ORIGINAL ARTICLE



# Synthesis of Alkyl Monoglucoside Citric Monoester and Properties of Its Sodium Salt

Zhu Jin<sup>1</sup> · Jun Zhang<sup>1</sup> · Xiuquan Yang<sup>1</sup> · Yuan Zhou<sup>1</sup>

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Abstract A series of disodium alkyl monoglucoside citric monoesters (AG-EC) were synthesized with an indirect method using glucosides, lauryl/decyl/octyl alcohol and citric acid. The structure and composition of the synthesized surfactants were defined by Fourier transform infrared spectroscopy (FTIR) and liquid chromatography-mass spectrometry (LC/MS). The surface properties, foaming ability and wetting ability were investigated. AG-EC surfactants exhibited excellent water solubility which eliminated the defect of long-chain alkyl glucoside. All three surfactants showed high surface activities. AG12-EC and AG10-EC showed remarkable foaming abilities in distilled water and hard water. Aqueous solutions of AG-EC surfactants spread slowly on a parafilm surface.

**Keywords** Alkyl glucosides · Citric monoester · Anionic surfactant · Surface properties

### Introduction

With the mass production and the reasonable price of alkyl polyglucosides (APG), derivatives such as the sulfonate and sulfosuccinate of APG have attracted researchers' interests [1–4]. Disodium alkyl polyglucosides citrate (APG-EC) based on corn starch, citrus juice and natural oil, is a type of sugar-based green anionic surfactant that is safe and mild [3]. APG-EC is obtained by esterification of citric

Xiuquan Yang apggroup@sina.com

acid with the hydroxyl groups of the APG molecule. On the one hand, it not only retains the excellent properties of APG but also overcomes many of its limitations such as poor water-solubility. In addition, APG-EC has reduced irritation to eyes and skin. Even if the mass fraction of APG-EC reaches 30 % in an aqueous product, no irritation of eyes is observed [5]. Because of its excellent watersolubility, APG-EC aqueous solutions remain clear and bright after prolonged storage near 100 °C [6]. APG-EC shows many improved performance attributes which includes excellent foaming, hard water resistance and water-solubility. It can be applied to cosmetics, beauty care products and detergents in general.

There are two main reaction schemes to synthesize APG-EC surfactants. One is the direct esterification method where APG is reacted with aqueous citric acid under reduced pressure at 120 °C. During the esterification progress, water must be removed by distillation to drive the reaction to completion. At high reaction temperatures, a nitrogen flow is necessary to protect the reactants from oxidation by air [7]. The products after the direct esterification method only contain about 60-80 % monoester of citric acid [8]. Di- and tri-esters of citric acid exhibit almost no surface activities. The indirect method uses anhydrous APG to react with citric acid anhydride. Citric acid anhydride is obtained by reacting anhydrous citric acid and acetic acid anhydride in the presence of acetic acid. In the indirect method, the esterification is carried out under reduced pressure at 90 °C and the reaction products are mostly monoesters of citric acid [8, 9]. Compared with the direct method, the indirect method economizes on starting materials and optimizes the synthesis of APG-EC.

The synthesis of APG 810-EC and APG 1214-EC using the indirect method and their properties has been reported previously [9]. However, the yields of the products were

<sup>&</sup>lt;sup>1</sup> China Research Institute of Daily Chemical Industry, 34# Wenyuan Str., Taiyuan 030001, Shanxi, People's Republic of China

determined from the ester value of the reaction mixture and the structures of the products were only characterized by infrared spectroscopy. The relative reactions and the properties involved with APG and APG-EC cannot be studied clearly since APG and APG-EC both are complex mixtures and it is hard to isolate the pure substance alkyl glucoside (AG) from APG [3]. At the same time, it is difficult to accurately calculate the yield of the reaction from the ester value of reaction mixture since the by-product also contains esters. In this work, a series of AG-EC with different hydrophobic chain lengths were synthesized by the indirect method from the natural materials glucose, fatty alcohol and citric acid. The AG purified from APG synthesized by the Fischer method, was reacted with citric acid anhydride, instead of APG. The pathway is given in Scheme 1. The yields of the products were determined by HPLC method. The structures of the products were characterized by infrared spectroscopy and liquid chromatography-mass spectrometry and the surface properties of the three products were investigated.

