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Journal of Colloid and Interface Science 291 (2005) 570–576
JOURNAL OF Colloid and Interface Science
www.elsevier.com/locate/jcis

Hydrolyzable nonionic surfactants: Stability and physicochemical properties of surfactants containing carbonate, ester, and amide bonds

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Received 6 April 2005; accepted 13 May 2005

Available online 23 June 2005

Abstract

A linear and a branched nonionic cleavable surfactants containing a carbonate bond have been prepared from tetra(ethylene glycol) and an alkylchloroformate. The stability of these carbonate surfactants was determined by investigating their hydrolysis and biodegradability characteristics. The hydrolysis was catalyzed by alkali or enzymes (esterase from porcine liver and lipases from *Mucor miehei* and *Candida antarctica* B) and was monitored using ^{1}H NMR. It was found that the stability toward alkali was higher for a carbonate surfactant than for a corresponding surfactant with an ester as weak bond. Biodegradation tests resulted in more than 60% degradation after 28 days for both carbonate surfactants. Physicochemical properties, such as critical micelle concentration (CMC), cloud point, area per molecule, and surface tension at the CMC, were determined and compared to those obtained from similar surfactants containing ester, amide, or ether bonds. It was found that the carbonate linkage is hydrophobic and that the oxycarbonyl part of the carbonate group is equivalent, in a formal sense, to an extra methylene group in the alkyl chain of the surfactant.

Keywords: Cleavable surfactant; Nonionic surfactant; Hydrolysis; Carbonate; Biodegradation; CMC; Amide; Ester

1. Introduction

The size of the global surfactant market was about 12 million tons for the year 2003 [1]. Consumption of such large quantities emphasizes the importance of these products not to accumulate when released into nature. Consequently, one of the most important factors to take into account when developing a new surfactant is its ability to biodegrade at a reasonable pace, i.e., that it has a good biodegradation profile.

One way to improve the biodegradation rate of a surfactant is to make it less stable by insertion of a weak bond in the molecular structure, i.e., to make a so-called cleavable surfactant [2]. The labile bond can be situated anywhere in the surfactant structure, but the most common approach is to place it between the hydrophobic and the hydrophilic groups. Cleavage of a bond at this location will result in separation of the polar head group and the hydrophobic tail and hence a loss of surface activity. This so-called primary degradation is often the first step in the biodegradation pathway. Thus, increasing the rate of this step often leads to an overall decrease in the time needed to reach ultimate biodegradation [3,4].

The present paper is part of an ongoing project in which cleavable surfactants with different hydrolyzable bonds are compared with regard to stability and physicochemical properties. We have recently reported on oxyethylene-based surfactants with an ester or an amide as labile bond [5–7]. Chemical and enzymatic hydrolysis were studied and compared with results obtained for the rate of biodegradation. It was found that both bonds are relatively stable toward chemical hydrolysis, but the surfactants nevertheless show good biodegradation profiles. The main focus of the present investigation is to describe the degradation characteristics of a

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0021-9797/$ – see front matter
doi:10.1016/j.jcis.2005.05.041

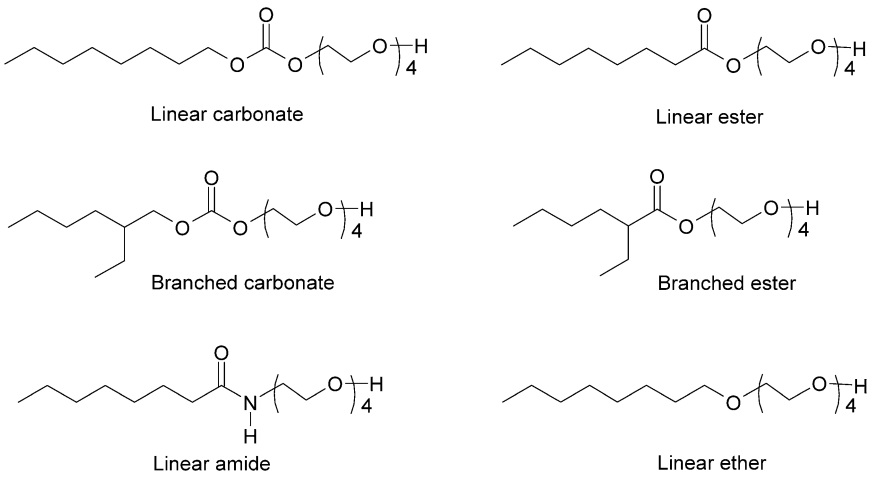

Fig. 1. Structures of the different nonionic surfactants used.

related surfactant with a carbonate as labile bond, a class of compound that has previously not attracted much attention [8–10].

