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Self-aggregation and antimicrobial activity of saccharide-cationic surfactants

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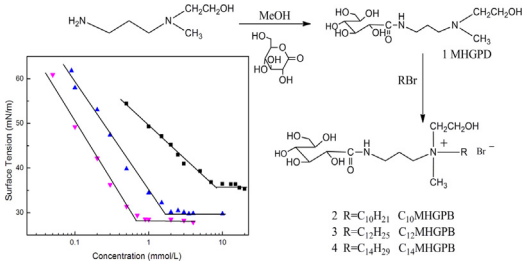
HIGHLIGHTS

- Three novel saccharide-amide cationic surfactants were designed and synthesized.
- Their surface activities, adsorption/aggregation behavior and antimicrobial activity were investigated.
- The cmc values of C_nMHGPB are higher with the longer chains.
- The saccharide-amide cationic surfactants have good antimicrobial activity.

GRAPHICAL ABSTRACT



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ABSTRACT

Saccharide-amide cationic surfactants containing hydroxyethyl group and a sugar moiety N-methyl-N-hydroxyethyl group-N [3-(gluconamide)-propyl]-N-alkylammonium bromide (C_nMHGPB where *n* represents hydrocarbon chain lengths of 10, 12, and 14) were synthesized and the effect of the alkyl chain length on aggregation and antimicrobial activity were investigated. Static/dynamic surface tension and conductivity were applied to study the adsorption and aggregation behavior. The antimicrobial activity was evaluated against *Escherichia coli* and *Staphylococcus aureus*. The most surprising result is that the cmc values of C_nMHGPB are higher with the longer chains. The results showed that dynamic surface tension results are affected more by the hydrophobic head group. The saccharide-amide cationic surfactants containing 10–14 carbon atoms in the alkyl chain showed antimicrobial activity at the concentration of 50–100 ppm, and C_{12}MHGPB surfactant had the best antimicrobial activity.

1. Introduction

A new generation of surfactants should be biodegradable and biocompatible, and thus fulfill the principles of green chemistry [1,2]. Saccharide surfactants may be wholly or partly derived from renewable resources, and these materials are currently of interest from both academic and commercial viewpoints [3,4]. Such products have great promise for the development of detergents, membrane recognition phenomena, nanostructured biological materials, new forms of cosmetics, or drug delivery systems [5,6]. In particular, glucocationic surfactants combine the mild of sugar-based surfactant and the effectiveness of cationic surfactants. Therefore these classes of surfactant show unique properties such as lower toxicity, higher biodegradability, and environmental compatibility [7,8]. So research in the field of cationic surfactants containing a glucose-based moiety has developed very quickly [9]. Quagliotto et al. [10] synthesized glucopyridinium cationic surfactants, and the surfactant showed the tendency to form premicellar aggregates in solution when the hydrophobicity is raised. And thermodynamics and biological properties of the aqueous solutions of the surfactant were studied [11]. Yoshimura et al. [12] studied adsorption and aggregation properties of heterogemini surfactants

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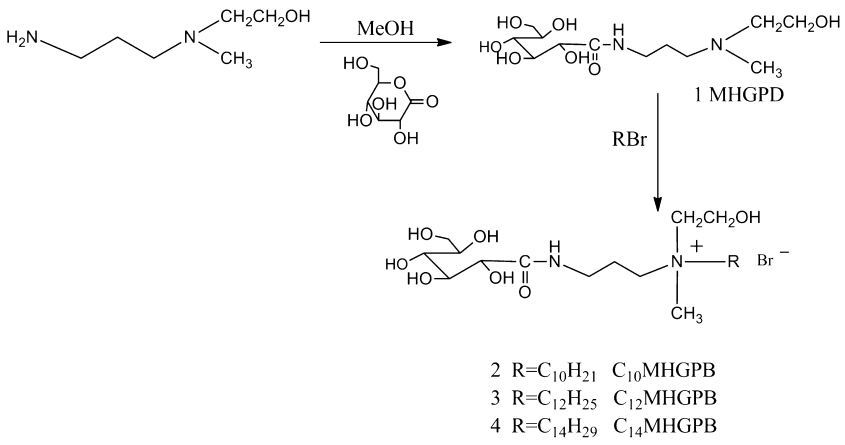

Scheme 1.

containing a quaternary ammonium salt and a sugar moiety. Nabel et al. [8] synthesized two series of gemini cationic surfactants based on glucose and fructose molecules and showed antimicrobial activity on gram-positive and gramnegative bacteria and antifungal activity equal to or comparable to commercially available controls. Viscardi et al. [13] reported a series of surfactants, including a new class of compounds: gluco-pyridinium surfactants. A few parameters, mainly the hydrophobicity of the headgroup, may play a role in finding more efficient antimicrobial structures. Reported in the literature, glucocationic surfactants are mostly based on the combination of the ether bond [14,15], very few examples of surfactants containing a quaternary ammonium salt and a saccharide-amide moiety are reported in the open literature.

