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Synthesis and Foaming Properties of New Cationic Surfactant with Multifunctional Groups

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A new cationic surfactant (HECA) was synthesized and characterized. The conditions of in the quaterization reaction were investigated including the temperature, reaction time and molar ratio. The critical micelle concentration (CMC) and foamability and foam stability were evaluated and the results showed that it reaches to 32.1 mN/m at the concentration of 1×10^{-3} mol/L, the minimum surface tension was around 28.9 mN/m beyond 1×10^{-2} mol/L. The foam foamability and foam stability measurement are consistent with those of critical micelle concentration.

Keywords: Cationic surfactant, Synthesis, Critical micelle concentration, Foamability, Foam stability.

INTRODUCTION

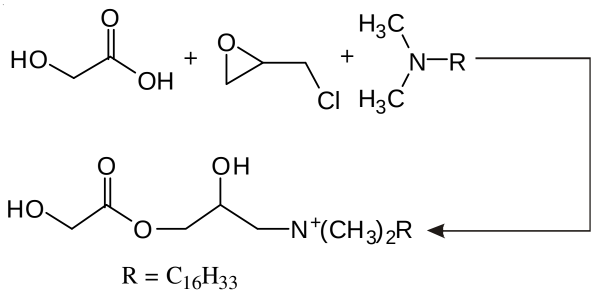
Quaternary ammonium cationic surfactants are widely employed in pharmaceutical and cosmetic industries and in many applications where they come into contact with the skin[1-4]. Furthermore, these surfactants have been included in liposomes in order to obtain cationic liposomes which have the ability to transfer DNA into cells through fusion witch the cell membranes, or to form spontaneously complexes with DNA and RNA[5-8]. The cationic surfactants such as long chain substituted imidazolines and their quarternized imidazolinium salts are frequently used as fabric softeners, dispersants, antistatic agents, bleach activators and emulsifiers not only because of their good performance but also for their mildness to eyes, skin and clothes and their biodegradability[9-12]. Despite having a positive charge, cationic surfactants have been known to have rather low solubility in water[13-15]. Increasing usage of cationic surfactants in industrial and household products has been causing environmental problems owing to poor biodegradability and thus much attention has been paid to develop environmental friendly, nontoxic and biodegradable cationic surfactants[16]. Also from an environment perspective, the most important property of cationic surfactants is that they strongly and rapidly adsorb to negatively charged surfaces of suspended solids and colloids. In view of this adsorption and antimicrobial behaviour they demonstrate poor primary biodegradation and no evidence of ultimate biodegradation. In this work, a new cationic surfactant was synthesized and characterized and the interfacial properties such as critical micelle concentration and foam stability of the synthesized cationic surfactants were investigated.

EXPERIMENTAL

Glycolic acid, isopropanol, *N*,*N*-dimethyldodecylamine and epichlorohydrin (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.

Synthesis and characterization: A certain amount of glycolic acid was added in to isopropanol and then one equivalent of epichlorohydrin was added in dropwised under stirring at certain temperature. The mixture was stirred for 4 h and then a certain equivalent of *N*,*N*-dimethyldodecylamine was added and reacted for another 4 h under the same conditions. After the reaction finished, the solvent was evaporated, then residue was washed with diethyl ether for three times, recrystallized by ethanol and dried under room temperature to produce the target compound (named as HECA). The reaction is described as shown in **Scheme-I**. The product was identified by FT-IR spectrophotometer.

Surface tension measurements: The surface tension measurements of the prepared aqueous surfactant solutions were measured at 25 °C using a Du Nuoy ring tensiometer



Scheme-I: Synthesis of the new cationic surfactant (HECA)

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.

The critical micelle concentration was determined by measuring the conductivity of aqueous solutions of the compounds of increasing concentrations. The solutions were thermostated at 25 °C and maintained under agitation with a magnetic stirrer during the measurements. The critical micelle concentration is given by the slope break in the conductivity *vs*. concentration curve.

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 solution was shaken vigorously for 10 s 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 and the average value was adopted as $t_{1/2}$. All measurements were performed at 25 °C.