### **Experiment Section**

### Materials

Anhydrous glucose, octanol, decanol, dodecanol, anhydrous ethanol, sodium hydroxide, acetone and anhydrous citric acid were purchased from Tianjin Kermel Chemical

Scheme 1 Preparation of AG-EC

Reagent Co. Ltd. (Tianjin China). Acetic acid and acetic acid anhydride were purchased from Tianjin Chemical Reagent Factory (Tianjin China). Squalane was purchased from Flower's Song Fine Chemical Co. Ltd. (Guangzhou China). All the chemicals were of analytical grade and used without further purification. Deionized water was used in all measurements.

### Synthesis and Purification of AG

About 0.3 mol anhydrous glucose powder, 1.8 mol lauryl/ decyl/octyl alcohol and 0.5 g *p*-toluene sulfonic acid were added in a four-neck flask equipped with a mechanical stirrer, a thermometer and a vacuum distillation unit. Under the condition that the stirring was about 300 rpm and the pressure was 45 mmHg, the reaction finished in 3.5 h at 105 °C. A 30 % NaOH aqueous solution was added to adjust the pH of product to 8.0 and the temperature was slowly increased to 230 °C to remove the excess lauryl/ decyl/octyl alcohol by vacuum distillation. The content of AG in the product was about 75 % (wt.).

The product was first dissolved in boiling water before 10 wt% acetone was added. The mixture was held at -10 °C for a couple of hours until crystals appeared. The crystals were then isolated by vacuum filtration and washed three times with ice cold acetone. The resulting white powder was held at 60 °C and 20 mmHg for 24 h. The purification process increased the purity of AG to 95 %.



#### Synthesis of Citric Acid Anhydride

Anhydrous citric acid powder (0.1 mol) and acetic acid anhydride (0.12 mol) reacted in the presence of 0.15 mol acetic acid as solvent at 52 °C in a closed flask equipped with a thermometer and a magnetic stir. After few hours, the reaction mixture changed to colorless solution which indicated that the reaction was finished. The yield of citric acid anhydride was 90 %.

### Synthesis and Purification of AG-EC

The ester was prepared by reacting 0.095 mol of AG (dispersed in squalene) with citric acid anhydride dissolved in acetic acid at 90 °C for about 2 h with stirring. The excess acetic acid and acetic acid anhydride were removed by vacuum distillation. After the esterification step, the alkyl monoglucoside citric monoester was extracted from the mixture by adding 50 mL anhydrous ethanol. NaOH (50 % aqueous) was added to adjust the pH to 8 with constantly stirring. The precipitated AG-EC was isolated and dried at 55 °C and pressure of 10 mmHg. The yield of AG12-EC, AG10-EC and AG08-EC determined by HPLC was about 95, 96 and 96 % respectively.

### Measurements

### **Structure Characterizations**

The mass spectrum of citric acid anhydride was measured using a Shimadzu LCMS-2020 mass spectroscope. Infrared spectroscopy (IR) measurements were performed using a Bruker VERTEX 70 FTIR spectrometer. Citric acid anhydride and AG-EC were mixed with anhydrous KBr powder and tableted. The molecular mass and component of the intermediate which contains mono-(alkyl monoglucoside) citrate were determined by liquid chromatography connected with mass spectrometry (LC–MS). The LC–MS analysis was performed using a Shimadzu LCMS-2020 spectroscope.

The LC separation used an Eclipse Plus C18 column (4.6  $\times$  100 mm, 3.5  $\mu$ m) and gradient elution with solvent A (methyl alcohol) and solvent B (water containing 0.02 % trifluoroacetic acid). The gradient composition was linearly changed within 10 min from 35 % solvent A plus 65 % solvent B to 60 % solvent A plus 40 % solvent B. This final composition was held for a further 8 min. The flow was 1 mL/ min. Mass scans were measured from *m*/*z* 50 up to *m*/*z* 1000, at 350 °C interface temperature, 250 °C DL temperature, -4500 V interface voltage, neutral DL/Qarray. Mass spectrometry data was acquired in the negative ionization mode.

