# Synthesis and Properties of a New Multifunctional Gemini Anionic Surfactant

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**Summary**: A new Gimini cationic surfactant (BHAC) was synthesized using succinic acid, epichlorohydrin and *N,N*-dimethyldodecylamine as raw reactants. The reaction conditions of in the quaterisation reaction were investigated including the temperature, reaction time, and molar ratio. The surface properties, including critical micelle concentration (CMC), foamability and foam stability, were evaluated. The results showed that the minimum surface tension was 28.1 mN/m at the concentration of $1\times10^{-3}$ mol/L, and the foamability and foam stability measurement are consistent with those of CMC.

Keyword: Gimini cationic surfactant, Synthesis, Critical micelle concentration, Foam, Corrosion inhibition.

## Introduction

Gemini surfactants have two hydrophobic tails and two hydrophilic head groups connected through a linkage adjacent to the hydrophilic head groups in one molecule [1-3], which have attracted great attention from industrial and academic fields as well, and the Gemini surfactants have been widely used in many fields [4-6]. Gemini surfactants has lower critical micelle concentration (CMC), a relevant foaming capacity and lower Krafft point, so as to display more potent abilities to form micelles reduce the interface tension compared with their corresponding conventional single-chain surfactant counterparts [7-11]. Quaternary ammonium cationic surfactants are widely used in pharmaceutical and cosmetic industries, for example, these surfactants have been used in liposomes mixture to form cationic liposomes which can transfer DNA into cells through fusion witch the cell membranes, or to form spontaneously complexes with DNA and RNA [12]. Besides, the cationic surfactants are widely used as fabric softeners, bleach activators, dispersants, anti-static agents, and emulsifiers not only because of their good performance but also for their mildness or friendly to human beings and their biodegradability [13, 14]. In this work, a new Gemini cationic surfactant was synthesized and characterized, and the interface properties, such as critical micelle concentration (CMC) and foam stability, of the new cationic surfactants will be investigated.

## Experimental

### *Materials*

Succinic acid, isopropanol, Hexadecyl dimethyl amine, epichlorohydrin and the solvent (99%) were purchased from China National Pharmaceutical Group Corporation and were used without any further purification. Solvents such as ethyl ether, ethanol, and isopropanol were also used without further purification. Hydrochloric acid was purchased from Xi'an Chemical Company. Water used for sample preparation was ultrapure having been double distilled and passed through an ion exchange system (Xi'an Deionized Water).

### *Synthesis and Characterization*

A certain amount of succinic acid was added in to isopropanol, and then two equivalent of epichlorohydrin was added in dropwised under stirring at certain temperature. The mixture was stirred for 4h, and then a certain equivalent of hexadecyl dimethyl amine was added and reacted for another 4h under the same conditions. After the reaction finished, the solvent was evaporated, then resident was washed with diethyl ether for three times, recrystalized by ethanol, and dried under room temperature to produce the target compound (named as BHAC). The product was characterized using Fourier transform infrared spectroscopy (FT-IR, Nicolet 5700) at 25℃. FT-IR spectra were recorded in KBr pellets with a Bruker Tensor 37 spectrometer in the 400–4,000 $cm^{-1}$ region. The NMR was operated on Varian XL-400 nuclear magnetic resonance appearance.

### *Surface Tension Measurements*

The surface tension measurements of the

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prepared aqueous surfactant solutions were measured at 25℃ using a Du Nuoy ring tensiometer with a platinum ring (Kruss K100, Germany). The platinum ring was cleaned several times by distilled water before each measurement to remove any residual deposit. Calibration was performed against a range of standard liquids to obtain an excellent agreement with the reference values. The surface tension was measured three times for each sample with a 40-min interval between each reading to ensure equilibrium data. The surface tension values were within an error less than or equal to ±1 mN/m.

*Gravimetric Measurements*

The corrosion tests were performed on Q235A with a composition (in wt.%) C: 0.22, P: 0.045, Si: 0.35, S: 0.05, Mn: 1.40, and Fe balance. The electrolyte solution was 1M HCl, prepared from analytical grade 38% HCl and distilled water. The concentrations of persimmon leaves extracts were employed as 10, 50, 100, 200, 500, and 1,000 mg/L. All tests have been performed in water solutions and at 60 ± 0.5 ºC for 5 h. The gravimetric tests were carried out according to the Standard of Petroleum and Natural Gas Industry of People's Republic of China (Method of SY/T5273-2000, Evaluation method for behavior of corrosion inhibitor for produced water of oilfield) with a few modifications. Each test was done with three specimens simultaneously to give reproducible results.

