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ORIGINAL ARTICLE

# The Relationship Between the Structure and Properties of Amino Acid Surfactants Based on Glycine and Serine

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**Abstract** Two series of surfactants based on glycine and serine were synthesized with aproic acid, octanoic acid, decanoic acid, dodecanoic acid, tetradecanoic acid and hexadecanoic acid. All the surfactants were characterized by MS and $^1$H NMR, the structures of the synthesized surfactants are correct and the signals in MS and $^1$H NMR can be explained. The reaction conditions, surface properties and foam properties were studied. For the two series of surfactants, critical micelle concentration (CMC) and $\gamma_{CMC}$ (surface tension at CMC) decrease and surface activity is enhanced as the length of carbon chain increases. The surfactants with tetradecanoyl and hexadecanoyl groups show a good foaming property and especially, the long-chain acyl-serine performs better. These are all related to the hydromethyl group in the serine.

**Keywords** Amino acid · Synthesis · Characterization · Surface tension · Foamability

## Introduction

Amino acids are the basic structural units of proteins. *N*-acyl acid surfactant molecules that contain an amino acid as the hydrophilic part and a long chain as the hydrophobic part constitute an interesting class of biocompatible compounds [1]. *N*-acyl amino acids, also referred to as lipo-amino acids [2], are a special kind of surfactant based on amino acids. Studies on lipo-amino acids have been of great interest in the last few years because of their high degree of biocompatibility and low toxicity. These advantages make lipo-amino acids very favorable for application in biology, especially as a vesicle or bilayer.

For synthesis of lipo-amino acid surfactants, according to the chemical structure of an amino acid, the long chain can be introduced through acyl, ester, amide or alkyl linkage at the amino or carboxyl groups [3]. The side chain could be another action point when a hydroxyl, amino or carboxyl group exists at the same time. There are many ways to introduce the long chain at the amino group. Ryonsuke and Takashi [4] used a mixed acid anhydride to react with the amino acids. This method is a simple and convenient process for preparing N-higher aliphatic acyl derivatives of amino acid, however, the fatty acid produced cannot continue to carry out the chemical reaction so that there is a huge amount of waste as a low atom economic reaction. Rao Valivety prepared a variety of amino acid-based surfactants ranging from simple monoesters to complex bola- and gemini-amphiphiles with lipases in 1998 [5]. Though the enzyme synthesis is a mild, eco-friendly, highly selective method, the low conversion, long reaction time, expensiveness and difficult reuse limit this method of lipase application. Compared with the above methods, Schotten–Baumann condensation is a widely-used method in industrial applications due to its simple synthesis process and mild reaction conditions [6].

Studies on the surface-active properties of different types of surfactants based on amino acids have been reported [7–9]. Akio et al. [8] prepared six kinds of *N*-hexadecanoyl amino acid surfactants, and discussed the relationship between the Krafft temperature and the amino acid residue. Mhaskar et al. [9] studied the effect of structural variation in fatty acid and amino acid moieties on the surfactant properties of sodium salts of *N*-acyl

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condensates of amino acids. In some studies, amino acid-based surfactants were used to mix with other surfactants to study the aggregation behavior including micelle and vesicle formation of the mixed system [10, 11]. Amino acid-based surfactants showed a nice compatibility because of their special structure in which the amide proton can easily form a hydrogen bond with other molecules. Critical micelle concentration (CMC) and foaming ability are two of physicochemical natures of surfactant molecules [12], which are primarily dependent on the chemical structure and properties of the adsorbed surfactant molecules at the interface. Many factors such as the adsorption rate from the solution to the liquid–gas interface, the surface tension of the liquid, the bulk viscosity of the liquid, the microstructure of the foaming solution, the presence of electrolyte as well as the external temperature and pressure could influence the foamability and foam stability [13]. Most studies of foaming ability basically focus on foam height and the change of foam height versus time for comparison of relative foam stability [14–16]. Therefore, the design and synthesis of series of amino acid surfactants are important to the study of the relationship between structure and properties. However, the purity of surfactants will be critical for the studies.

In this work, two series of amino acids surfactants (total 12 compounds, based on glycine and serine, respectively) were designed and synthesized by Schotten–Baumann condensation. Serine surfactants possess an extra hydroxymethyl group compared with glycine surfactants so that the studies of the hydroxyl group effect can be carried out, because the hydrogen bond is helpful for the aggression of the surfactant molecules, water solubility can also hold out more applications in the future. All the surfactants were characterized by MS and $^{1}$H NMR. The relationship between structure and surface activity and foamability of the two series are discussed.

## Experimental Procedures

### General

Caproic acid, octanoic acid, decanoic acid, dodecanoic acid, tetradecanoic acid and hexadecanoic acid were purchased from the Tianjin Guangfu Fine Chemicals Research Institute, China, (99.0 % pure). Glycine and serine were purchased from the Jizhou Huayang Chemical Co., Ltd., China. Phosphorus trichloride was purchased from the Tianjin Chemical Reagent Factory, China, (99.55 % pure). Sodium hydroxide was purchased from Tianjin Kemio Chemical Co., Ltd., China, (≥96.0 % pure). Concentrated hydrochloric acid (31 %) was purchased from Shenzhen Kailixing Chemical Co., Ltd., China. Petroleum ether was of analytical grade. Deionized water was used in all measurements.