Here we also relate the properties of the carbonate surfactants to those of ester, amide, and ether surfactants of similar structure, see Fig. 1. Our intention was to investigate how different cleavable bonds affect the physicochemical properties of the surfactants. We were also interested in the effect of branching in the surfactant's hydrophobe on the degradation characteristics and on the physicochemical properties.

2. Experimental

2.1. Chemicals

Octanoyl chloroformate (>95%) and 2-ethylhexyl chloroformate (>95%) came from Tokyo Kasei. Tetra(ethylene glycol) (99%), pyridine (>99%), and sodium deuteroxide (40 wt% solution in D_2O) were purchased from Aldrich. The D_2O and the deuterium chloride (20% in D_2O) were 99.8 and >99.5 atom% D, respectively, both obtained from Dr. Glaser AG. Lipase from *Mucor miehei* (Lot 40K2600, 5280 units/mg) and esterase from porcine liver (Lot 123K7033, 24 units/mg) came from Sigma, lipase from *Candida antarctica* B (Novozym CALB L PPW6354, 13,000 units/g) was kindly provided by Novozymes A/S. All chemicals were used as received. All solutions were prepared using water obtained from a Millipore (Milli-Q) water purification system. All chemicals used for biodegradation tests were of reagent grade and deionized water containing no more than 0.01 mg/L Cu was prepared in a water purification system.

2.2. Synthesis of carbonic acid, octyl 2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl ester (linear carbonate surfactant)

Octanoyl chloroformate (3 ml, 15 mmol) was added dropwise during 0.5 h to a mixture of tetra(ethylene glycol) (53 ml, 0.30 mol), pyridine (1.5 ml, 19 mmol), and 60 ml dry dichloromethane (DCM) at −5 °C under nitrogen atmosphere. After 2.5 h the solution was allowed to reach room temperature and was stirred overnight. The reaction was aborted by evaporation under reduced pressure. The crude was diluted in 250 ml ethyl acetate and extracted with brine (3 × 200 ml) to remove the main part of the excess tetra(ethylene glycol). The organic phase was evaporated and the residue was dissolved in DCM, filtered and evaporated. The residue was purified by flash chromatography (silica) using ethyl acetate as eluent giving 4.3 g (79%) of colorless oil. TLC (ethyl acetate) R_f 0.3; ^{1}H NMR (400 MHz $CDCl_3$–TMS) δ 0.88 (t, 3H), 1.22–1.44 (m, 10H), 1.66 (m, 2H), 2.56 (t, 1H), 3.60–3.76 (m, 14H), 4.13 (t, 2H), 4.29 (t, 2H). No traces of unreacted starting materials or byproducts could be detected by TLC or ^{1}H NMR.

2.3. Synthesis of carbonic acid, 2-ethylhexyl 2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl ester (branched carbonate surfactant)

The surfactant was prepared from 2-ethylhexyl chloroformate according to the route described for the preparation of linear carbonate resulting in a colorless oil (96% yield). TLC (ethyl acetate) R_f 0.2; ^{1}H NMR (400 MHz $CDCl_3$–TMS) δ 0.89 (t, 6H), 1.26–1.44 (m, 8H), 1.60 (m, 1H), 2.48 (t, 1H), 3.59–3.76 (m, 14H), 4.05 (m, 2H), 4.29 (t, 2H). No traces of unreacted starting materials or byproducts could be detected by TLC or ^{1}H NMR.

2.4. Tensiometry

The critical micelle concentration, CMC, of the surfactants was determined by measuring the equilibrium surface tension as a function of surfactant concentration with a Sigma 70 tensiometer equipped with a Pt–Ir du Noüy ring. The surface tension isotherms were measured at 18 °C and repeated twice. The area per molecule, A_{CMC}, was calculated from the surface excess, Γ, through the relation $A =$