*Electrochemical Measurements*

The electrodes were mechanically abraded with a series of emery papers (800 and 1,200 grades), then rinsed in acetone and double-distilled water before their immersion in the experimental solution. Electrochemical measurements were conducted in a conventional three-electrode thermostated cell. The electrode was inserted into a Teflon tube and isolated with polyester so that only its section (0.5 cm2) was allowed to contact the aggressive solutions. A platinum disk as counter electrode and standard calomel electrode (SCE) as the reference electrode have been used in the electrochemical studies.

*Scanning Electron Microscopy (SEM)*

The surface morphology of the sample under study in the absence and presence of inhibitors was investigating using a Digital Microscope Imaging scanning electron microscope (model SU6600, serial no. HI-2102-0003) at accelerating voltage of 20.0 kV. Samples were attached on the top of an aluminum stopper by means of carbon conductive adhesive tape. All micrographs of the specimen were taken at 5009 magnification.

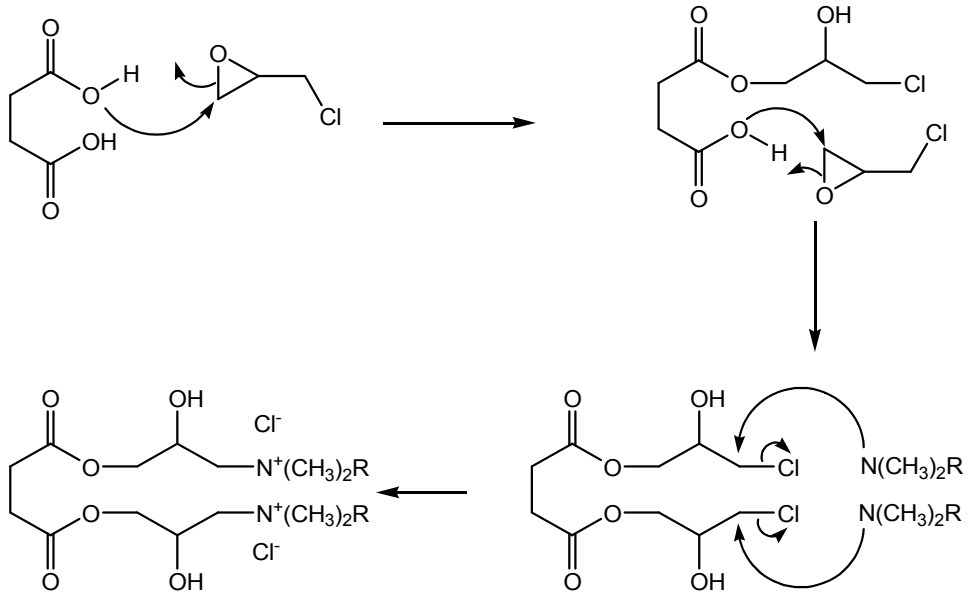
*Foamability and Foam Stability Measurements*

A calibrated 100 mL glass cylinder with a stopper was used for the measurement of foam stability and foamability. Twenty milliliters of surfactant solution (0.1 wt%) was poured into the calibrated cylinder. The foamability was measured by Ross-Miles method, and the volume of the foam were monitored and recorded at different times. The initial foam volume was reported as the foamability. Foamstability was characterized by time, $t_{1/2}$, needed for the collapse of foam to half its initial volume. The experiments were repeated at least three times, the volumes were within an error less than or equal to ±5ml, and the average value was adopted as $t_{1/2}$. All measurements were performed at 25 ºC