The mass spectra were obtained with a High Performance Liquid Chromatography/Mass selective Detector (HP America, model HP1100LC/MSD). NMR analysis was carried out with a Bruker 400-MHz instrument (Bruker, France, Model AVANCE 400 MHz). The surface tension was determined with a processor tensiometer (KRUSS, Germany, Model K100C) by the Wilhelmy plate technique.

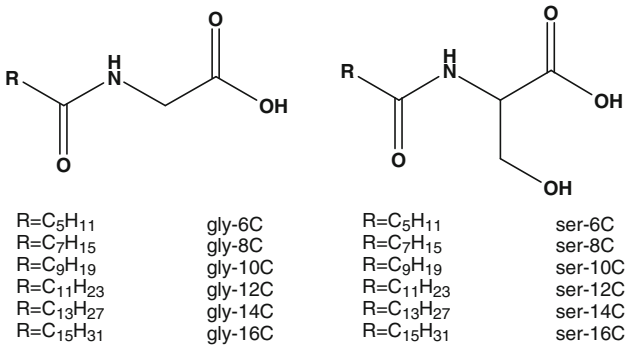
The structures of the synthesized lipo-amino acid are shown in Scheme 1. The surfactants based on glycine are recorded as a glycine series (gly-6C ~ gly-16C, according to their numbers of carbons in the hydrophobic chain). In a similar way, the serine series (ser-6C ~ ser-16C) represents the compounds in the series of serine-based surfactants, are also shown in Scheme 1.

### Synthesis

In the Schotten–Baumann condensation method, the hydrophobic chain is introduced at the amino group with acyl chloride. The process is shown in Scheme 2. All the products exist in the form of lipo-amino acids because of the instability of their sodium salts in the alkaline condition. The sodium salts of lipo-amino acids are obtained by adding an equal amount of sodium hydroxide before use.

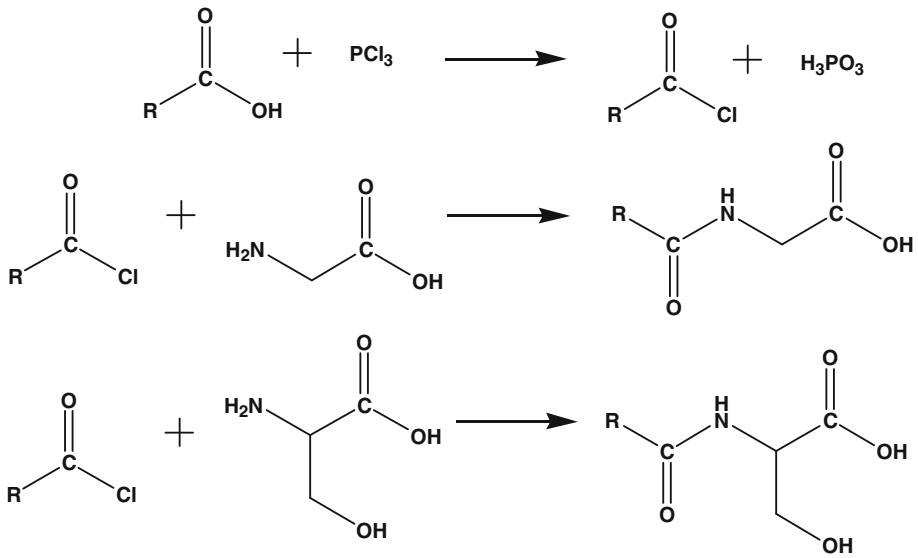
#### *Synthesis of Long-Chain Carbonyl Chlorides*

To take the preparation of decanoyl chloride as an example, as shown in Scheme 2, in order to remove trace water in the materials, decanoic acid (17.2 g, 0.1 mol) was added to a three-necked flask and heated at 100 °C for about 1 h. When the temperature had cooled down to 40 °C, $PCl_3$ (6.88 g, 0.05 mol) was added dropwise into the flask. Later the mixture was stirred at 55 °C for 2 h, and then was transferred into a separating funnel for another 2 h. The upper liquid layer was decanoyl chloride. Other long-chain carbonyl chlorides were obtained in the same way except the reaction temperature [15].




**Scheme 1** The general structure of synthesized lipo-amino acids

**Scheme 2** The synthesis routes of lipo-amino acids




*Synthesis of gly-6C ~ gly-16C*

Gly-10C is taken as an example. Glycine (7.5 g, 0.1 mol) was dissolved in a mixture of acetone (30 mL) and deionized water (15 mL). Then 10 % (wt %) NaOH aqueous solution was added dropwise into the mixture until the pH was 8.5–9.5. Then, decanoyl chloride (9.5 g, 0.05 mol) was added dropwise with vigorous stirring at 0–5 °C. During the reaction process, the pH was kept within a range of 8.5 to 10.5 with 10 % (wt %) aqueous solution of NaOH. Then, the mixture was stirred at 0–5 °C for another 2.5 h and allowed to stand at room temperature overnight. The solvent was removed by vacuum distillation, and then a mixture of concentrated hydrochloric acid and water (1:1 by volume) was added to the residues until the pH was 1–2. A white solid gradually precipitated. The white solid obtained by vacuum filtration was washed with deionized water until the pH of the filtrate was 7 and then with petroleum ether three times [17]. The target product was recrystallized from methanol three times, and the yield was 36.07 %. Other products of the glycine series were obtained in the same way, and the yields for this series were about 30 %.

