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Novel succinic acid based polymeric surfactants: Synthesis and performance investigation

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ABSTRACT

Three novel succinic acid based polymeric surfactants, MAPEG-OSO_3Na (M_{PEG} = 1000, 2000, 4000), were designed and synthesized by reaction of maleic anhydride (MA) and polyethylene glycols (PEG) of different molecular weight. Their surface activities, adsorption, spreading performances, aggregation behaviors and dispersion in aqueous solution were investigated by static/dynamic surface tension measurements, contact angle techniques, transmission electron microscope (TEM) and particle size distribution (PSD) at 25 °C. Surface tension measurement for all three surfactants are about 30 mN/m. From the results of static surface tension measurements, we could estimate the CAC/C_{20} ratio, adsorption efficiency (pC_{20}), maximum surface excess concentration (Γ_{max}) and minimum surface area per molecule (A_{min}) at air/liquid interface. The dynamic surface tension results indicated that adsorption process of aqueous solutions at air/liquid interface is mixed diffusion-kinetic adsorption mechanism. TEM analysis of MAPEG-OSO_3Na solutions revealed that surfactant molecules can self-assemble into spherical micelles. PSD and TEM results showed that the application prospect of these surfactants is dispersant in aqueous solution.

1. Introduction

In recent years, surfactants have been widely applied as wetting agents [1,2], emulsifiers [3,4] and leather finishing agents [5] for the purpose of reducing surface tension. Increasing requirement of energy industry leads most researchers to focus their eyes on the exploitation of polymeric surfactants. Polymeric surfactants are a kind of substance that have characteristic molecular structure consisting of hydrophobic chain together with hydrophilic portion [6]. In comparison to traditional surfactants, they exhibit excellent properties such as dispersion, cohesion, thickening and emulsification. Due to their unusual properties, they are widely used as dispersers [7], flocculants [8,9], rheology modifiers [10].

It is known that PEG has a number of benign characteristic, for example, PEG is miscible with water and is biocompatible that can be utilized in tissue culture media. Also PEG has been found to be stable to acid, base and high temperature systems [15]. Furthermore, MA not only has high reactivity so that it can occur addition reaction, esterification and polymerization reaction, but also there is no byproduct produced in reaction process, which corresponding to the demands of green chemistry [16]. Sulfate polymeric surfactants containing the structure of PEG and MA are widely used in the field of washing industry, textile industry, coating technology and other fields. For instance, Rizvi et al. [11] synthesized the polymeric alkenoxy amino acid surfactants with sulfate head group, derived from leucinol, iso-leucinol, and valinol. They found that the sulfate surfactants have lower CMC and are very useful at low pH conditions due to improved solubility in acidic media. The sulfate polymers provide equally good chiral separation of the analytes investigated. Quan and co-workers [12] prepared the polystyrene-supported PEG-bound sulfonic acid, which widely used as catalyst due to the polystyrene linker can increase the mass transfer ratio of product from the reactants. Shahab [13] synthesized a polymerized surfactants with a sulfate headgroup, namely, poly(sodium undecylenic sulfate). The polymerized surfactants can be effectively as pseudostationary phases over a wide range of concentrations, and used for the separation of polycyclic aromatic hydrocarbons (16 PAHs). Zhang [14] obtained two environmentally friendly succinic acid mono-fluoroalkyl sulfonate surfactants and discovered that the Krafft points are below 0 °C and the surfactants have good thermostability. However, these surfactants seldom used in the dispersion of inorganic pigment and the sulfating agents in the literatures mentioned above are chlorosulfonic acid and concentrated sulfuric acid, in addition, the solvent is dichloroethane. In the process of sulfating reaction, waste acid and chlorine-containing compounds can cause some economic and environmental problems. Therefore, a new sulfating method is that the sulfating agent is changed to gas sulphur trioxide (SO_3). There are no water and waste acid to produce in the reaction process, and the dosage of the SO_3 can close to the theory of consumption, which are helpful for

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environmental protection [17,18]. On the basis of these characteristics, we envision a new surfactant, containing two sulfate groups and long chains (—CH_2CH_2O—), that can not only further enhance solubility, but also provide steric effect and electrostatic repulsive force for dispersion stabilization.

In this paper, we make full use of advantages of MA and PEG to prepare an environmentally friendly and biocompatible succinate sulfate surfactants (MAPEG-OSO_3Na, see Scheme 1) using gas sulphur trioxide as sulfating agent. The physicochemical performances, including surface tension, adsorption and spreading ability, were investigated systemically by various measurements.

2. Materials and methods

2.1. Materials

MA was purified by crystallization from chloroform three times. Absolute ethanol, sodium hydroxide, ethyl acetate and PEGs (number average molecular weight M = 1000, 2000, 4000) were purchased by Tianjin Kermel Chemical Reagent Co., Ltd. (China). *P*-toluenesulphonic acid (PTSA) was supplied by Tianjin Guangfu Research Institute of Fine Chemical Industry. Fuming sulfuric acid (65%) were supplied by Tianjin Shentai Chemical reagent Co., Ltd. (China). All of other reagents were analytical grade and used without further purification except MA. The deionized water with a resistivity of 18.25 MΩ·cm was prepared by a UPD-II ultrapure water purifier.

2.2. Synthesis of MAPEG-OSO_3Na polymer

The disodium sulfates of succinic acid diesters were prepared through three steps reaction in accordance with Scheme 1. MAPEG-OSO_3Na was synthesized by esterification reaction of PEG and MA. Then sulfate groups were introduced by reacting with sulphur trioxide (SO_3). Finally, the esterified product was neutralized by 30 wt% aqueous sodium hydroxide to pH = 8 gradually. An example of the typical procedure which involves MA and PEG1000 is as follows:

MA (22.54 g, 0.23 mol), PEG (493.20 g, 0.49 mol), and PTSA (10.31 g) were mixed and put into round-bottom flask in the presence of nitrogen. The reaction was to continue until the acid value was constant essentially (about 6 h). After esterification reaction, catalyst was neutralized by alkali and filtrated with absolute ethanol.

Liquid SO_3 was collected by the condensation of SO_3 vapor evaporating from fuming sulfuric acid. In the process of sulfate reaction, SO_3 vapor was mixed with nitrogen which has a constant flow rate of 0.11 m^3/h. Then the mixed gas was passed into a three-neck round-bottom flask containing MAPEG (165.05 g) obtained from first step at 80 °C. The esterified products (MAPEG-OSO_3H) were neutralized by aqueous sodium hydroxide to pH = 8, filtered out inorganic salts with absolute ethanol and purified by extracting the unreacted MAPEG with ethyl acetate. The final product (yield is about 60%), presenting a viscous but pourable light yellow liquid at 60 °C and waxy solid at room temperature, was obtained after removing solvent by reduced pressure distillation.

2.3. Characterization

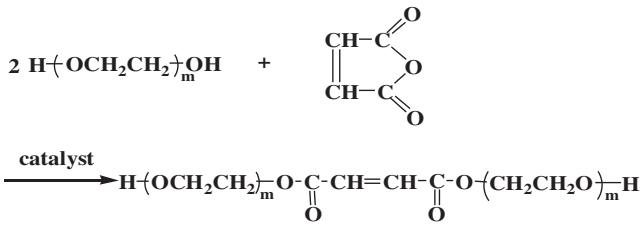
2.3.1. Fourier transform infrared analysis spectroscopy (FT-IR)

Fourier transform infrared (FT-IR) spectra were recorded using a Bruker Vertex-70 spectrometer at room temperature. A small amount of sample was smeared onto the KBr tablets to detect the structure information of products. The wavelength range of FT-IR spectra was measured from 500 cm^{-1} to 4000 cm^{-1}.

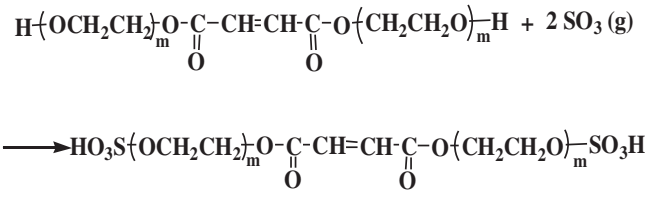
2.3.2. Nuclear magnetic resonance (^1H NMR) spectrum

The ^1H-nuclear magnetic resonance (^1H NMR) spectra were obtained with a Varian INOVA-400 MHz spectrometer, using deuterochloroform ($CDCl_3$) as the solvent.

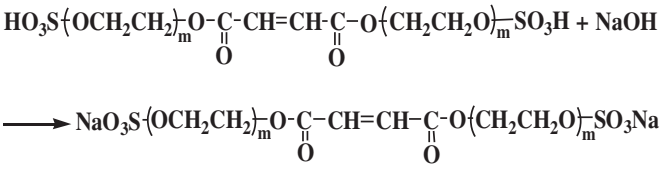
Step 1



Step 2



Step 3



Scheme 1. The synthetic route of MAPEG-OSO_3Na.