**Results and Discussion**

*Chemistry*

During the synthesis of target molecule (BHAC), the succinic acid reacts with epichlorohydrin at the first step with the molar ratio of 1:2. The N atom, with a free pair of p electron, attacks the α-C atom of the Cl by a typical substitution reaction to form the di-esters. In the second step, hexadecyl dimethyl amine quarterizated with two chloro primary carbon and produced the final quaternary ammonium Gemini surfactants with two hydroxyl groups. All the reaction process was summarized in Scheme-1. The synthesized cationic surfactants having two hydroxyl groups and two cations as well as two ester groups, and the counter ion is chloride. The specific bands likes O–H stretching band (3415 cm-1), $sp^3$ C–H stretching band (2922 $cm^{-1}$, 2851 $cm^{-1}$), O=O stretching band (1685 $cm^{-1}$), C–H bending band (1482 $cm^{-1}$), C–N stretching band (1121 cm-1), and C–O stretching band (1102 $cm^{-1}$) can be determined through IR spectra. BHAC: $^1$H NMR ($CD_3OD$, 400 MHz, TMS), δ: 0.88–0.92 (t, 6H, $CH_3$), 1.276–1.386 (m, 52H, $CH_2$), 2.50 (t, 4H, $CH_2$), 3.45 (s, 12H, $CH_3$), 3.52 (d, 4H, $CH_2$), 4.31 (d, 4H, $CH_2$), 4.8 (m, 2H, CH).



Scheme-1: The mechanism of the hydroxyl Gemini anionic surfactant synthesis.

*Reaction Condition Optimizing*

The conditions of in the second step were investigated including the temperature, reaction time, and molar ratio. The temperature was investigated at first with the reaction time of 4h, and molar ratio of succinic acid : epichlorohydrin : hexadecyl dimethyl amine = 1: 2.2: 2.2. The result was shown in Fig. 1. It can be found that the temperature play a important role in this reaction, low temperature leads to low yield, and it becomes ineffectively above 80 ºC. The yield reaches to 85% at 80 ºC, and at the boiling point of the solvent (84 ºC) the yield reaches to 86%. So the reaction temperature can be selected as 80 ºC

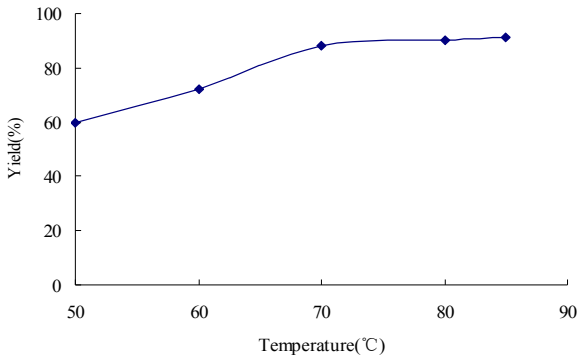



Fig. 1: The effect of temperature on the yield of BHAC.

The reaction time was investigated with the temperature of 80 ºC, and molar ratio of succinic acid: epichlorohydrin : hexadecyl dimethyl amine = 1: 2.2: 2.2. The result was shown in Fig. 2. It shows that the yield reach to the highest at 4 h with the yield of 85%, and further lasting the reaction time will lead to a slight decrease to the yield, so the reaction time was selected as 4 h.

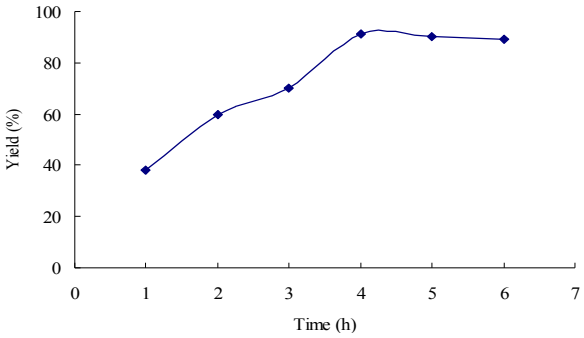



Fig. 2: The effect of reaction time on the yield of BHAC.

The amount of hexadecyl dimethyl amine was investigated with the temperature of 80 ºC, reaction time of 4h. The result was shown in Fig. 3. It shows that the yield reach to 85% with using 2.2 equivalent, and further increasing the equivalent just lead the yield a slight increase to 86%, so the amount of hexadecyl dimethyl amine was selected as 2.2.

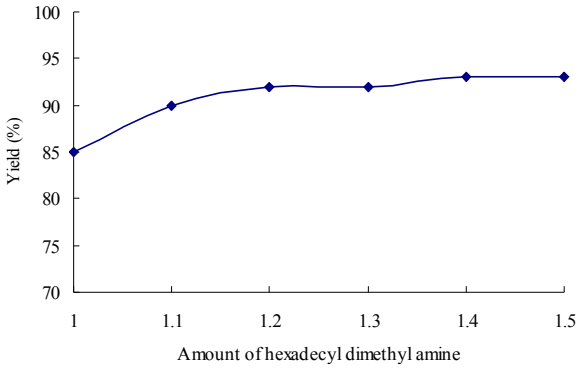



Fig. 3: The effect of amount of hexadecyl dimethyl amine on the yield of BHAC.