The mass spectrograms, $^1$H-NMR parameters, and the yields of glycine series were as follows:

Gly-6C

MS (negative): *m/z* 172.1 $[M - H]^-$, 208.1 $[M + Cl]^-$, 286.0 $[M + CF_3CO_2]^-$, 345.0 $[2\ M - H]^-$

$^1$H NMR (400 M, MeOD) δ0.90 (3H, t, $CH_3$), 1.32 (4H, m, 2 × $CH_2$), 1.62 (2H, quint, $CH_2$), 2.24 (2H, t, $CH_2$), 3.89 (2H, s, $CH_2$), yield 20.46 %.

Gly-8C

MS (negative): *m/z* 200.1 $[M - H]^-$, 236.1 $[M + Cl]^-$, 314.0 $[M + CF_3CO_2]^-$

$^1$H NMR (400 M, MeOD) δ0.90 (3H, t, $CH_3$), 1.32 (8H, m, 4 × $CH_2$), 1.62 (2H, quint, $CH_2$), 2.24 (2H, t, $CH_2$), 3.89 (2H, s, $CH_2$), yield 30.05 %.

Gly-10C

MS (negative): *m/z* 228.2 $[M - H]^-$, 264.0 $[M + Cl]^-$, 342.2 $[M + CF_3CO_2]^-$

$^1$H NMR (400 M, MeOD) δ0.90 (3H, t, $CH_3$), 1.32 (12H, m, 6 × $CH_2$), 1.62 (2H, quint, $CH_2$), 2.24 (2H, t, $CH_2$), 3.89 (2H, s, $CH_2$), yield 36.07 %.

Gly-12C

MS (negative): *m/z* 256.2 $[M - H]^-$, 296.2 $[M + Cl]^-$

$^1$H NMR (400 M, MeOD) δ0.90 (3H, t, $CH_3$), 1.32 (16H, m, 8 × $CH_2$), 1.62 (2H, quint, $CH_2$), 2.24 (2H, t, $CH_2$), 3.89 (2H, s, $CH_2$), yield 33.54 %.

Gly-14C

MS (negative): *m/z* 284.2 $[M - H]^-$, 320.2 $[M + Cl]^-$

$^1$H NMR (400 M, MeOD) δ0.90 (3H, t, $CH_3$), 1.32 (20H, m, 10 × $CH_2$), 1.62 (2H, quint, $CH_2$), 2.24 (2H, t, $CH_2$), 3.89 (2H, s, $CH_2$), yield 30.38 %.

Gly-16C

MS (negative): *m/z* 312.3 $[M - H]^-$, 348.3 $[M + Cl]^-$

$^1$H NMR (400 M, MeOD) δ0.90 (3H, t, $CH_3$), 1.32 (24H, m, 12 × $CH_2$), 1.62 (2H, quint, $CH_2$), 2.24 (2H, t, $CH_2$), 3.89 (2H, s, $CH_2$), yield 35.32 %.

*Synthesis of ser-6C ~ ser-16C*

L-Serine (6.3 g, 0.6 mol) and sodium bicarbonate (9.54 g, 0.9 mol) were suspended in 50 mL of water and 20 mL of THF. Under vigorous stirring, four portions of decanoyl chloride were added within 4 h. After 16 h of additional stirring, the organic layer was evaporated and the aqueous solution was quenched to a pH of 2 with concentrated

hydrochloric acid. The precipitated solid was filtered off and dried. Recrystallizing from diethyl ether gave *N*-decanoyl-L-serine as white crystals [18].

The mass spectrograms, $^1$H NMR and the yields of serine series are listed below.

Ser-6C

MS (negative): *m/z* 202.1 $[M - H]^-$, 237.9 $[M + Cl]^-$, 405.1 $[2\ M - H]^-$, 441.0 $[2\ M + Cl]^-$

$^1$H NMR (400 M, DMSO-d6) δ0.86 (3H, t, $CH_3$), 1.26 (4H, m, 2 × $CH_2$), 1.48 (2H, quint, $CH_2$), 2.13 (2H, t, $CH_2$), 3.62 (2H, m, $CH_2$), 4.26 (1H, sext, CH), 7.89 (1H, d, NH), 12.48 (1H, s, COOH), yield 24.79 %.

Ser-8C

MS (negative): *m/z* 230.1 $[M - H]^-$, 266.0 $[M + Cl]^-$, 344.0 $[M + CF_3CO_2]^-$, 483.3 $[2\ M - 2H + Na]^-$

$^1$H NMR (400 M, DMSO-d6) δ0.86 (3H, t, $CH_3$), 1.26 (8H, m, 4 × $CH_2$), 1.48 (2H, quint, $CH_2$), 2.13 (2H, t, $CH_2$), 3.62 (2H, m, $CH_2$), 4.26 (1H, sext, CH), 7.89 (1H, d, NH), 12.48 (1H, s, COOH), yield 49.85 %.

