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ORIGINAL ARTICLE

Preparation and Surface Activity of Phosphated Alkyl Oligoglucosides

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Abstract A family of phosphated alkyl oligoglucoside surfactants was prepared by reacting alkyl oligoglucosides with phosphorus oxychloride. The alkyl oligoglucosides were obtained by an usual method in which the glucose is reacted with a fatty alcohol containing 10–18 carbon atoms. These novel phosphated surfactants have been found to exhibit good surface tension, foaming and wetting power. The critical micelle concentration was found to increase with the length of hydrocarbon chain of the surfactant. The surface excess concentration and the interfacial area per surfactant molecule are reported. These phosphated surfactants also exhibit a good performance to improve the whiteness and wetting of cotton fabrics in a hydrogen oxide bleaching system, and they are also found to be more biodegradable than conventional surfactants.

Keywords Synthesis · Phosphated glucoside · Surfactant · Biodegradable

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Introduction

During the past few years, many natural waters have been polluted by chemicals from various sources. Some of them are surfactants which originate mainly from household detergents, personal care products, washing agents, and processing supplies used in industry. A great deal of work has been done in trying to take into account biodegradability in the use of surfactants [1–3].

Alkyl polyglucosides, derivatives of carbohydrates like glucose (hydrophilic moiety) and long chain fatty alcohols (hydrophobic moiety), exhibit an amphiphilic structure similar to the traditional surfactants, with more biodegradability and toxicologically safety [3]. Strictly speaking, alkyl polyglucosides are not new surfactants, but they have been again reconsidered recently, because of increasing environmental concerns. Some studies investigating the properties of these derivatives and their application in detergents, personal care and industrial processes have been reported recently [4–9]. In general, the alkyl polyglucosides are classified as nonionic surfactants and only limited information [10] is available with regard to anionic derivatives of alkyl polyglucoside as detergents or as auxiliaries in industrial uses, such as fabric dyeing processes.

In our previously study, we reported the preparation and surface active properties of a series of biodegradable dextrin derivatives [7–9]. In this paper we present the preparation and surface properties of a series phosphated alkyl oligoglucosides. These surfactants are prepared by the anionic modification of alkyl oligoglucosides with phosphorus oxychloride [11]. The alkyl oligoglucosides were obtained by an usual method in which glucose is reacted with fatty alcohol containing 10–18 carbon atoms in the presence of a catalyst. The properties studied in this paper

include surface tension, contact angle, foaming properties, and the influence of surfactants on the bleaching process of cotton fabrics. The biodegradability of these surfactants was evaluated by the determination of the ratio of BOD/COD [2].

Experimental

Materials

Glucose, *p*-toluene sulfonic acid, fatty alcohol and phosphorus oxychloride, solvents, and other chemicals purchased from Hayash Pure Chemical Co. were reagent grade. Sodium dodecylbenzene sulfonate (SDBS) was supplied by Sigma–Aldrich Co. and used to compare the biodegradability of phosphated alkyl oligoglucosides surfactants. The BOD and COD test reagents were purchased by Merk Co. and used without further purification. A commercial grey cotton fabric was used for the scouring and bleaching experiments.

Preparation and Analyses

Although the actual reaction mechanisms are much more complicated [3], the preparation of phosphated alkyl glucoside derivatives may be split into three steps as represented in Fig. 1. In the initial step, the alkyl oligoglucosides were obtained by the reaction of 1 mol glucose with 1 mol fatty alcohol with 1 g of acid catalysis (*p*-toluene sulfonic acid) according to a usual method reported elsewhere [3–5]. The fatty alcohols used in this study had 10–18 carbon atoms. In the second step, 1 mol alkyl oligoglucoside obtained from step 1, was reacted with 1 mol phosphorus oxychloride and 1 mol of solvent (chloroform) to obtain an anionic derivative. The phosphorus oxychloride was used in the present study because it was the proper agent to attain a pure anionic product. Then, in step 3, the modified glucosides were reacted with 1 mol sodium hydroxide aqueous solution to form the sodium salt. The products were purified by using ethanol to remove the impurities; the analyses of the final products are shown in Table 1.

The structure of the final products was confirmed by infrared (IR), proton nuclear magnetic resonance (NMR) spectral analysis and elemental analysis. IR spectra were obtained with a Japan Spectroscopic FT/IR-3 spectrophotometer and NMR spectra were acquired with a Varian 360 L NMR spectrometer.

Surface Activity Measurements

The surface tension was determined at room temperature with a Japan Kaimenkaguka CBVP-A3 surface tensiometer.

