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Surface activity and emulsification properties of hydrophobically modified dextrins

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ABSTRACT

Novel modified dextrins were prepared in which propylene glycol polyglucosides are reacted with various fatty alcohols (C10–C18). We measured the surface activities of these compounds in terms of the critical micelle concentration (CMC), the surface tension at the CMC (γ_{cmc}), the surface excess concentration, the surface area occupied per molecule, and the standard free energy of micellization per mole of monomer unit (ΔG°_{m}). Emulsification measurements revealed that the smallest emulsion droplet size (i.e., most stable emulsion) was also obtained when the number of carbon atoms in the alkyl chain was 14. The biodegradability of the modified dextrins was also compared to that of sodium dodecylbenzene sulfonate and octyl phenol ethoxylate and it was found that the compound possessed the more highly biodegradable.

1. Introduction

Surface-active compounds synthesized from renewable resources, such as fatty alcohols and polyols, are of increasing interest because of their high performance, benefits to the health of consumers, and environmental compatibility relative to those of petrochemical-derived standard products [1]. Because dextrins are nontoxic to human beings and biodegradable, they are perfect raw materials for use in personal care formulations and food emulsifiers.

Dextrins, which consist of a carbohydrate moiety as the hydrophilic group and a fatty alcohol as the hydrophobic group, are valuable nonionic surfactants. Vesicles containing nonionic surfactants, such as dextrin ether, can encapsulate both hydrophilic and hydrophobic drugs, thereby protecting them against acidic and enzymatic degradation in the gastrointestinal tract.

Carbohydrate fatty alcohols are excellent oil-in-water (O/W) nonionic emulsifiers suitable for use in food, cosmetic, and pharmaceutical applications. For a surfactant to act as an emulsifier, it must exhibit good surface activity and produce a low surface tension in the particular system in which it is to be used. Thus, it must have a tendency to migrate to the air–water interface, rather than remain dissolved in either one of the bulk phases.

Changes to the molecular structures of surfactants can affect the physicochemical properties and applications of their solutions. Magdassi and co-workers [2–4] found that human immunoglobulin G that had been hydrophobically modified with alkyl chains possessed a different surface activity and improved functional properties. For micelles, increasing the length of the surfactant hydrophobic tail decreases the critical micelle concentration (CMC) [5–8]. Although many studies have been devoted to the preparation of hydrophobically modified polysaccharides, their surface activities have been discussed less frequently [9]. In previous papers, we described the preparation and surface activities of a novel series of biodegradable surfactants prepared from modified dextrin- and oxirane-containing materials [10,11].

In this paper, we describe the surface activities of a series of biodegradable modified dextrins possessing hydrophilic/hydrophobic amphipathic structures, prepared by covalently linking long-chain fatty alcohols to the dextrin. To study how these modifications influenced the dextrin surface activity at the air–water interface, we measured the surface hydrophobicities of the modified dextrins in terms of their surface tension, conductivity, and fluorescence.

2. Materials and methods

2.1. Materials

Dextrin was obtained from ACROS (Acros Organics, NJ, USA). Triethanol amine, fatty alcohols (n = 8, 10, 12, 16), and all other reagents were purchased from Hayashi Pure Chemicals and used without further purification. The preparation of the modified dextrins has been described previously [10]; their structures are displayed in Fig. 1. Sodium dodecylbenzene sulfonate (SDBS) and Triton X-100 were supplied by Sigma–Aldrich Co. and used to com-

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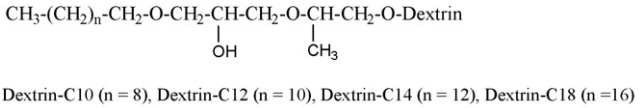

Fig. 1. Structures of the modified dextrins.

pare the biodegradability of modified dextrins. The BOD and COD test reagents were purchased by Merk Co. and used without further purification. The fluorescence probe, pyrene, was supplied by Fluka Chemicals.

2.2. Measurements

Surface tensions were determined at room temperature using a Kaimenkaguka CBVP-A3 surface tensiometer (Japan) that was calibrated with ultra-pure water prior to use. The Pt plate was cleaned through flaming; the glassware was rinsed sequentially with tap water and ultra-pure water. The surfactant solution was freshly prepared as a stock solution and then diluted to the desired concentration for each measurement. Surface tension was measured three times for each concentration; an average error of less than 0.5 dyne/cm was obtained routinely.