Ser-10C

MS (negative): *m/z* 258.2 $[M - H]^-$, 294.0 $[M + Cl]^-$, 372.1 $[M + CF_3CO_2]^-$

$^1$H NMR (400 M, DMSO-d6) δ0.86 (3H, t, $CH_3$), 1.27 (12H, m, 6 × $CH_2$), 1.48 (2H, quint, $CH_2$), 2.16 (2H, t, $CH_2$), 3.62 (2H, m, $CH_2$), 4.26 (1H, sext, CH), 7.93 (1H, d, NH), 12.48 (1H, s, COOH), yield 53.04 %.

Ser-12C

MS (negative): *m/z* 286.0 $[M - H]^-$, 322.1 $[M + Cl]^-$, 400.0 $[M + CF_3CO_2]^-$

$^1$H NMR (400 M, DMSO-d6) δ0.86 (3H, t, $CH_3$), 1.27 (16H, m, 8 × $CH_2$), 1.48 (2H, quint, $CH_2$), 2.16 (2H, t, $CH_2$), 3.64 (2H, m, $CH_2$), 4.26 (1H, sext, CH), 7.88 (1H, d, NH), 12.48 (1H, s, COOH), yield 57.84 %.

Ser-14C

MS (negative): *m/z* 314.0 $[M - H]^-$, 350.0 $[M + Cl]^-$, 428.0 $[M + CF_3CO_2]^-$

$^1$H NMR (400 M, DMSO-d6) δ0.86 (3H, t, $CH_3$), 1.27 (20H, m, 10 × $CH_2$), 1.48 (2H, quint, $CH_2$), 2.16 (2H, t, $CH_2$), 3.64 (2H, m, $CH_2$), 4.26 (1H, sext, CH), 7.88 (1H, d, NH), 12.48 (1H, s, COOH), yield 61.22 %.

Ser-16C

MS (negative): *m/z* 342.3 $[M - H]^-$, 378.3 $[M + Cl]^-$, 456.2 $[M + CF_3CO_2]^-$

$^1$H NMR (400 M, DMSO-d6) δ0.86 (3H, t, $CH_3$), 1.27 (24H, m, 12 × $CH_2$), 1.48 (2H, quint, $CH_2$), 2.16 (2H, t, $CH_2$), 3.64 (2H, m, $CH_2$), 4.26 (1H, sext, CH), 7.88 (1H, d, NH), 12.48 (1H, s, COOH), yield 83.87 %.

### *Determination of CMC and $\gamma_{CMC}$*

The surface tension of different concentrations of *N*-acyl amino acid sodium solutions was measured by the Wilhelmy plate technique with a processor tensiometer (KRUSS, Germany, Model K100C) at 25 °C. All surface tension values shown were the average of four measurements. The CMC and $\gamma_{CMC}$ were determined from the breakpoint of the plot of the surface tension of their aqueous solutions versus concentration.

### *Foamability*

First, 30 mL of the sodium of lipo-amino acids aqueous solution was added into a 100-mL stoppered cylinder. Then the stoppered cylinder was violently shaken 40 times. The total volume and the volume of the aqueous solution left were recorded at 0 min (time 0 min is set after the shaking), 1, 2, 5, 10 and 30 min. The differences between the two values was the volume of the foam.

## Result and Discussion

### Synthesis of *N*-Acyl Amino Acid

The hydrophobic chain is introduced by acyl chloride. However, the instability of acyl chloride in an aqueous solution is deadly during the preparation process of long-chain acyl-amino acid. For acyl-glycine, the pH must be exactly controlled at 8.5–9.5 with sodium hydroxide, and this pH range is helpful for the nucleophilicity of the amino group and makes it possible to reduce the hydrolysis reaction of acyl chloride as much as possible. For the preparation of long-chain acyl-serine, in order to avoid the hydrolysis reaction as much as possible, the pH was controlled with sodium carbonate, the dropping speed of acyl chloride should be necessarily slow.

### Proton NMR Spectroscopy

The $^1$H-NMR spectra of *N*-acyl amino acids were all recorded. Taking *N*-caprylyl glycine as an example of the glycine series, the chemical shifts of the constituent protons are shown in Fig. 1. A triplet is observed at a $\delta$ value of 0.8, which is characteristic of methyl protons adjacent to methylene protons in long-chain alkyl group. The methylene [$(-CH_2)_4-$] proton resonance is observed at $\delta$ of 1–2 as a multiplet. The two methylene groups adjacent to the amide group give the signals at $\delta$ of 1.62 (quint) and 2.24 (t). The signals at $\delta$ of 3.89 are the resonance of protons in the methylene in the structure of glycine. The rest are solvent signals. There are no signals revealing the protons of the acylamino group and carboxy group in $CD_3OD$.