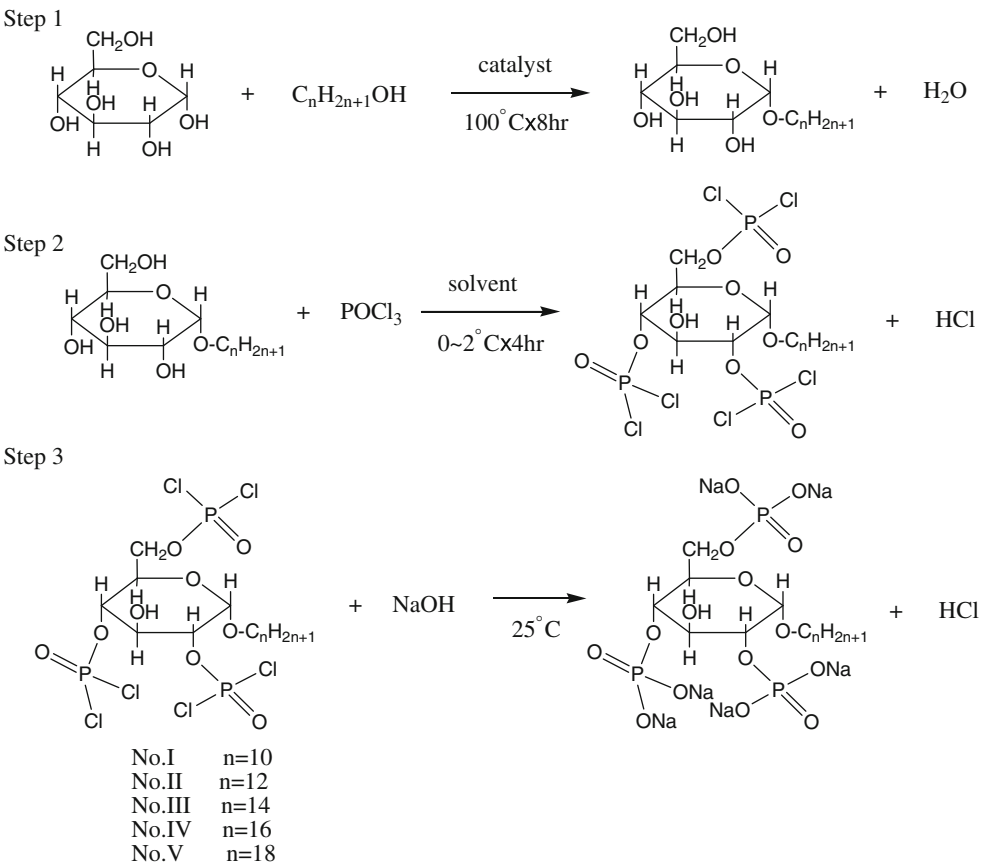

Fig. 1 Preparation of anionic modified alkyl oligoglucosides

Table 1 Analyses of anionic modified alkyl oligoglucosides

Compound	Anionic group	Molecular weight	Elemental analysis			
			C (%)		H (%)	
			Found	Calc.	Found	Calc.
I	3.300	729.2	26.33	23.53	3.81	3.43
II	3.421	772.3	27.97	25.59	4.17	3.79
III	3.538	814.7	29.46	27.52	4.42	4.13
IV	3.652	856.9	30.81	29.33	4.81	4.44
V	3.824	906.2	31.78	31.03	4.98	4.74

The critical micelle concentration (CMC) and the surface tension at the CMC were determined from the breakpoint of the plot of surface tension versus the logarithm of the concentration. The surfactant surface excess concentration at the air/solution interface (Γ) in mol m^{-2} was calculated using the following Gibbs adsorption isotherm equation [12, 13]:

$$\Gamma = -(1/iRT)(d\gamma/d \ln C)$$

in which γ represents the surface tension in m Nm^{-1}, R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature, C is the surfactant concentration, and ($d\gamma$/d ln$C$) is the slope below the CMC in the surface tension plots. The area occupied by the surfactant molecule at the air/solution interface, A_{cmc}, was obtained from the saturated adsorption as follows:

$$A_{cmc} = 1/N\Gamma_{cmc}$$

in which N is Avogadro's number, and Γ_{cmc} represents the surface excess concentration at the CMC. The value of i represent the number of species at the interface for which the concentration changes with the surfactant concentration. The alkyl polyglucosides are classified as nonionic surfactant, for mixtures of ionic and nonionic surfactants in aqueous solution in the absence of added electrolyte, so the coefficient $i = 1$ for the dilute solution (10^{-2} M or less) of phosphated alkyl oligoglucosides surfactants [14, 15].