# Surface Tension and Critical Micelle Concentration (CMC)

The surface tension was measured with a Krüss K12 tensiometer at 25  $\pm$  0.1 °C using a platinum plate at a series of concentrations. An average value was recorded after repeating each measurement three times. Before measurement, the surface tension of de-ionized water was confirmed at 72.0  $\pm$  0.3 mN/m. The accuracy of the surface tension measurements was within 0.01 mN/m. The uncertainty limits on the critical micelle concentration (CMC) of AG12-EC, AG10-EC and AG08-EC are estimated to be  $\pm 2$ ,  $\pm 2$  and  $\pm 4$  %, respectively.

The uncertainties in the surface tension at the CMC  $(\gamma_{CMC})$  are estimated to be less than 1 %.

The maximum surface excess concentration ( $\tau_{MAX}$ ) and the minimum surface area ( $A_{min}$ ) per molecule were calculated according to the equations derived from the Gibbs adsorption isotherm [10].

$$\tau_{\rm MAX} = -\frac{1}{2.303nRT} \left(\frac{\partial\gamma}{\partial LgC}\right)_T \tag{1}$$

$$A_{\min} = \frac{10^{18}}{N_A \tau_{\text{MAX}}} \; (\text{nm}^2) \tag{2}$$

*R* is the gas constant, *T* is the absolute temperature;  $\left(\frac{\partial \gamma}{\partial L_g C}\right)_T$  is the slope of the surface tension *versus* the *LgC* curve; *N*<sub>A</sub> is Avogadro's constant. The surfactant anion and counterion were both adsorbed at the surface with increasing surfactant concentration hence *n* equals 2 [10, 11]. The adsorption efficiency (pC<sub>20</sub>) was determined by the value of the negative logarithm of the surfactant concentration C<sub>20</sub> at which the surface tension of water is reduced by 20 mN/m.

### Foaming Property

Foaming properties were measured by the Ross–Miles method [12] at 50 °C. The foam volume at 30 s and 5 min was measured. The foam volume at 30 s represents the foaming power of the sample; the ratio the volume of 30 s and 5 min was used to obtain the stability of the foam.

### Wetting Property

The contact angle of the products (aqueous, 1 %) on parafilm were measured using a Kruss DSA25 Video based contact angle measuring device. The measurement was repeated five times and an average value was determined.

### **Results and Discussion**

### **Structure Characterization**

Structures of AG-EC and citric acid anhydride were characterized by FTIR. The structure of lauryl monoglucoside citric monoester, the intermediate to synthesis  $AG_{12}$ -EC was measured by LC–MS.

The FTIR spectra of AG-EC and citric acid anhydride are shown in Fig. 1. The major absorption bands of AG12-EC are:  $3450 \text{ cm}^{-1}$  (-OH), 2924 and 2853 cm<sup>-1</sup> (C-H),  $1730 \text{ cm}^{-1}$  (ester carbonyl), 1591 and 1392 cm<sup>-1</sup> (-COONa), and 1053 cm<sup>-1</sup> (C–O–C in ester);the major absorption bands of AG10-EC are:  $3442 \text{ cm}^{-1}$  (-OH), 2927 and 2853 cm<sup>-1</sup> (C-H), 1732 cm<sup>-1</sup> (ester carbonyl), 1581 and  $1406 \text{ cm}^{-1}$  (-COONa), and  $1053 \text{ cm}^{-1}$  (C–O–C in ester); the major absorptions of AG08-EC are: 3435 cm<sup>-1</sup> (-OH), 2925 and 2856 cm<sup>-1</sup> (C–H), 1733 cm<sup>-1</sup> (ester carbonyl), 1580 and 1406  $\text{cm}^{-1}$  (-COONa), and 1053 cm<sup>-1</sup> (C-O-C in ester). The major absorptions of citric acid anhydride are  $3492 \text{ cm}^{-1}$  (-OH), 2945 cm<sup>-1</sup> (C-H), 1868 and 1768 cm<sup>-1</sup> (anhydride carbonyl), 1697  $\text{cm}^{-1}$  (acid carbonyl), 1230  $\text{cm}^{-1}$  (C–O in cycle-anhydride). Compared with citric acid anhydride, the signals of ester and -COONa in the FTIR spectra of AG-EC indicate successful synthesis of AG12-EC, AG10-EC and AG08-EC.

The mass spectrum of citric acid anhydride is shown in Fig. 2, the major peaks (m/z, negative) are 60.1 (McLafferty rearrangement), 111.2 [M-60-H]<sup>-</sup>, 173.2 [M-H]<sup>-</sup>, and 191.2 [M<sub>citric acid</sub> –H]<sup>-</sup>. Starting raw material citric acid and the by-product (acetate of citric acid) are seldom observed in the mass spectrum.

In the LC chromatogram of lauryl monoglucoside citric monoester shown in Fig. 3a, peaks a and e represent



Fig. 1 The FTIR spectra of AG-EC and citric acid anhydride



Fig. 2 The mass spectrum of citric acid anhydride

unreacted citric acid anhydride and AG12, respectively. Peaks b, d, f and g indicate lauryl monoglucoside citric monoester and isomers which were obtained by citric acid anhydride reacting with hydroxyl at different loci on the AG12. In Fig. 3b, corresponding to the peak c in the LC chromatogram, the mass spectrum of lauryl monoglucoside citric monoester was characterized by a molecular ion  $[M-H]^-$  at m/z = 521. In Fig. 3c, corresponding to the peak e in the LC chromatogram, the mass spectrum of lauryl glucoside was characterized by the peaks (m/z, negative) at 347  $[M-H]^-$ , 379  $[M + CH_3OH-H]^-$ , 695  $[2 M-H]^-$ , and 718  $[2M + Na-H]^-$ .

### **Surface Activity**

The surface tension and the surface activity parameters of AG-EC in water are shown in Fig. 4 and Table 1, respectively. Table 1 shows that AG12-EC, AG10-EC and AG08-EC reduced the surface tension of distilled water to a range of 30-34 mN/m, which indicated that AG-EC molecules could adsorb at the air-water interface strongly. Similar to normal surfactants, the CMC decreased with increasing length of the hydrophobic carbon chain [10]. The  $\gamma_{CMC}$  values of AG-EC first increased and then decreased with increase in the hydrocarbon chain length. The  $\tau_{MAX}$  values of AG-EC first decreased and then increased with increasing hydrocarbon chain length. The lowest  $\tau_{MAX}$  value of AG<sub>10</sub>-EC could be explained by the co-effect of the electrostatic repulsion between the large head groups of AG10-EC molecules and the attractive forces between the AG<sub>10</sub>-EC molecules. The style of AG10-EC packing at air-water surface is different from AG12-EC and AG08-EC, which occupied more surface area per surfactant headgroup. The Amin of AG10-EC which shows the packing densities [13] is smallest among the three surfactants demonstrated the assumption above. The  $\gamma_{CMC}$  of AG08-EC is lower than AG12-EC which may be due to the hydrophobic carbon chain of AG08-EC much



Fig. 3 The LC-MS spectrum of lauryl monoglucoside citric monoester



Fig. 4 Surface tension versus the logarithm of the aqueous molar concentration of the AG-EC at 25  $^{\circ}\mathrm{C}$ 

shorter than AG12-EC. The molecules of AG08-EC packing are closer than AG12-EC molecules at water/air interface so that AG<sub>08</sub>-EC obtained a smaller  $A_{min}$ , a bigger  $\tau_{MAX}$  and a lower  $\gamma_{CMC}$  [14–16].

With the increase in the tail length, the pC20 values of AG-EC increased. The efficiency of adsorption of a surfactant at the water surface is represented by the pC20 values. These surfactant molecules of a larger pC20 are adsorbed at the water/air interface more efficiently and reduce surface tension of water more efficiently [10, 17].

### **Foaming Ability**

Due to poor water solubility, the foaming ability of AG is also rather poor [18]. By introducing the -COONa head group, the solubilities of AG-EC in water are greatly improved. As seen in Fig. 5, AG12-EC and AG10-EC show excellent foaming power. With the increasing carbon atom number of hydrophobic groups, the foaming power of AG-EC increased in both distilled water and hard water. The longer the hydrophobic groups, the lower the CMC and the more efficient the surfactant is as a foamer [10]. The foam stabilities of AG-EC increased with increasing hydrocarbon chain length. On the one hand, the increased hydrophobic chain length enhances the attraction between molecules, which makes the surface film more stable [10, 19]. On the other hand, the viscosity of surface film increases and the rate of liquid drainage slows down which improves the foam stability [10, 20]. With regard to AG08-EC, a short hydrocarbon chain causes poor foam stability and a high CMC (2.6 g/L) beyond the concentration used in the foaming test. The AG08-EC monomers cannot transfer to the new air/water interface because of the insufficient micelle in bulk water [21]. So the AG08-EC exhibited poor foam ability.

The foaming power and foaming stability of AG-EC were better in hard water than in distilled water. The  $Ca^{2+}$  in the hard water was adsorbed into the surface layer by the negative surfactant ions. As divalent counterions,  $Ca^{2+}$  drove the surfactant molecules to pack tighter which decreased the cross-sectional area of surfactant monomers and the electrostatic repulsion between charged head groups and improved the strength of the surface film [10, 20–22].

### Wetting Ability

As shown in Fig. 6, the wetting abilities of AG-EC are not ideal. The contact angles of AG12-EC, AG10-EC and AG08-EC solutions (1 %, wt.) on paraffin film are 73.5°, 70.9° and 62.3° respectively. The large electrostatic repulsion between the head group yields a loosened assembly at the solid–liquid interface [10]. Not in agreement with normal surfactants, the contact angles of AG-EC decrease with decreasing hydrocarbon chain length [10].

**Table 1** Values of CMC,  $\gamma_{CMC}$ ,  $\tau_{MAX}$ ,  $A_{min}$  and pC<sub>20</sub> for AG-EC

Surfactant	CMC (mmol/L)	γCMC (mN/m)	$\tau_{\rm MAX}~(\mu {\rm mol/m}^2)$	$A_{\min} (\mathrm{nm}^2)$	pC <sub>20</sub>
AG12-EC	0.23	31.94	1.74	0.95	4.64
AG10-EC	1.04	33.60	1.59	1.05	4.01
AG08-EC	5.10	29.72	1.80	0.92	3.39

characterized by FTIR and LC-MS. Moreover, the surface

properties of the products were also investigated. The

lowest surface tension values obtained with 0.23 mmol/L

AG12-EC, 1.04 mmol/L AG10-EC and 5.10 mmol/L

AG08-EC are 31.94, 33.60 and 29.72 mN/m respectively.

AG12-EC and AG10-EC show good foam ability in both

distilled water and hard water. The contact angles of these

1 % aqueous solutions of AG12-EC, AG10-EC and AG08-

EC on parafilm are 73.5°, 70.9° and 62.3°, respectively.

Because they show many excellent properties in surface

activity and nonirritating effects on humans, AG-EC may

be used in wide applications in cosmetics and personal care

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Fig. 5 The foaming properties of AG-EC



Fig. 6 The contact angles of AG-EC aqueous solutions on parafilm versus time

The contact angles cannot reach equilibrium within 100 s because of the slow diffusion rate of AG-EC molecules. The charged head groups of the surfactant reduce the adsorption rate [23]. The contact angle of AG08-EC is smaller and descends faster than others, resulting from the shorter hydrocarbon chain the faster the surfactants in bulk solution diffused to the new interface [24].

## Conclusion

The surfactants AG12-EC, AG10-EC and AG08-EC were synthesized by the indirect process with yields of 95, 96 and 96 % respectively. The structure of the products was

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**Zhu Jin** is a postgraduate student at the China Research Institute of Daily Chemical Industry under the supervision of Prof. Yang Xiuquan. His main research field is the synthesis and properties of surfactants of alkyl polyglucosides derivatives.

**Jun Zhang** is a chemical engineer at the China Research Institute of Daily Chemical Industry. He received his M.Sc. from Shanxi University in 2009. His current research interests are surfactant analysis and formulation design.

Xiuquan Yang obtained his M.Sc. in fine chemicals from Dalian University of Technology in 1990. He is now the Vice-Chief Engineer at the China Research Institute of Daily Chemical Industry. His research focuses are on synthesis, application of natural-derived fine chemicals and the transfer of technological achievements.

**Yuan Zhou** is a chemical engineer at the China Research Institute of Daily Chemical Industry. She received her M.Sc. from Shanxi University in 2011. Her research focuses on the synthesis and investigation of natural-derived surfactant.