Due to the structural similarities between the glycine and serine series, some similar signals can be seen in the $^1$H-NMR spectra from Figs. 1 and 2. Taking *N*-caprylyl serine as an example (shown in Fig. 2), the protons in the

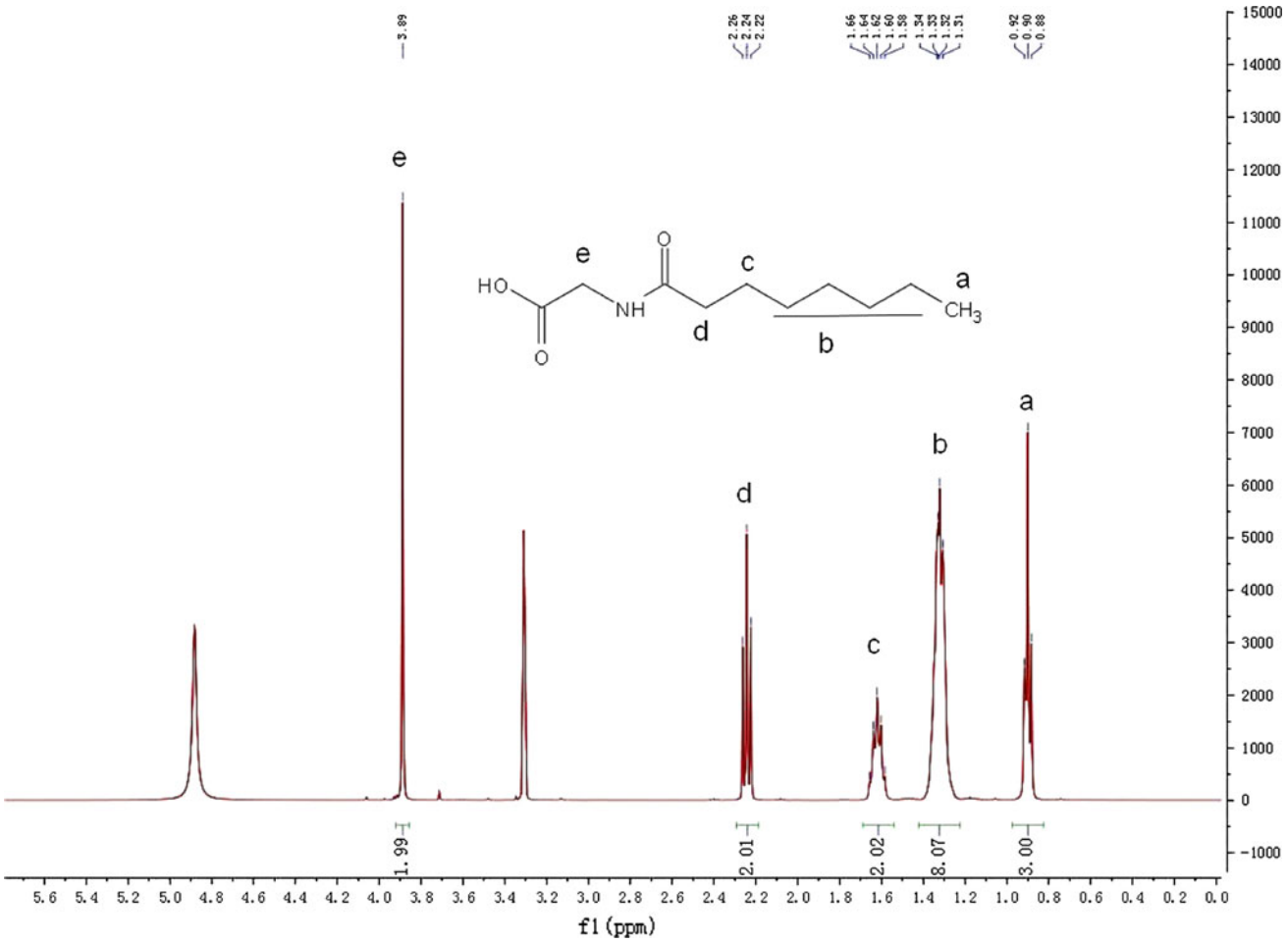



**Fig. 1** The $^{1}$H-NMR spectra of *N*-caprylyl glycine

long chain also show similar series of signals at $\delta$ of 0–3 (peak a, b, c, d). The methine proton resonance is observed at $\delta$ of 4.2 for the influence of hydroxymethyl group. Two quartets are observed at a value of 3.5–3.8, which is characteristic of methine proton in the hydroxymethyl group. However, the signals of active hydrogen in the structure are observed at $\delta$ of 12.48 (COOH), 7.89 (CONH) in DMSO-d6.

Two active groups in the structure of serine are the hydroxyl group and the amino group, both have the possibility to react with acyl chloride, an acylation reagent. Which group will be preferable to react with acyl chloride, the hydroxyl group or amino group? In Fig. 2, the methine proton resonance in the serine structure shows a signal at $\delta$ of 3.5–3.8. This shows that the methane group is adjacent to the hydroxyl group rather than the ester group, which should give a signal at $\delta$ over 4.0. So the hydroxyl group in the molecular structure can imply that it is the amino group reacted with acyl chloride instead of the hydroxyl group.