In previous work, we have investigated the synthesis of the N,N-dimethyl-N-[3-(gluconamide/lactobionamide)]propyl-N-alkylammonium bromides (C_nDGPB and C_nDLPB, where n represents hydrocarbon chain lengths of 10, 12, and 14) and their adsorption and aggregation properties [16]. It was found that the vesicles formation for C_{14}DGPB may be significantly dependent on its chain length increase and hydrophilic head group decrease. As a continuation of our research aiming to characterize this new class of surfactants, we present a novel family of saccharide-amide cationic surfactants containing hydroxyethyl group and a sugar moiety (Scheme 1). We have investigated the effects of surfactant structure on adsorption and aggregation behavior in aqueous solution. The adsorption and aggregation properties were studied using static/dynamic surface tensiometry, and conductivity. A large number of cationic surfactant has the ability to inhibit the growth and metabolism of microorganisms [17–19]. This study was also intended to provide an improved understanding of the structural parameters affecting biological activity of long chain saccharide cationic surfactants. The research is expected to further the development of saccharide cationic surfactants as multifunctional compounds. In antimicrobial tests, gluco-cationic surfactants, which are expected to be more environmentally friendly, showed moderate activity.

2. Experimental

2.1. Materials

D (+)-Glucose δ-lactone was purchased from Aldrich Chemical Co. *n*-Decyl, *n*-dodecyl, or *n*-tetradecyl bromide were purchased from Acros. N-Methyl-N-(2-hydroxyethyl)-1, 3-propanediamine (MHP) was purchased from Zhangjiagang city, David additives Co., Ltd. N,N-Dimethyl-N [3-(gluconamide)-propyl]-N-alkylammonium bromide (C_nDGPB) and N,N-dimethyl-N [3-(lactobionamide)-propyl]-N-alkylammonium bromides (C_nDLPB) were synthesized as described in our previous study [16]. Other reagents and solvents were of analytical grade. Double distilled water was used for all analyses and measurements of primary properties.

Fourier transform infrared spectroscopy (FT-IR) was performed with a Hitachi 270-30 spectrometer. The examples were mixed with KBr and pressed to a plate for measurement.

Proton nuclear magnetic resonance spectroscopy (^{1}H NMR) was recorded in DMSO as solvent with a Varian Inova-400 MHz spectrometer.

2.2. Synthesis of N-methyl-N-hydroxyethyl group-N′-gluconamide-1, 3-propanediamine (MHGPD)

A mixture of D (+)-glucose δ-lactone (26.7 g, 150 mmol), N-Methyl-N-(2-hydroxyethyl)-1, 3-propanediamine (20.33 g, 154 mmol), and methanol (100 mL) was stirred at reflux temperature for 8 h. After the solvent was removed by evaporation, the residue was washed several times with ether and dried under reduced pressure to a constant mass. Yield: 92.1% (Brown–yellow syrup). IR (KBr): 1651 cm^{-1} (ν(C=O) in amide) and 1542 cm^{-1} (δ (N–H) in amide). ^{1}H NMR (D_2O, ppm) δ: 1.62 (m, 2H, $CH_2\mathbf{CH_2}CH_2$), 2.14 (s, 3H, $N\mathbf{CH_3}$), 2.37 (t, 2H, $NHCH_2CH_2\mathbf{CH_2}$), 2.47 (t, 2H, $N\mathbf{CH_2}CH_2OH$), 3.16 (t, 2H, $NH\mathbf{CH_2}CH_2CH_2$), 3.60–4.18 (8H, protons of the sugar moiety and $NCH_2\mathbf{CH_2}OH$).

2.3. Synthesis of N-methyl-N-hydroxyethyl group-N[3-(gluconamide)-propyl]-N-alkylammonium bromide (C_nMHGPB)

A mixture of MHGPD (54 mmol), *n*-alkyl bromide (60 mmol), and methanol (80 mL) was stirred at reflux temperature for 20 h. After the solvent was removed by evaporation, the residue was washed three times with ether and dried under reduced pressure to a constant mass.

C_{14}MHGPB: Yield: 87% (Brown–yellow syrup), ^{1}H NMR (D_2O, ppm) δ: 0.78 (t, 3H, $(CH_2)_{11}\mathbf{CH_3}$), 1.20 (m, 22H, $(\mathbf{CH_2})_{11}CH_3$), 1.68 (m, 2H, $\mathbf{CH_2}(CH_2)_{11}CH_3$), 1.86 (m, 2H, $NHCH_2\mathbf{CH_2}CH_2$), 1.97 (t, 2H, $\mathbf{CH_2}CH_2(CH_2)_{11}CH_3$), 2.71 (s, 3H, $N\mathbf{CH_3}$), 3.03 (m, 4H, $N(\mathbf{CH_2})_2$), 3.12 (t, 2H, $NH\mathbf{CH_2}CH_2CH_2$), 3.48–4.23 (8H, protons of the sugar moiety and $NCH_2\mathbf{CH_2}OH$).

C_{12}MHGPB: Yield: 89% (Brown–yellow syrup), ^{1}H NMR (D_2O, ppm) δ: 0.79 (t, 3H, $(CH_2)_9\mathbf{CH_3}$), 1.21 (m, 18H, $(\mathbf{CH_2})_9CH_3$), 1.68 (m, 2H, $\mathbf{CH_2}(CH_2)_9CH_3$), 1.87 (m, 2H, $NHCH_2\mathbf{CH_2}CH_2$), 1.98 (t, 2H, $\mathbf{CH_2}CH_2(CH_2)_9CH_3$), 2.72 (s, 3H, $N\mathbf{CH_3}$), 3.03 (m, 4H, $N(\mathbf{CH_2})_2$), 3.13