Application Measurements

Foaming properties were determined by the Ross-Miles method. Foam production was measured by the height of the foam initially produced, and foam stability was measured by the height after 3 min. The contact angle was measured by a FACE CA-5 contact angle meter. A 0.2% (by weight) surfactant solution was prepared. The ageing time of the drop is 1 min. The biodegradability of these surfactants was evaluated by the determination of the ratio of BOD/COD as previously reported [2].

A rapid laboratory dyeing machine was used to study the bleaching of a grey cotton fabric by hydrogen peroxide. The bleaching recipe included: H_2O_2 (20%) 10 g/L, NaOH 5 g/L, $NaSiO_3$ 3 g/L, auxiliaries 2 g/L, liquor ratio 30:1, temperature 80 °C, time 40 min. After the bleaching, the reflectance of the cotton fabric was measured using an ACS spectrophotometer and the results were used to calculate whiteness [16]. The bleached fabrics was also used to evaluate the wetting ability by the measured height of water penetrating into fabric [17].

Results and Discussion

Preparation

The alkyl oligoglucosides used in the present study are prepared by reacting fatty alcohol with glucose. It is known that the reaction products are present as a mixture of mono-, di- and higher glucosidized compounds (which are known as alkyl oligoglucosides). Next, these alkyl oligoglucoses were reacted with phosphorus oxychloride and neutralized by sodium hydroxide to obtain the anionic surfactant species. It is known that the chemistry of alkyl oligoglucose phosphates derivatives is much more complicated, because the reaction between an alkyl oligoglucoside and phosphorus oxychloride readily forms two ester bonds of the mono- or the diester. Nevertheless, an idealized and simplified preparation process of phosphated alkyl oligoglucoside may be represented as in Fig. 1. A typical IR spectrum of the phosphated alkyl glucoside derivatives displays bands at 3,365 cm^{-1}(O–H), 2,851–2,940 cm^{-1} (C–H), 1,040–1,110 cm^{-1}(C–O), 957–1,150 cm^{-1} (P–O–C) which are characteristic of the desired compound. Compound structure was further supported by the ^{1}H-NMR spectrum, which exhibits signals at δ 0.8–1.0 ppm (R–CH_2), 1.2–1.4 ppm (–CH_2), 3.3–4.0 ppm (–CH_2–OH).

Surface Tension

The phosphated derivatives of alkyl oligoglucosides prepared in this study exhibit an amphiphilic structure similar to conventional surfactants. The glucose, hydroxyl and phosphated groups compose the hydrophilic moieties, whereas the aliphatic chain containing 10–18 carbon atoms is the hydrophobic tail. The surface-active molecules is concentrated at the surface and reduces the surface tension, as shown in Fig. 2. The results indicate that an increase in the chain length of the alcohol tends to decrease the surface activity. These results are opposite to the reported results of the influence of alkyl groups for almost all conventional surfactants. It may be due to the increase of the average number of D-glucose unit per alkyl chain (degree of polymerization of alkyl polyglucosides) as the length of long-chain alcohol increases and the hydrophilicity of the

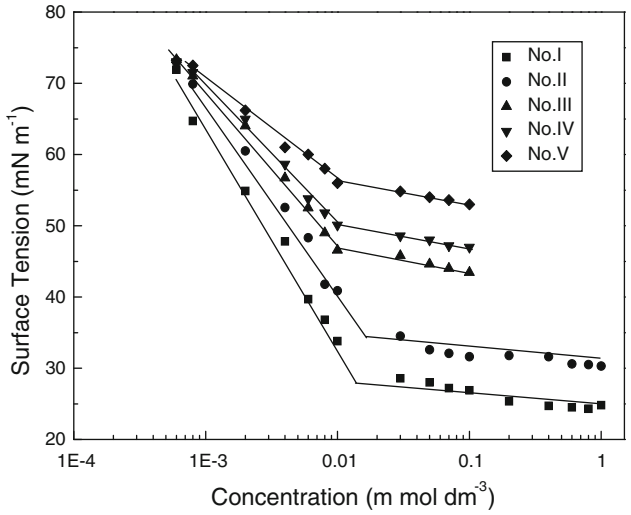

Fig. 2 Plots of surface tension against concentration of anionic modified alkyl oligoglucosides

surfactant rises. As would be expected, the increase in the hydrophobicity of surfactants result in an increased surface activity. The present results indicate that the increased hydrophilicity of the surfactants provided by the anionic and nonionic hydrophilic moieties more than compensate for the increased hydrophobicity produced by longer alkyl groups [18].

Surface Excess Concentration and Occupied Area

The CMC of conventional ionic surfactants is known to decrease with an increasing number of carbon atoms in the hydrophobic groups. In this study, the CMC increases with a longer hydrocarbon chain. These phosphated surfactants have a higher CMC than the anionic surfactants with amide groups, as reported by Yoshimura et al. [18]. The surface excess concentration and area occupied by the surfactant molecule at CMC were calculated from the surface data according to the Gibbs adsorption equation, and the results are summarized in Table 2. It is shown that the excess concentration of surfactant decreases as the length of the alkyl chain increases. These results indicate that the decreasing of the length of the alkyl chain produces a higher surface activity.