At the same time, the serine series are also a kind of chiral molecule. From Scheme 3, for the influence of charity center, $H_a$, $H_b$ and $H_c$ form an ABX system. $H_a$ and $H_b$ are observed as two quartets $[(1 + 1)\cdot(1 + 1)]$ at $\delta$ of 3.5–3.7 in Fig. 2. $H_c$ is in a system ABMX, which contained $H_a$, $H_b$, $H_c$ and the hydrogen in the amino group. Because the coupling constants of $H_a$, $H_b$ and $H_c$ are almost same, $H_c$ gives a sextet signal $[(2 + 1)\cdot(1 + 1)]$ at $\delta$ of 4.2–4.3.

## Surface Properties

The surface tension of the two series of surfactants at different concentrations was measured by the Wilhelmy plate technique at 25 °C. The curves of surface tension versus concentration (see Figs. 3, 4) were drawn to obtain the CMC and $\gamma_{CMC}$values, which are shown in Table 1.

For the same series, CMC and $\gamma_{CMC}$ decrease gradually as the chain length increases. The trend is consistent with

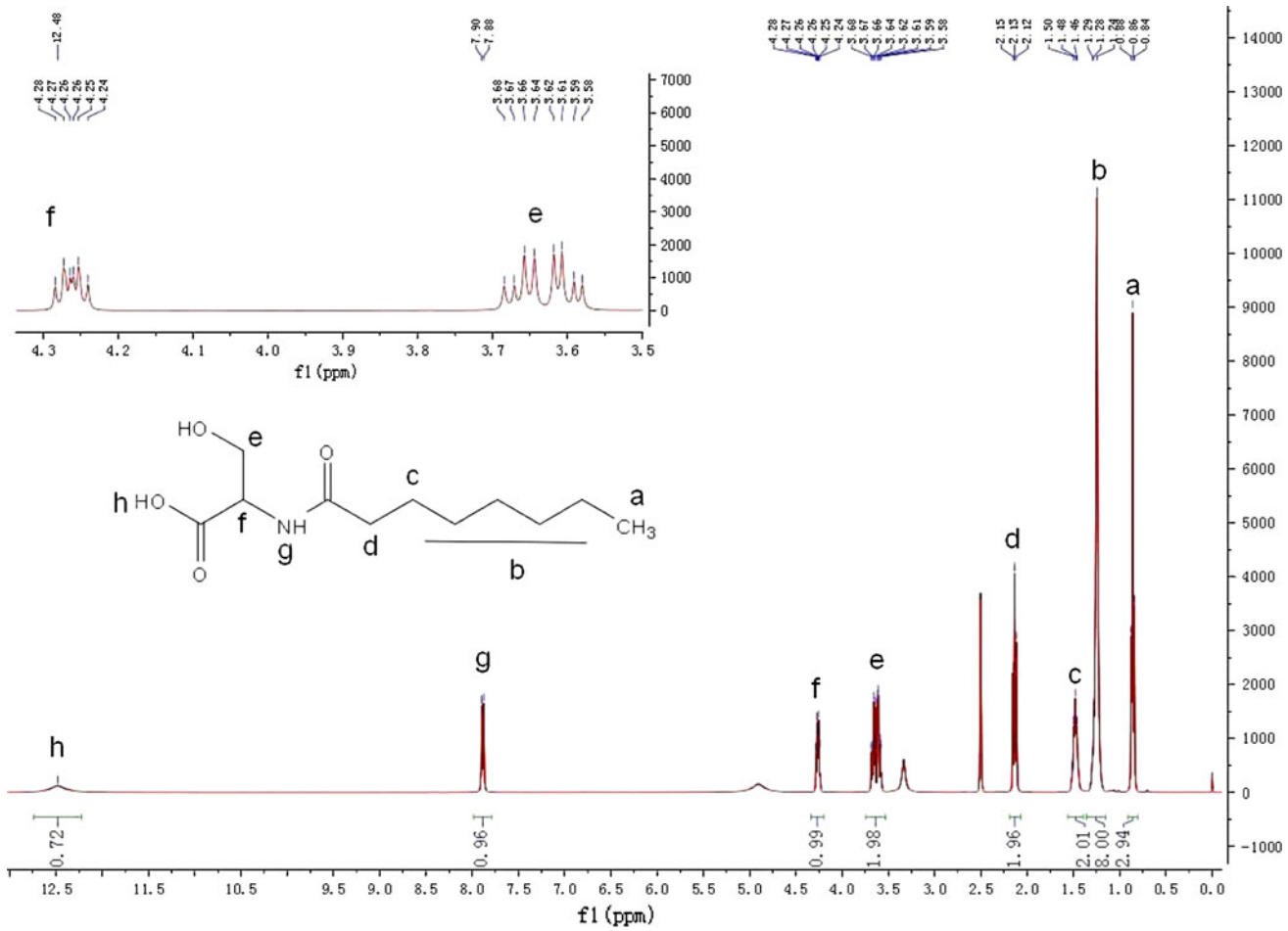
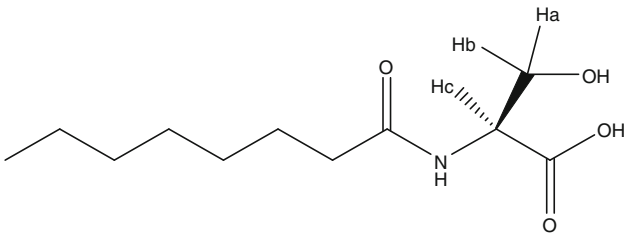