The CMC and the surface tension at the CMC were determined from the breakpoint of the surface tension and the logarithm of the concentration curve. The surfactant surface excess concentration at the air–solution interface (Γ; units: mol m^{-2}) was calculated using the Gibbs adsorption isotherm equation [7,12]

$$\Gamma = -\left(\frac{1}{iRT}\right)\left(\frac{d\gamma}{d\ln C}\right)$$

where γ represents the surface tension (units: mN m^{-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:

$$A_{cmc} = \frac{1}{N \cdot \Gamma_{cmc}}$$

where N is Avogadro's number and Γ_{cmc} represents the surface excess concentration at the CMC. The value of i represents the number of species at the interface for which the concentration changes with the surfactant concentration. The standard free energy of micellization per mole of monomer unit (ΔG°_{m}) with reference to the standard state of the unit mole fraction for the nonionic surfactants was calculated using the relation [13]

$$\Delta G^{\circ}_{m} = RT \ln \mathrm{CMC}$$

The emission spectra of the solutions were measured using an Aminco–Bowman Series 2 luminescence spectrometer. The excitation wavelength was 335 nm; the emission was measured between 350 and 450 nm. Hydrophobicity was evaluated in terms of the ratio between peak 1 (I_1) at 374 nm and peak 3 (I_3) at 394 nm in the emission spectra of pyrene in 10^{-6} M aqueous solutions. Each pyrene solution was prepared by evaporating the solvent from 0.1 ml of 10^{-4} M pyrene in ethanol, adding 10 ml of the product solution, and then sonicating it for 15 min in an ultrasonic bath.

Conductivity measurements were performed using a COND 720 digital conductivity meter (cell constant: 0.475 cm^{-1}); the experimental temperature was maintained at 298 K (water bath). To perform each series of measurements, an exact volume of distilled water (50 ml) was introduced into the bath and the conductivity measured after each addition.

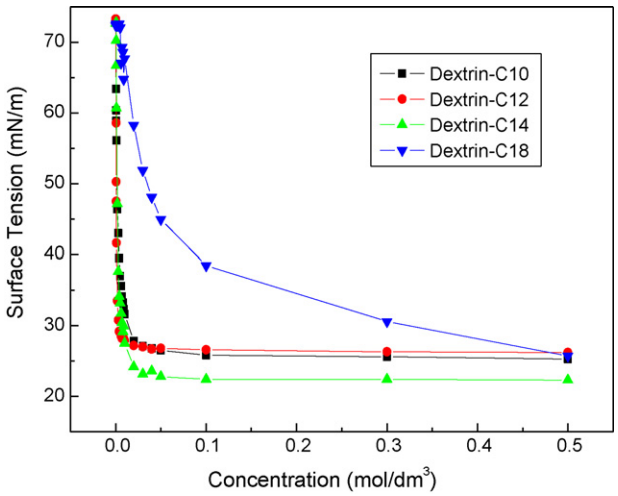

Fig. 2. Plots of surface tension against concentration of the modified dextrins.

The 10 wt% O/W emulsions were prepared by adding soybean oil (10 g) to the modified dextrin solutions (90 g) and then homogenizing (IKA Labortechnik Ultra-Turrax T25 homogenizer) at 11,000 rpm for 5 min. The average diameter (by volume) and size distribution of the emulsion droplets were measured using a Microtrac S3000 apparatus. A ZetaProbe (Colloidal Dynamics) was used to measure the zeta potentials of the modified dextrin emulsions at 298 K. The surface morphology of the emulsions was analyzed using an AETC-M100A electron microscope (AETC Toshi). The surface morphological images of the emulsions pretreated by Pt deposition were examined with scanning electron microscopy (SEM, model S-3000N, Hitachi)

3. Results and discussion

3.1. Surface tension

Dextrins are water-soluble polymeric compounds that exhibit little surface activity because of their lack of hydrophobic groups. After modification with hydrophobic groups (e.g., fatty alcohols), the resulting amphiphilic derivatives concentrate at air–water surfaces, with their hydrophobic chains pointing to the air and their hydrophilic backbones lying on the surface, to reduce surface tension. Fig. 2 displays the surface tension plotted with respect to the concentration of aqueous solutions of the modified dextrins at 298 K.

When a modified dextrin is dissolved in water, it migrates to the surface of the solution to reduce the surface tension. Because the hydrophobic part of the molecule repels water molecules, it faces the air; the head of the molecule remains in the solution, resulting in a reduction of the surface tension at the air–water boundary. Increasing the concentration of the modified dextrin increases the migration of the molecules to the surface, up to a defined concentration (the CMC) at which the surface becomes saturated. The modified dextrin molecules that remain in the bulk solution at this concentration form micelles through aggregation of the tails, with the heads of the modified dextrins forming the outer surfaces of the micelles. Beyond this CMC, no further change in surface tension occurs to the solution.

Table 1 lists the CMCs, surface tensions at the CMCs (γ_{cmc}), maximum surface excess concentrations (Γ_{cmc}), standard free energies ($\triangle G^{\circ}_{m}$), and surface areas per molecule (A_{cmc}) at the air–water interface for the modified dextrins. The driving force for molecular association and formation of micelles from the surfactants is the hydrophobic interaction of hydrocarbon chains: