



# Influence of branched quaternary ammonium surfactant molecules as levelers for copper electroplating from acidic sulfate bath



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## ABSTRACT

A family of branched quaternary ammonium surfactants (compounds **1a–1c**) with different carbon chains were synthesized for levelers applied in copper electroplating. Their inhibitory actions on copper electroplating were characterized by cyclic voltammetry (CV). Compound **1b**, as representative structure type, was tested by means of different electrochemical methods including CV, polarization curve and electrochemical impedance spectroscopy (EIS) with different concentrations. The interaction between compound **1b** and copper surface was investigated using atomic force microscope (AFM) and X-ray photoelectron spectra (XPS). The results indicated that our newly synthesized compounds, particular **1b**, were effective levelers used for copper electroplating. Compound **1b** could adsorb on copper surface to form an adsorption layer. The adsorption behavior of compound **1b** on copper surface indicated that compound **1b** could inhibit the copper electrodeposition, which provided favorable conditions used as a leveler. Moreover, the addition of compound **1b** could increase the cathodic polarization, which was attributed to the adsorption of compound **1b** during copper electroplating process. In addition, various surface morphologies and crystalline orientation of the plated copper films caused by different concentrations of compound **1b** were characterized by scanning electron microscope (SEM) and X-ray diffraction (XRD) respectively. Effects of compound **1b** on refining the grain size and changing the preferential orientation of the plated copper films were exhibited.

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## 1. Introduction

Copper electrodeposition technique is of great interest for industrial usage. It is a straight forward process for the production of functional copper films with low cost and easy control [1]. However, to get copper deposit in good performance, it is not enough to accomplish electroplating process without additive. Copper electroplating from acidic sulfate electrolyte with small amounts of certain additives has been investigated extensively and those additives lead to significant changes in the properties and orientation of the deposit [2]. Hence, for the purpose of controlling the surface morphology or other certain properties of the copper deposit, additives play a key role in copper electroplating. Thus, the systematic investigation on the additives used in copper electroplating

increased remarkably over the 5-decade due to the increasing demands of the relevant application field [3–5].

Organic additives for electroplating of copper have their different functions and these organic molecules are generally divided into three categories: inhibitors/suppressors, brighteners/accelerators and levelers. Suppressors which sometimes denominated inhibitors are usually high molecular weight polyether compounds which can adsorb on the cathode surface uniformly, forming a monolayer film which is regarded as a barrier to the diffusion of Cu<sup>2+</sup> to the surface and polarizing the cathode. Their synergistic effect with chloride ion has been studied thoroughly [6]. Brighteners also known as accelerators, usually the molecules comprising sulfur-containing, are added to refine and orientate the grain structure of the copper deposit. They change the nucleation process by accelerating charge transfer process at the copper interface and providing active growth sites. Levelers include polyamines and the reaction product of amines with alkylene oxide or epihalohydrin [7,8]. These classified additives' names allotted to the above-mentioned compounds sometimes do not necessarily correspond strictly to specific and clearly separated actions on the deposit morphology [9].

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Recently, many new levelers have been evaluated to identify their effectiveness as additives applied in copper electroplating and these new levelers also have the quaternary ammonium cations [3,10–13]. Among them, quaternary ammonium surfactants as one class of leveler compounds have been used extensively in industry. The existence of amphiphilic groups in one molecule makes surfactants possess some unique properties such as enrichment at interface, which greatly decreases the surface tension of water. The adsorption of amphiphilic molecules from solution onto metals has received some attention in the past as a way of controlling the electrochemistry at metal surfaces [14,15]. In terms of action mechanism, most of these levelers could ionize a cation with quaternary ammonium and halide ion in aqueous solution [16,17]. Quaternary ammonium salts with a large organic cation, which can adsorb on the cathodic surface, form hemimicelle barrier and block the active sites on the metallic surface, change potential distribution of electrode/solution interface and consequently promote inhibition [18].

The investigations in regards to novel structures of quaternary ammonium salt were usually reported in patents [19,20]. In literature, such levelers as cetyltrimethylammonium bromide (CTAB), Janus green B (JGB) and triethyl-benzyl-ammonium chloride (TEBA), were generally used to investigate the function mechanism or structure–function relationship of the quaternary ammonium levelers [3,10–12]. It was enough to demonstrate that an electrolyte containing cationic surfactant could significantly inhibit the copper deposition kinetics and readily form on the copper surface [10].

Herein, a new effective family of branched quaternary ammonium surfactants (compounds **1a–1c**) with different carbon chains, shown in Fig. 1, were synthesized. In this paper we focus on the effects of the innovative structures regarded as levelers in copper electroplating. To the best of our knowledge, there were few reports on this kind of organic additives applied in copper electroplating. Through a series of electrochemical tests, inhibitory efficiencies of branched quaternary ammonium surfactant molecules **1a–1c** and the relationship with their CMC values were verified. The interaction between compound **1b**, as the representative structure type, and the copper surface was showed by AFM and XPS patterns. Effects of compound **1b** on refining the grain size and changing the preferential orientation of the plated copper films were exhibited.

## 2. Experimental

### 2.1. Synthesis of the additives

Melting points were determined with an X-4 apparatus and  $^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra were recorded on a Bruker Avance 400 spectrometer using  $\text{CDCl}_3$  or  $\text{D}_2\text{O}$  as solvent and chemical shifts recorded were internally referenced to  $\text{Me}_4\text{Si}$  (0 ppm) to determine the structure of the compounds. Mass (ESI) spectra were recorded on a Micromass GCTM mass spectrometer.

Initial material, compound **2**, was synthesized by a method according to the literature procedures proposed in our previous research work [21]. Then compounds **8a–8c** were prepared in excellent yield by refluxing an acetonitrile solution of compound **2** and three kinds of primary amines (compounds **7a–7c**) separately in the presence of an excess of potassium carbonate. Among these primary amines, compounds **7a** and **7b** were purchased as commercial reagents. And yet compound **7c** was synthesized in accordance with another three literatures [22–24]. Then compounds **8a–8c** dissolved in acetonitrile were quaternized by small active molecule iodomethane in a sealed tube. After that, ester groups were removed by acidolysis with anhydrous formic acid at room temperature. Finally, in order to increase the solubility

of target molecules in water, six carboxyl groups were converted into sodium carboxylic acid by sodium methylate, now that we obtained the target molecules **1a–1c** resulting in a 62–72% overall yield of compounds **1a–1c** from **2**. Almost each step just needed simple handling of purification. Detail synthetic routes were shown in Schemes 1 and 2.

#### 2.1.1. Synthesis of intermediate compound **8**

Typical procedure for the preparation of intermediate compound **8a**: A mixture of compound **2** (6.50 g, 12.12 mmol), **7a** (0.63 g, 4.87 mmol) and  $\text{K}_2\text{CO}_3$  (4.02 g, 29.09 mmol) in  $\text{CH}_3\text{CN}$  (80 mL) was refluxed for 12 h. After completion of reaction (monitored by TLC), the precipitate was filtered at room temperature and the filtrate was then evaporated off. The resulting residue was purified by silica gel column chromatography using petroleum ether and ethyl acetate (5:1) to give the pure product as a pale yellow solid (3.75 g, yield: 82%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  0.86 (t,  $J=6.8$  Hz, 3H), 1.23–1.25 (m, 12H), 1.41 (s, 54H), 1.97 (t,  $J=8.4$  Hz, 12H), 2.20 (t,  $J=8.4$  Hz, 12H), 2.52 (t,  $J=7.6$  Hz, 2H), 3.08 (s, 4H), 6.97 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  14.09, 22.63, 27.37, 27.57, 28.08, 29.31, 29.50, 29.69, 29.76, 29.88, 31.79, 55.92, 57.34, 59.32, 80.53, 169.83, 172.72. HRMS (ESI):  $m/z$  [ $\text{M}+\text{H}$ ] $^+$  calcd for  $\text{C}_{56}\text{H}_{101}\text{N}_3\text{O}_{14}$ : 1040.7367; Found: 1040.7362. Compounds **8b** and **8c** were synthesized by the same procedure.

Compound **8b**: A pale yellow solid. Yield: 90%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  0.87 (t,  $J=6.8$  Hz, 3H), 1.24–1.27 (m, 28H), 1.42 (s, 54H), 1.98 (t,  $J=8.4$  Hz, 12H), 2.21 (t,  $J=8.4$  Hz, 12H), 2.52 (t,  $J=7.6$  Hz, 2H), 3.10 (s, 4H), 6.97 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  14.14, 22.70, 27.42, 27.58, 28.09, 29.37, 29.67, 29.72, 29.76, 29.87, 31.93, 55.94, 57.35, 59.31, 80.55, 169.84, 172.73. HRMS (ESI):  $m/z$  [ $\text{M}+\text{H}$ ] $^+$  calcd for  $\text{C}_{64}\text{H}_{117}\text{N}_3\text{O}_{14}$ : 1151.8536; Found: 1151.8534.

Compound **8c**: A pale yellow oil. Yield: 85%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  1.25–1.28 (m, 2H), 1.42 (s, 54H), 1.74–1.80 (m, 2H), 1.98 (t,  $J=8.4$  Hz, 12H), 2.20 (t,  $J=8.4$  Hz, 12H), 2.67 (t,  $J=7.6$  Hz, 2H), 3.14 (s, 4H), 7.10 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  18.66, 28.01, 28.20, 28.44, 29.56, 29.66, 29.70, 29.80, 29.89, 30.02, 30.11, 54.79, 57.53, 59.06, 80.61, 169.58, 172.77. HRMS (ESI):  $m/z$  [ $\text{M}+\text{H}$ ] $^+$  calcd for  $\text{C}_{59}\text{H}_{90}\text{F}_{17}\text{N}_3\text{O}_{14}$ : 1387.6151; Found: 1387.6150.

#### 2.1.2. Synthesis of target compound **1**

Typical procedure for the preparation of target compound **1a**: A mixture of compound **8a** (3.70 g, 3.56 mmol) and an excess of  $\text{CH}_3\text{I}$  in  $\text{CH}_3\text{CN}$  (50 mL) was refluxed for 12 h in a sealed tube. In a period of the reaction, additional  $\text{CH}_3\text{I}$  was necessary to complete the quaternization. After the evaporation of the solvent, the residue was stirred in  $\text{HCOOH}$  (20 mL) for 24 h. The solvent was removed by reduced pressure distillation to afford a red oil, which was washed with acetone ( $3 \times 20$  mL) to give a white solid (2.34 g, yield: 78%). Then it was added to a stirred solution of  $\text{CH}_3\text{ONa}$  (0.89 g, 16.60 mmol) dissolved in  $\text{CH}_3\text{OH}$  (50 mL) and the mixture was stirring for 24 h at the room temperature. After the reaction, the solvent was removed by rotary evaporation, affording a pale yellow solid.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ , 400 MHz):  $\delta$  0.71 (t,  $J=6.8$  Hz, 3H), 1.12–1.19 (m, 10H), 1.62 (s, 2H), 1.79–1.83 (m, 12H), 1.98–2.02 (m, 12H), 3.27 (s, 3H), 3.52–3.57 (m, 2H), 4.12 (q,  $J=15.2$  Hz, 4H), 8.30 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{D}_2\text{O}$ , 100 MHz):  $\delta$  13.34, 21.88, 21.96, 22.09, 25.23, 28.01, 28.05, 30.45, 30.84, 31.53, 50.50, 59.43, 61.85, 64.07, 162.87, 182.38. HRMS (ESI):  $m/z$  [ $\text{M}+6\text{H}-6\text{Na}-\text{I}$ ] $^+$  calcd for  $\text{C}_{33}\text{H}_{56}\text{N}_3\text{O}_{14}$ : 718.3757; Found: 718.3762. Compounds **1b** and **1c** were synthesized by the same procedure.

Compound **1b**: A pale yellow solid.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ , 400 MHz):  $\delta$  0.73 (t,  $J=6.8$  Hz, 3H), 1.14–1.21 (m, 26H), 1.63 (s, 2H), 1.79–1.83 (m, 12H), 1.99–2.03 (m, 12H), 3.25 (s, 3H), 3.53–3.57 (m, 2H), 4.16 (q,  $J=15.2$  Hz, 4H), 8.31 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{D}_2\text{O}$ , 100 MHz):  $\delta$  13.50, 22.13, 25.38, 28.28, 28.54, 28.70, 28.65, 28.85, 28.93, 30.47, 31.30,

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