RESULTS AND DISCUSSION

In the synthesis of HECA, there was three components participate the reaction. In the first step, glycolic acid reacts with epichlorohydrin with the molar ratio of 1:1 by a typical substitution reaction to produce a chloro hydroxyl glycolic ester. The proton of the carbonyl group is more active than that of the H of hydroxyl group, which makes the carbonyl proton bonds to oxygen atom of epichlorohydrin by hydrogen bond much easier than that of hydroxyl proton. So the reaction will produce the tartaric ester rather than ether. In the second step, *N*,*N*-dimethyldodecylamine quarterizated with the chloro hydroxyl glycolic ester and produced the final quaternary ammonium surfactants. The synthesized cationic surfactants having two hydroxyl groups and one ester group and the counter ion is chloride. All the reaction process was summarized in **Scheme-II**. The specific bands likes O-H stretching band (3410 cm^{-1}), sp^3 C-H stretching band (2921, 2850 cm^{-1}), O=O stretching band (1687 cm^{-1}), C-H bending band (1482 cm^{-1}), C-N stretching band (1121 cm^{-1}) and C-O stretching band (1102 cm^{-1}) could be able to determine through IR spectra.

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 4 h and molar ratio of glycolic acid: epichlorohydrin: *N*,*N*-dimethyldodecylamine = 1: 1: 1.2. 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 °C. The yield reaches to 92 % at 80 °C and at the boiling point of the solvent (84 °C) the yield reaches to 93 %. So the reaction temperature can be selected as 80 °C.

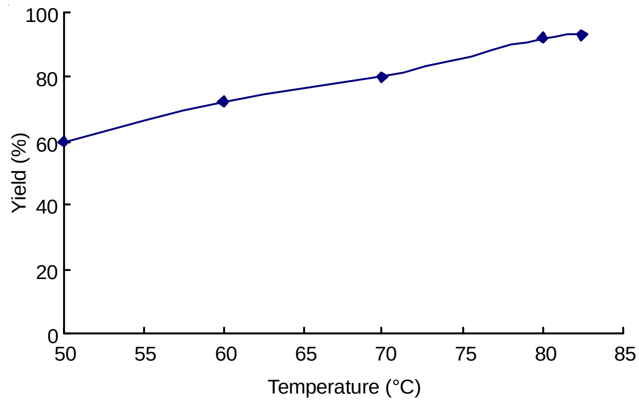
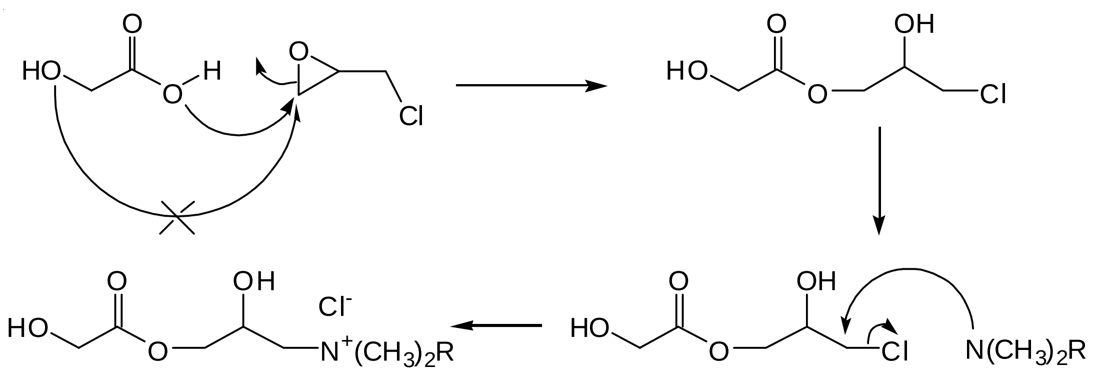


Fig. 1. Effect of temperature on the yield of HECA

The reaction time was investigated with the temperature of 80 °C and molar ratio of glycolic acid: epichlorohydrin: *N*,*N*-dimethyldodecylamine = 1: 1: 1.2. The result was shown in Fig. 2. It shows that the yield reach to the highest at 4 h with



Scheme-II: Reaction mechanism of the HECA synthesis

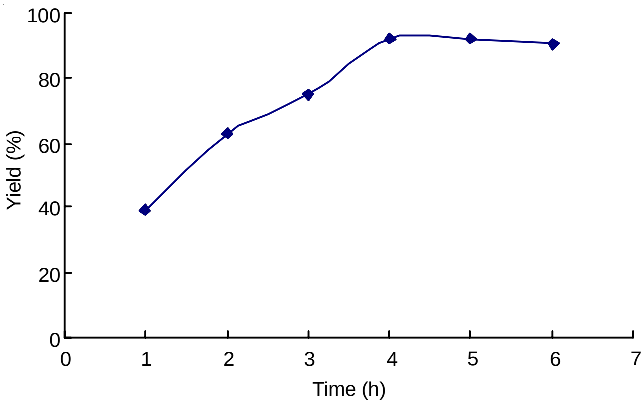


Fig. 2. Effect of reaction time on the yield of HECA

the yield of 92 % and further lasting the reaction time will lead to a slight decrease to the yield, so the reaction time was selected as 4 h.