Table 2 Surface active properties of anionic modified alkyl oligoglucosides

Compound	CMC (mmol dm^{-3})	γ_{cmc} (mN m^{-1})	Γ_{cmc} ($\times 10^{-6}$ mol m^{-2})	A_{cmc} (nm^2 $molecule^{-1}$)
I	13.65	27.78	3.77	0.441
II	16.56	34.60	3.39	0.490

The occupied area per molecule for the surfactants gives some information on the packing degree of adsorbed molecules. In the present case, this value increases with increasing chain length. This may indicate that the interaction between hydrocarbon chains might not be attractive but sterically repulsive. It is worth noting that the area occupied by the phosphated alkyl oligoglucoside is larger than that of the sugar-based surfactants with the same hydrocarbon chain length [10], which could be attributed to the electrostatic repulsion between neighboring anionic head groups.

Wetting Power

The wetting power of a surfactant is one of its most important properties. For example, in laundry cleaning or textile processing use, the wetting power of surfactants may accelerate the diffusion or penetration of alkali chemicals and dyes into the fibers and improve the detergency or dyeing effects.

The contact angles formed between solutions of alkyl glucoside derivatives and an acrylic plastic plane and cotton fabric are shown in Table 3. The angles are found to be smaller than those found with water, indicating that all the solutions of all products possessed the power to wet the acrylic plastic and the fabric.

Foaming Properties

Foaming is a complex matter and by no means well understood, although foam is of great practical importance, for instance in cosmetics, or because it must be suppressed owing to its unfavorable effects. However, the low-foaming tendency of surfactants is an important property in some applications, such as in the use of mechanical dishwashing agents and dyeing auxiliaries in modern textile-dyeing processes.

Table 4 shows the foaming properties, as the initial height of produced foam and the foam height after 3 min. In comparison to other alkyl polyglucosides, for example a higher alcohol reacting directly with polyglucoses, the

Table 3 Contact angles of anionic modified alkyl oligoglucosides

Compounds	Contact angle (°)	
	Acrylic plastic	Cotton fabric
H_2O	74	124
I	50	72
II	54	81
III	61	91
IV	64	96
V	70	108

Table 4 Foaming properties of anionic modified alkyl oligoglucosides

Compounds	Foam height (cm)	
	Initial	After 3 min
I	2.7	1.8
II	2.3	0.9
III	4.2	3.7
IV	2.0	1.6
V	1.0	0.7

derivatives prepared in this paper exhibit a lower foamability. This lower foaming is probably due to the presence of multi-hydrophilic groups causing a considerable increase in area per molecule and thus reducing the surface cohesive force [19, 20].

Biodegradability

After use, the surfactants contained in household detergents, personal care products, washing agents and processing materials used in industry, end up in wastewaters. Consequently ecological issues are of first concern for this class of compounds. The results of the total biodegradation of the derivatives prepared in this study are shown in Table 5. After 10 days their biodegradation is greater than 60% and consequently, they should be regarded as readily biodegradable. Apparently, they are considerably more biodegradable because they would be natural foods of bacteria present in sewage or river water.

Influence on Bleaching of Cotton Fabrics

In the processes of textile industry, scouring and bleaching are carried out to prepare cloths for dyeing. The scouring and bleaching treatments do not rely primarily on the use of surfactants. Nevertheless, rapid and even wetting of the cloths is of major importance, and to assist this, some auxiliaries may be added. The ability of phosphated alkyl glucoside surfactants to improve the whiteness and the wetting power of cotton fabrics in a hydrogen peroxide bleaching system are shown in Table 6. The presence of surfactants increases the effects of oxidation in bleaching baths and prepare the more purified fabrics for the next processes of dyeing or printing.

Table 5 Biodegradability of anionic modified alkyl oligoglucosides

Compound	COD	BOD_5	BOD_{10}	BOD/COD (%)	
				5 days	10 days
I	1,107	520	708	47.0	63.9
III	944	550	634	58.3	67.2
V	949	585	685	61.6	72.2
SDBS[a]	1,040	114	249	10.9	23.9

[a] Sodium dodecylbenzenesulfonate

Table 6 Ability of surfactants to improve the wetting power and whiteness

Compounds	Height of water adsorption	Whiteness of bleached fabrics (E313)
I	6.6	55.42
II	4.9	55.02
III	1.7	54.66
IV	1.1	54.25
V	0.7	54.03
Blank	0	53.21

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