**Fig. 2** The $^{1}$H-NMR spectra of *N*-caprylyl serine




**Scheme 3** The charity structure of *N*-caprylyl L-serine

the general rules of amphipathic molecules, that is, for the amphipathic chain, the efficiency of reducing surface tension increases and the CMC decreases. Compared to the glycine series, the serine series shows a lower surface tension below 30 mN m$^{-1}$. Obviously, different molecular structures between the serine series and the glycine series are the key factors to make the distinct changes in surface tension. The hydroxymethyl group in the serine series could increase the water soluble ability so that a relatively lower surface tension can be observed. The surfactants with hydrocarbon chains of 6 and 8 carbon atoms have such a high CMC value (over $10^{-1}$ M) that large amounts of the samples are needed and it is difficult to obtain the CMC and $\gamma_{CMC}$, so no data are listed in Table 1.

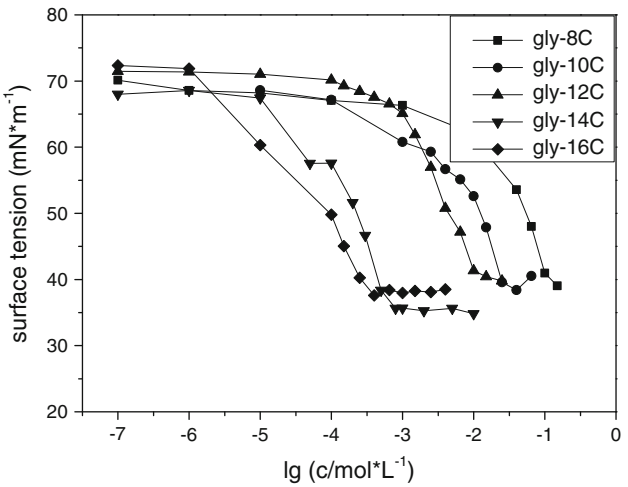



**Fig. 3** Surface tension ($\gamma$) versus lg(c/mol L$^{-1}$) of long-chain acylglycine at 25 °C

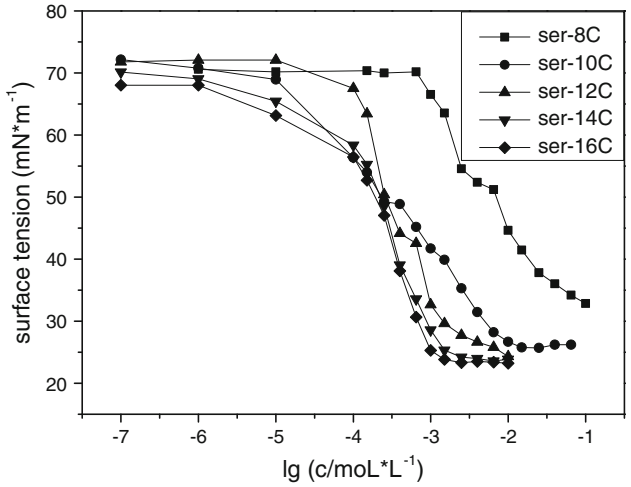



**Fig. 4** Surface tension ($\gamma$) versus lg(c/mol $L^{-1}$) of long-chain acyl-serine at 25 °C

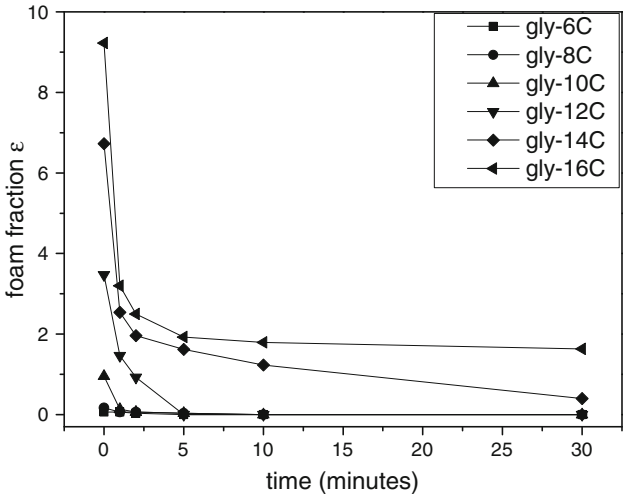



**Fig. 5** The foam fraction $\varepsilon$ against time of long-chain acyl-glycine at 25 °C

**Table 1** The CMC and $\gamma_{CMC}$ values of all the synthesized amino acid surfactants

| Surfactants | CMC (mol $L^{-1}$) | $\gamma_{CMC}$ (mN $m^{-1}$) |
|---|---|---|
| Gly-6C | – | – |
| Gly-8C | – | – |
| Gly-10C | $2.51 \times 10^{-2}$ | 38.98 |
| Gly-12C | $1.00 \times 10^{-2}$ | 41.17 |
| Gly-14C | $5.01 \times 10^{-4}$ | 35.61 |
| Gly-16C | $3.16 \times 10^{-4}$ | 38.24 |
| Ser-6C | – | – |
| Ser-8C | – | – |
| Ser-10C | $1.00 \times 10^{-3}$ | 26.21 |
| Ser-12C | $1.58 \times 10^{-3}$ | 29.97 |
| Ser-14C | $1.58 \times 10^{-3}$ | 24.42 |
| Ser-16C | $1.26 \times 10^{-3}$ | 23.14 |

