F NMR. The micellization and aggregation properties of PFPE-Na surfactant in aqueous solution were studied systematically using equilibrium surface tension, electrical conductivity, dynamic surface tension, steady-state fluorescence, transmission electron microscopy (TEM) and contact angle methodologies. The results of equilibrium surface tension at 25 °C showed that the critical micelle concentration (CMC) and the surface tension at CMC (γ_{CMC}) of PFPE-Na aqueous solution are lower than sodium perfluorooctanoate [NaPFO, $C_7F_{15}COONa$], which revealing that as a kind of environment-friendly surfactant, PFPE-Na is a perfect substitute of NaPFO. Electrical conductivity measurements implied that the micellization of PFPE-Na in aqueous solution was an exothermic and entropy-driven process in the range of temperature investigated. Steady-state fluorescence and transmission electron microscopy (TEM) may indicate that PFPE-Na self-assemble in aqueous solution to form larger spherical aggregates with the increase of concentration. In addition, dynamic surface tension measurements of PFPE-Na solution showed an extremely efficient adsorption at concentrations above CMC while the determination of contact angle of PFPE-Na showed the wetting ability was general.

Introduction

Fluorocarbon surfactants are seen as special surfactants compared with traditional surfactants [1] for they possess unique properties called “three-high” and “two-loathe”, which mean high surface activity, great heat resistant, chemical resistant, oil repellent and water proof [2]. Fluorocarbon surfactants are widely used not only in numerously industrial and household fields, but also in the fields of enlarged applications where hydrocarbon surfactants cannot be used [3]. Fluorocarbon surfactants have motivated a worldwide interest due to their excellent properties [4]. However, long perfloroalkyl chain of fluorocarbon surfactants like perfluorooctanoic acid (PFOA) are hard to biodegrade leading to the accumulation in nature environment which can become potential carcinogens to human. So PFOA has been banned in many industry areas. Polyfluoroalkylpolyether compounds have low-melting point and great degradability. The insertion of oxygen atoms into the polyfluoroalkyl chain not only increase the elastic characteristic but also the solubility of the chain [5]. Perfluoropolyether surfactants have low surface energy, high stability, and low toxicity. Furthermore, the components after degradation have no negative effects to the environment. So they have attracted much attentions in basic industry and cutting-edge scientific fields such as military, aerospace and nuclear industry [6,7]. Developing a new type of perfluoropolyether surfactant to replace PFOA has a profound significance and application prospect. Perfluoropolyether carboxylic acid is one of the primary choices of PFOA alternatives. As an important intermediate, perfluoropolyether carboxylate can satisfy the synthesis of downstream productions. However, the micellization and aggregation properties of these surfactants in aqueous solutions were scarce.

In this work, PFPE-Na was synthesized and its properties were investigated systematically, such as micellization thermodynamic, adsorption properties, aggregation behaviors and wetting ability.

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http://dx.doi.org/10.1016/j.jiec.2016.07.026

The main purpose of this article is to enrich our knowledge of fluorocarbon surfactant and to provide a more comprehensive foundation of PFPE-Na.

Experimental

Materials

2,5-Bis(trifluoromethyl)-3,6-dioxaundecafluorononanoyl fluoride (PFPF) was obtained from Lisheng Regent Biochemistry Technology Co., Ltd. (Guangdong, P.R. China). Diethyl ether was purchased from Tianjin Kemel Chemical Reagent Co., Ltd. (Tianjin, P.R. China). Sodium hydroxide and sodium chloride were obtained from Shentai Reagent Co., Ltd. (Tianjin, P.R. China). Pyrene (99%) was achieved from Alfa Aesar. Benzophenone was purchased from China National Medicine Group Shanghai Chemical Reagent Company. (Shanghai, P.R. China). Water we used in all experiments was deionized water (18.2 MΩ).

Synthesis of PFPE-Na

PFPE-Na was prepared according to the procedures reported previously by the neutralization method [8,9]. The completely hydrolyzed PFPF (4.98 g) in deionized water was neutralized by 2.00 mol/L NaOH aqueous solution (30 mL) at room temperature and coprecipitated with saturated salt water, then filtered and dried sequentially to obtain a product. The product solubilized in diethyl ether was filtered off insoluble inorganic salt and evaporated the solvent of diethyl ether under depression and then dried under a vacuum for 48 h to get a solid product (yield, 93.6%).

Structural analyses

The chemical structures of PFPF and PFPE-Na were characterized by nuclear magnetic resonance spectroscopy (NMR) and fourier transform infrared spectroscopy (FT-IR). ^{19}F NMR spectra were recorded on a Varian INOVA-400 Hz spectrometer using $CDCl_3$ (PFPF) and D_2O (PFPE-Na) as the lock solvent and CF_3CO_2H as the reference. FT-IR spectra were obtained using a Bruker Vertex-70 spectrometer.