*Conformation*

The conformation of the surfactant will affect the interface its characters [15]. The stable conformation of BHAC was calculated using Chem3D 10.0, and it was shown in Fig. 4. The optimized geometries evidence that the nonpolar part, the two hexadecyl groups adopts a significantly linear conformation, which seems to result in a more efficient packing in the solid state, inducing a strong trend to pack together but not compensated by the increase of hydrophilicity, and thus inducing a higher Krafft temperature [16]. The hydrophilic part is strictly compensated by a poor trend to crystallize, but they may bond together by the H-bonds due to the –OH and ester groups.

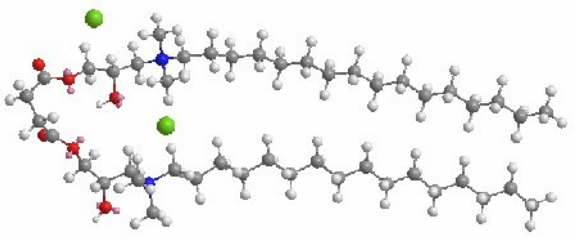


Fig. 4: The stable conformation of BHAC.

*Interfacial Properties and CMC Investigation*

Surface tension of aqueous BHAC solution was measured by a Du Nuoy ring tensiometer at 25ºC. The CMC was determined by measuring the surface tension of the surfactant under deferent concentrations. The CMC was measured as the concentration until the surface tension of the aqueous solution does not decrease any more, and the results at CMC condition are summarized in Fig. 5. It was shown in Fig. 5 that the surface tension of the aqueous surfactant solution decreases with increasing the concentration and reach to 28.5 mN/m at the concentration of $1\times10^{-3}$ mol/L, and further increasing does not decrease the surface tension effectively. The minimum surface tension was around 28.0 mN/m. The critical micelle concentration (CMC) of BHAC was deter-mined from the breakpoint of the surface tension versus thelogarithm of surfactant concentration plot (Fig. 5), and the CMC is $3.8\times10^{-3}$ mol/L.

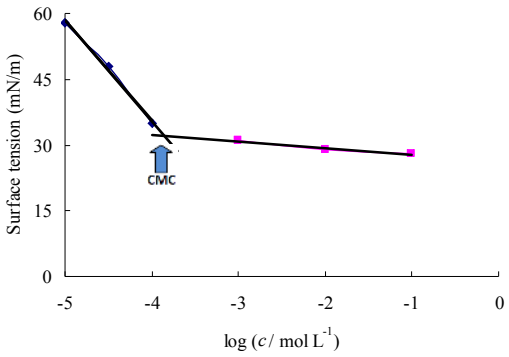



Fig. 5: Variation of the surface tension *vs* Logarithm of concentration for BHCA in water at 25 ºC.

*Corrosion Inhibition and Mechanism*

The efficiency of corrosion inhibitors is defined by the following expression (1):

$$E\% = 100 \times \frac{W_0 - W}{W_0} \qquad (1)$$

where W0 and W are the corrosion rates in the absence and presence of inhibitors, respectively. The inhibition efficiency (IE) of BHAC was investigated in the concentration range 10 to 200 mg/L in 1 M HCl, and the changes of IE (%) with the inhibitor concentration are summarized in Table 1. From the table, it is apparent that BHAC inhibit the corrosion with different efficiency under different concentrations, and the IE increases with increasing concentration, and the IE reaches to 95.8% with the BHAC concentration of 200 mg/L. This result could be attributed to the strong hydrophobicity of gemini surfactants BHAC. The adsorption arised from hydrophobic interactions between surfactant ions and the adsorption arised from a binding of individual gemini surfactantsoncharged sites of steel surface via

electrostatic interaction could occur basically in the same concentration range.

Table-1: The inhibition efficiency of BHAC measured by weight loss.

| Concentration (mg/L) | Corrosion Rate ($g/m^2 \cdot h$) | Inhibition Efficiency (%) |
|---|---|---|
| — | 90.62 | 0 |
| 10 | 53.19 | 41.3 |
| 20 | 35.43 | 60.9 |
| 50 | 15.67 | 82.7 |
| 100 | 4.89 | 94.6 |
| 200 | 3.81 | 95.8 |

Potentiodynamic polarization curves for mild steel in 1 M HCl solution at 30 ºC without and with various concentration of BHAC are presented in Fig. 6. Since the largest displacement exhibited by BHAC is 7 mV, BHAC is considered as a mixed-type inhibitor. Nevertheless, Fig. 6 shows that the decreases in the anodic part are more pronounced than in the cathodic part, meaning that addition of BHAC to 1.0 M HCl solution will reduce anodic dissolution of mild steel more than the cathodic hydrogen evolution reaction.