The amount of *N*,*N*-dimethyldodecylamine was investigated at 80 °C, reaction time of 4 h. The result was shown in Fig. 3. It shows that the yield reach to 92 % with using 1.2 equivalent and further increasing the equivalent just lead the yield a slight increase to 93 %, so the amount of *N*,*N*-dimethyldodecylamine was selected as 1.2.

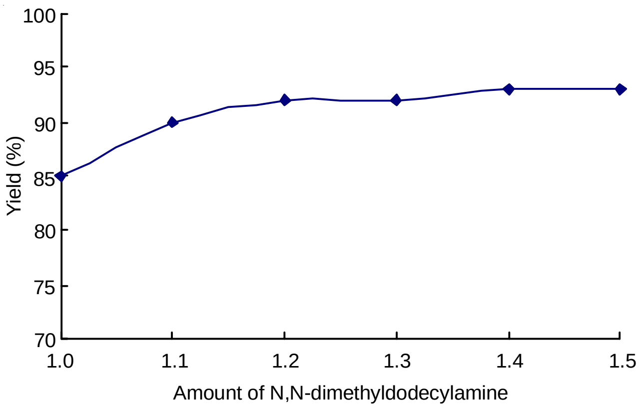


Fig. 3. Effect of amount of *N*,*N*-dimethyldodecylamine on the yield of HECA

Interfacial properties: Critical micelle concentration is defined as the concentration of surfactants above which micelles form and all additional surfactants added to the system go to micelles. The critical micelle concentration was taken as the concentration beyond which the surface tension of the aqueous solution does not decrease any more. The critical micelle concentration was determined by measuring the surface tension of the surfactant as a function of concentration. Surface tension of aqueous surfactant solution was measured by a Du Nuoy ring tensiometer at 25 °C and the results at critical micelle concentration condition are summarized in Fig. 4. As shown in Fig. 4, before reaching the critical micelle concentration, the surface tension changes strongly with the concentration of the surfactant. After reaching the critical micelle concentration, the surface tension remains relatively constant or changes with a lower slope. The surface tension of aqueous surfactant solution decreases with increasing the concentration and reaches to 32.1 mN/m at the concentration of 1×10^{-3} mol/L and further increasing does not decrease the surface

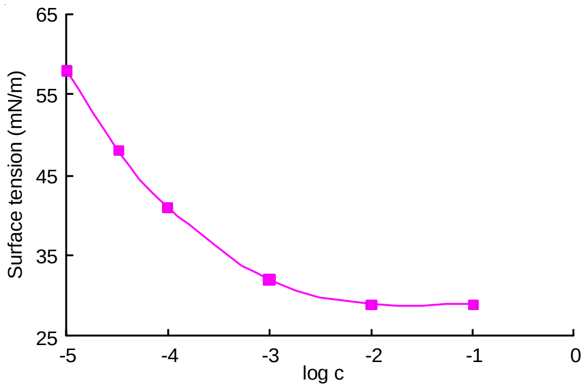


Fig. 4. Surface tension of HECA

tension effectively. The minimum surface tension is around 28.9 mN/m beyond 1×10^{-2} mol/L.

Foamability and foam stability: The stability of foams made with aqueous surfactant solutions against coalescence and diffusion expansion of bubbles 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) is a parameter widely used as a characteristic of foam stability. The foamability and foam stability of HECA solution were investigated and summarized in Table-1. From the table, it can be found that the foam volumes of two surfactants come to the maximum at the concentration of 5×10^{-3} mol/L and further increasing can not increase the volume anymore. It also showed that the results for foam stability measurement are consistent with those of critical micelle concentration.

TABLE-1
FOAMABILITY AND FOAM STABILITY OF HECA SOLUTION

Concentration (mol/L)	Foam volume (mL)	$t_{1/2}$ (s)
1×10^{-4}	260	122
5×10^{-4}	310	175
1×10^{-3}	455	202
5×10^{-3}	555	246
1×10^{-2}	575	260
2×10^{-2}	575	262

Conclusion

In this study, a new cationic surfactant was synthesized by the condensation reaction of glycolic acid and epichlorohydrin followed by the quarternization with dimethyl amine. The reaction conditions were investigated and the structure of the resulting products was elucidated by FT-IR. The critical micelle concentration of the aqueous surfactant solution has been found to increase with increasing the hydrophilicity of a surfactant and the minimum surface tension was around 28.9 mN/m. It has been observed that the results for foam stability measurement are consistent with those of critical micelle concentration.

ACKNOWLEDGEMENTS

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