The CMC was determined by the intersection point of two tangents, which were drawn at the front and back of the curve's breakthrough point. The $\gamma_{CMC}$ is the surface tension at the CMC

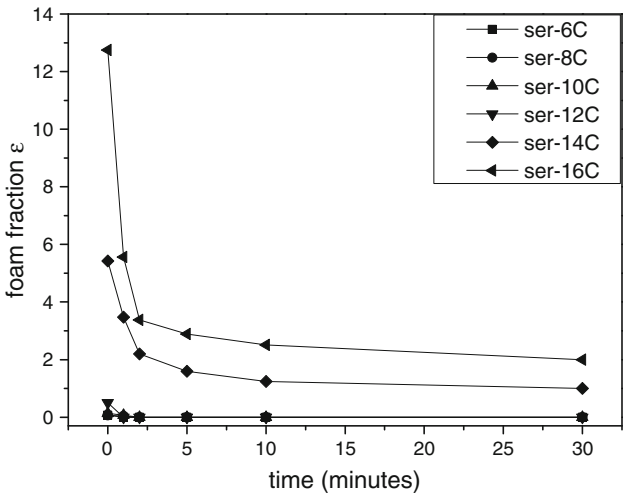
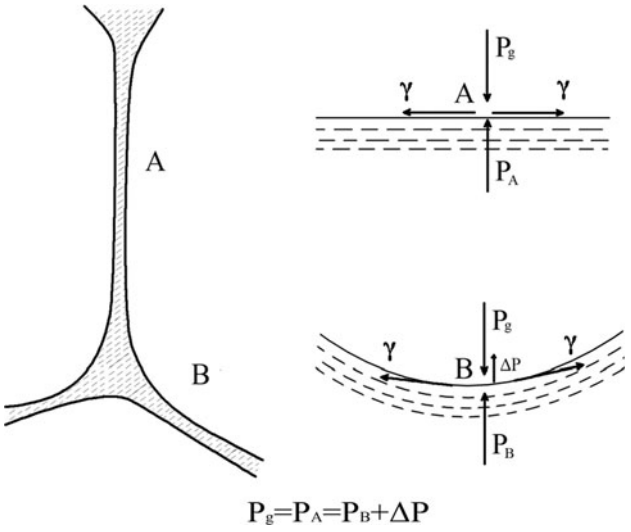



**Fig. 6** The foam fraction $\varepsilon$ against time of long-chain acyl-serine at 25 °C

## Foamability and Foam Stability

A bubble refers to a dispersion system in which gas is scattered inside a liquid. The process of bubbles from their production to their bursting consisting of two parts: liquid drops and gas escapes. In order to characterize the foamability, the foam fraction $\varepsilon$ ($\varepsilon$ = volume of foam/volume of liquid) is introduced. The results are shown in Figs. 5 and 6. All the curves almost flatten after 5 min, which means the system is virtually balanced. The time before the system becomes balanced and the value of $\varepsilon$ at equilibrium will characterize the foamability and foam stability, the longer the time and the larger the $\varepsilon$, the better will be the foamability and foam stability.

From the curves in Figs. 5 and 6, it could be found that, for the two series of surfactants, a better foamability and stability are observed as the length of the hydrophobic chain increases, especially when the carbon number is 14 and 16. This phenomenon is related to the surface tension of the surfactants. Taking the serine series as an example, the surface tension (at $10^{-3}$ mol $L^{-1}$) changes from 66.52 to 25.37 mN $m^{-1}$ as the length of hydrophobic chain changes from 8 to 16 carbons. A possible mechanism to explain the relationship between surface tension and foamability and stability is presented in Scheme 4. Both A and B represent two typically different situations in the wall of a bubble. In general, the pressure inside the liquid is equal to that of air in the bubble, just like the situation at point A ($P_g = P_A$). However, at the point B, it changes ($P_g = P_B + \Delta P$). The pressure on the liquid surface has additional pressure




**Scheme 4** The microstructure of the bubble wall

because of the surface tension. So there is a pressure difference between A and B to make the liquid flow from point A to point B. The film at point A has a tendency to be thinner and the bubble is easily burst.

According to the Laplace Equation (Eq. 1):

$$\Delta P = \gamma\left(\frac{1}{r_1}+\frac{1}{r_2}\right). \quad (1)$$

The increment is proportional to the surface tension ($\gamma$), the smaller the surface tension, the smaller pressure difference between points A and B. That means the low surface tension weakens the tendency at which the liquid flows from point A to point B, and consequently, the bubble shows better stability.

Compared with the glycine series, the serine series showed a better stability of foam, the stability of ser-16C and gly-16C was especially obvious. It is mostly attributable to the single head group between the two series. An extra hydroxymethyl in the serine series could form a hydrogen bond among the surfactant molecules, and make the surfactants form a more ordered arrangement on the gas–liquid interface, then, contributing to a stronger film of the bubble than that of glycine series.

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