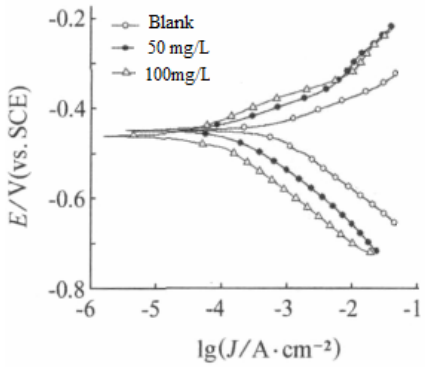



Fig. 6: Tafel plots of BHAC in 1 M HCl.

*Scanning Electron Microscopy*

SEM micrographs of the surface of the mild steel specimens in both acid media in the absence and presence of BHAC are shown in Fig. 7a. From the figs it is clear that, in the absence of BHAC, the mild steel surface was damaged with pitted areas (Fig. 7a), which is typical of pitting corrosion. Fig. 7b shows a smooth surface with deposited extract on the specimens in acid solutions containing 100 mg/L of BHAC. This is due to the formation of an adsorbed film of BHAC on the surface of mild steel. The results of SEM analysis support the inhibitive action of BHAC on the corrosion of mild steel in acid solutions.

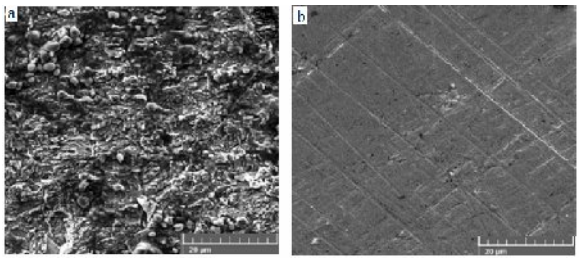



Fig. 7: SEM images of mild steel specimens in a HCl, b HCl with 100 mg/L of inhibitor.

*Foamability and Foam Stability*

The stability of foams made with aqueous surfactant solutions under different concentrations is characterized by the variation of the dispersity with time. The time for complete destruction (or the disappearance of a certain portion of a column) has been widely used as a characteristic of foam stability [17, 18]. The foamability and foam stability of BHAC solution were investigated and summarized in Table-2. From the table, it can be found that the foam volumes of the surfactant come to a high level with a foam volume of 595 ml at the concentration of $5\times10^{-4}$ mol/L, and further increasing can not increase the volume obviously. As the concentration was raised to $2\times10^{-3}$ mol/L, the foam volume just raised to 612 ml. It also showed that the results for foam stability measurement are consistent with those of CMC with a $t_{1/2}$ of 299 s under $5\times10^{-4}$ mol/L.

Table-2: Foamability and foam stability of BHAC solution.

| Concentration (mol/L) | Foam volume (ml) | $t_{1/2}$ (s) |
|---|---|---|
| $1\times10^{-5}$ | 302 | 160 |
| $5\times10^{-5}$ | 388 | 230 |
| $1\times10^{-4}$ | 510 | 282 |
| $5\times10^{-4}$ | 595 | 299 |
| $1\times10^{-3}$ | 610 | 300 |
| $2\times10^{-3}$ | 612 | 300 |

## Conclusions

In this study, a new cationic surfactant was synthesized by the condensation reaction of succinic acid and epichlorohydrin followed by the quarternization with dimethyl amine. The reaction conditions were investigated and optimized, and the structure of the resulting products was characterized by FT-IR. The surface intension of the aqueous surfactant solution was found to increase with increasing the hydrophilicity of a surfactant, and the CMC was about $1\times10^{-3}$ mol/L with the surface

tension of 28.5 mN/m. The foam stability and foam stability were found to consistent with those of CMC. The foam volumes of the surfactant come to a high level at the concentration of $5\times10^{-4}$ mol/L with a foam volume of 595 ml. It also showed that the results for foam stability measurement are consistent with those of CMC with a $t_{1/2}$ of 299 s under $5\times10^{-4}$ mol/L.

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