Measurements

Equilibrium surface tension measurements

The equilibrium surface tension of PFPE-Na aqueous solutions were measured with Krüss K12 (Krüss Company, Germany) Processor Tensiometer by Wilhelmy plate technique at (25 ± 0.1) °C. Before the measurements, each PFPE-Na aqueous solution was equilibrated for 24 h.

Electrical conductivity measurements

Measurements of electrical conductivity were performed with a conductivity analyzer (model DDS-11A, Shanghai Leici-Chuangyi Instrument and Meter Co., Ltd., Shanghai, China). All surfactant solutions were prepared with distilled water putting at least 24 h before the measurements. The temperature was controlled by a thermostatic water bath and each electrical conductivity data is an average value measured three times to minimize data errors.

Dynamic surface tension measurements

The dynamic surface tension was determined by a Krüss BP100 bubble-pressure tensionmeter (Krüss Company, Germany, accuracy ±0.01 mN/m) at (25 ± 0.1) °C to achieve the measurement of the maximum pressure which was necessary to blow a bubble in a liquid from the tip of a capillary. The measurements were conducted with effective surface ages ranging from 10 to 200,000 ms.

Steady-state fluorescence measurements

Fluorescence measurements were carried out using Flspectorophotomet (F-4600, Hitachi, Japan)at (25 ± 0.1) °C. The slit widths for emission and excitation were fixed at 2.5 and 5.0 nm, respectively and pyrene concentration was kept at 5.00×10^{-6} mol/L for each solution. I_1/I_3 was used to indicate the intensity ratio of the first (373 nm) and the third (384 nm) vibronic peaks of pyrene.

Transmission electron micrographs (TEM)

To investigate micro-morphology of PFPE-Na aggregates in aqueous solutions, TEM was performed with a JEM-1011 transmission electron microscope (Jeol Company, Japan) at 100 kV. All sample solutions were deposited on a carbon-coated copper grid and negatively stained with 2 wt% phosphotungstic acid.

Contact angle measurements

The wetting ability of PFPE-Na was completed under air by using Krüss DSA 25 instrument (Krüss Company, Germany) to measure the contact angle. A paraffin film was chosen as the solid substrates. The temperature and environmental humidity were kept constant at (25 ± 0.1) °C, (50 ± 5) %, respectively.

Results and discussion

Characterization of PFPE-Na

PFPE-Na was synthesized by hydrolysis reaction with PFPF and sodium hydroxide solution. The structures of PFPF and PFPE-Na were characterized by ^{19}F NMR and FT-IR. Fig. 1 gives the ^{19}F NMR spectra of PFPF and PFPE-Na. The signal at $\delta = 101.9$ ppm is the characteristic absorption peak of $-COF^i$ and the signal between $\delta = -2$ to -3 ppm is the peak of $CF_3{}^a$. Influenced by adjacent groups, the signals of $CF_3{}^e$ and $CF_3{}^h$ move to the peaks between $\delta = -4$ to -7. The peak at $\delta = -53.5$ ppm is $CF_2{}^b$ and the peaks between $\delta = -54$ to -55 ppm are CF^d and CF^g. The characteristic peaks of $CF_2{}^f$ and $CF_2{}^c$ move to low field in near $\delta = -9$ to -10 because of the effect of adjacent oxygen. It can be clearly identified that the functional group of $-COF^i$ has completely disappeared in the product by analyzing the signal at $\delta = 101.9$ [10]. Fig. 2 shows the FT-IR spectra of PFPF and PFPE-Na. FT-IR results show little difference between raw material and product. The carbonyl

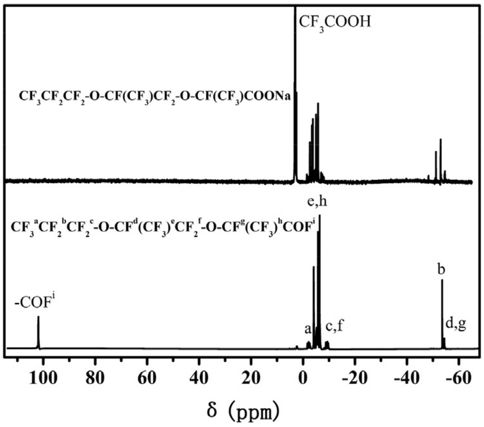

Fig. 1. ^{19}F NMR spectra of PFPF and PFPE-Na.