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Cationic ester-containing gemini surfactants: Chemical hydrolysis and biodegradation

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Abstract

Two cationic gemini surfactants having ester bonds between the hydrophobic tail and the cationic moiety have been synthesized. The ester bonds were either with the ester carbonyl group away from the positive charge (esterquat type arrangement) or facing the positive charge (betaine ester type arrangement). The chemical hydrolysis of the surfactants was investigated and compared with the hydrolysis of the corresponding monomeric surfactants. The betaine ester type of surfactants was found to hydrolyze much faster than the esterquat surfactants. It was also seen that above the critical micelle concentration the gemini surfactants were much more susceptible to alkaline hydrolysis than the corresponding monomeric surfactants. The biodegradation of the geminis and the monomeric surfactants were also studied. It was found that whereas the monomeric surfactants were rapidly degraded, the two gemini surfactants were more resistant to biodegradation and could not be classified as readily biodegradable. The 60% biodegradation was reached after 35–40 days. Thus, there was no correlation between rate of chemical hydrolysis and rate of biodegradation.

Keywords: Gemini surfactants; Synthesis; Biodegradation; Esterquats; Hydrolysis; Cleavable

1. Introduction

Surfactants are used in many applications and in many areas of human activity. The vast majority of the surfactants is discharged after use into industrial effluents and/or sewage and may ultimately reach rivers, lakes, and oceans. The degradation of the surfactants by microorganisms in biological treatment plants and in aquatic ecosystems is important to ensure low environmental concentrations and is thus a major driving force for the development of novel surfactants [1,2].

Gemini or dimeric surfactants are novel surfactants composed of two monomeric surfactant molecules with the head groups chemically bonded together by a spacer [3,4]. They possess two hydrophilic and two hydrophobic entities. The two hydrocarbon tails can be short or long; the two polar head groups can be cationic, anionic or nonionic; the spacer can be short or long, flexible or rigid, polar or non-polar. The main advantages of gemini surfactants in comparison with the corresponding conventional ones are higher surface activity [5,6], lower critical micelle concentration (CMC) [4], higher solubilization capacity [7], and interesting viscoelastic properties [8]. The greater efficiency and effectiveness of geminis over comparable conventional surfactants can make them more cost-effective [6,9].

Cationic gemini surfactants are attracting particular interest because their synthesis is relatively straightforward [9]. However, cationic surfactants in general have higher aquatic toxicity than other surfactants and various approaches are taken to circumvent this problem. One approach is to introduce an easily cleavable bond into the surfactant structure. An illustrative example of such "cleavable surfactants" is the surfactant family of esterquats, cationic surfactants with an ester bond inserted between the hydrocarbon tail(s), and the quaternary ammonium

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head group. Esterquats have replaced the conventional stable quats in many large-scale applications, such as fabric softeners, and environmental concern has been the dominating driving force for this transition. Early uses of normal esterquats were as textile auxiliaries and as dye leveling agents [10].

The purpose of this work was to prepare and characterize cationic gemini surfactants with ester bonds inserted between the hydrocarbon tails and the positively charged head groups and to evaluate their hydrolysis and biodegradation profiles. Two types of ester surfactants were studied, one with the carbonyl carbon of the ester bond facing the hydrophobic tail and one with the opposite orientation, i.e., with the bridging oxygen of the ester bond facing the tail. The former type is referred to as esterquat surfactants because the structure is that of the so-called esterquats that are widely used as fabric softeners (although these are usually twin-tailed, single head-group surfactants) [11]. The latter type is referred to as alkyl betainates. Monomeric betaine surfactants have been relatively much studied in recent years in search of very rapidly degradable cationic surfactants [12–14]. The susceptibility of the gemini surfactants to chemical hydrolysis was investigated and their rate of biodegradation was determined. The values obtained were compared with those of the corresponding monomeric surfactants.

2. Experimental

A collection of the *chemicals used* as well as of the procedures for *synthesis* of the different surfactants can be found in Supplementary material.

2.1. CMC measurements

The critical micelle concentrations (CMC:s) of the surfactants were determined by the conductivity method. Measurements were performed with a CDM 210 conductometer (Radiometer, France), using a water bath with stirring to control the temperature. For each series of measurements an exact volume of 25 ml Millipore water (resistivity ∼18 MΩ) was introduced into the vessel and the specific conductivity of the water was measured. The solution was then titrated with the surfactant solution and the conductivity was measured after each addition. The concentration at which there was a break on the curve of conductivity vs surfactant concentration was taken as the CMC.

2.2. Micelle ionization degree (α)

The counterion distribution in a micellar solution can be assessed from electrical conductivity vs concentration plots. The counterion binding to micelles was determined from the ratio between the slopes above and below the CMC [15].

2.3. Krafft temperatures

Weighted quantities of surfactant and water were heated to 50 °C to form clear solutions of known concentrations. These solutions were placed in a refrigerator for 24 h. Precipitation of dodecyl betainate monomer and gemini surfactants occurred rapidly in 1 h. No precipitation was seen for dodecyl esterquat monomer and gemini surfactant solutions. The temperature of the precipitated systems was slowly increased under constant stirring. The conductance was monitored by a CDM 210 conductometer (Radiometer, France) equipped with a thermocouple that was immersed in the solution. The Krafft temperature was taken as the temperature at which the conductance vs temperature plot showed an abrupt change in slope [16]. It should be noted that the real Krafft point is defined as the temperature at which the solubility of the unimer becomes equal to the CMC [17].

2.4. Biodegradability tests

The Closed Bottle test, a standardized method (OECD 301 D), was used for evaluating the biodegradability of the test substances. This method has been described in detail before [18, 19] and will be discussed only briefly here. Activated sludge obtained from a plant treating predominantly domestic wastewater was used as inoculum. Prior to inoculation of the bottles with 2.0 mg/L of dry weight, the activated sludge was kept aerated by continuous stirring for one week to reduce the endogenous respiration. The concentration of the test substances was 2.0 mg/L and the incubation temperature was 20 °C. The biodegradation was measured by following the course of the oxygen decrease in the bottles. To this end, dissolved oxygen in the bottles was monitored with an oxygen electrode (WTW Trioxmatic EO 2000) and an oxygen meter (WTW OXI 530, Retsch, Ochten, The Netherlands). The biodegradation was expressed as the percentage of the biological oxygen demand to the theoretical oxygen demand.

Inherent biodegradability was determined in the modified Semi-Continuous Activated Sludge (SCAS) test performed according to OECD guideline 302 A [20]. The experiment was conducted in 0.15 L test vessels dosed with domestic wastewater spiked with 50 mg/L of test substance (test unit) and domestic wastewater (control unit). The SCAS test was operated semi continuously with one cycle of fill and draw per day. Activated sludge was not deliberately wasted. The SCAS tests operated at 20 °C had a hydraulic retention time of 36 h. The removal of the test substances was assessed by measuring the non-purgeable organic carbon (NPOC) content in the effluents of both SCAS units. Before the determination of the NPOC, the effluents were filtered using cellulose nitrate filters with pores of 8 µm (Schleicher and Schuell, Dassel, Germany) to remove sludge particles. Filtered samples were acidified prior to injection in a total organic carbon analyzer model Vcpn (Shimadzu, Kyoto, Japan).

2.5. Preparation of phosphate buffer based on D_2O

A 100 mM phosphate buffer was prepared by mixing 50 mL of 200 mM potassium dihydrogen phosphate and 32.1 mL of 200 mM sodium hydroxide to a total volume of 100 mL in D_2O. The glass electrode pH meter (744 Metrohm, Switzerland), which was calibrated in H_2O-based buffers, showed a