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Studies On the Synthesis, Surface Activity and the Ability to Form pH-regulated Wormlike Micelles with Surfactant Containing Carboxyl Group

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ABSTRACT

In this article, a series of pH regulated surfactants with different hydrophobic chain length and carboxyl group molecular structure positions were designed and synthesized. The molecular structure of pH regulated surfactants was analyzed by mass spectrometry and ¹H NMR spectroscopy. The results of the surface activity test show that the pH regulated surfactants have lower surface tension, which indicates that it is easier to adsorb directionally at the gas-liquid interface and to aggregate in solution. Both inorganic and organic counterions can improve the viscosity of the system to some extent, but the viscosity-increasing ability of organic counterions is

much higher than that of inorganic counterions. The results of rheology and dynamic light scattering show the transition from spherical micelles to wormlike micelles was observed when pH increased from 5 to 8 in the Docos-13-enoylamino-acetic acid (Gly-22)/ Trimethylstearylammmonium chloride (ODAC) system. The results of Cryo-transmission electron microscopy verify this result directly. Also, the experimental results show that the Gly-22/ODAC system has excellent pH cycle regulation performance, which can significantly reduce the application cost of the system.

Keywords: pH regulated surfactant; Surface activity; Wormlike micelles; Molecular self-assembly.

1. Introduction

In the past decade, the fabrication of smart responsive materials has been a hot research area in the field of soft materials¹. Smart responsive materials can dynamically change their structural and functional requirements in response to environmental changes. In these studies, the surfactant is one of the hot research objects, which has the characteristic of changing the structure spontaneously under the stimulation of the environment and then inducing the change of the macroscopic properties such as viscosity and elasticity of the solution². At the same time, the molecular structure of the surfactant remains intact, so that it is recycled. The external stimuli that regulate changes in the molecular structure of surfactants are known as

“switches”. The main types of the switch are light, carbon dioxide, temperature, magnetic, pH and so on³.

Up to now, extensive and in-depth research has carried out on the synthesis and application of regulated surfactant. Although some progress has been made, the shortcomings still exist. The light-regulated surfactant can adjust the wavelength and duration of light precisely, but it has some disadvantages such as longer response time, incomplete change of molecular structure, reduced light transmittance, environmental limitation and high requirement of equipment⁴. The pollution degree of redox-regulated surfactant is small, but the complex molecular structure, the expensive ferrocene derivatives, and the difficulty of viscosity reduction limit the application of this kind of regulated surfactant in the practical production⁵. The CO₂ regulated surfactant has little pollution to the environment, but the system has poor temperature resistance, slow response period, complicated and expensive ventilation equipment⁶. The temperature regulated surfactant has little pollution to the system. However, it is challenging to realize precise control and narrow temperature control window. In contrast, the stable, biocompatibility, highly surface-active, and inexpensive pH regulated surfactant has the potential to achieve large-scale industrial applications⁷.

pH regulated surfactant is a class of molecules that can respond to pH environment changes in the system. These surfactants mainly through cis-trans, electrostatic repulsion, protonation, and other ways to cause changes in physical and

chemical properties of surfactant. Hongsheng Lu⁸ et al. studied the wormlike micelle system with pH regulation ability, which was formed by *N,N*-dimethyloleamide alone. By changing the pH value, the micelles can change from spherical micelles to vesicles in a reversible way. Wang⁹ et al. designed and synthesized a series of single-chain surfactant C₁₈N₃ with multi-amino groups, and studied the aggregation behavior of C₁₈N₃ in aqueous solution under different pH conditions. With the increase in pH value, the surface tension of C₁₈N₃ solution also increases, and the aggregation also changes from spherical micelles to lamellar micelles. Yiyang Lin¹⁰ et al. synthesized a single chain pH-responsive surfactant *N*-dodecyl phosphate (DPA), which changes its degree of ionization by adjusting pH value. The morphology of aggregates in the mixture of CTAB and DPA has been investigated. With decreasing in pH value, the self-assembly structure of the system has many changes, such as spherical micelles, rod micelles, wormlike micelles, lamellar liquid crystals, and vesicles.

Because carboxyl groups are environmentally friendly, responsive, and salt-tolerant, selecting it as pH regulating groups can achieve excellent physicochemical properties of pH regulated surfactant¹¹. However, the pH regulated surfactant containing carboxyl group has not been deeply investigated. Therefore, we designed and synthesized a series of pH regulated surfactants with different hydrophobic chain length and carboxyl group molecular structure positions. The structures and abbreviations of pH regulated surfactants are depicted in Scheme 1. Second, the molecular structures of pH regulated surfactants were analyzed by mass

spectrometry and ^1H NMR spectroscopy. Besides, the effect of different types of inorganic and organic counterions on the apparent viscosity of the mixed system was investigated^{12, 13}. Finally, the morphological changes of aggregates formed by self-assembly of surfactant in a mixed system with different pH values were studied utilizing rheology, dynamic light scattering, and Cryo-Transmission Electron Microscopy.

2. Experiment and methods

2.1. Materials and synthesis method

Dichloromethane, toluene, ethyl acetate, acetone, thionyl dichloride, sodium hydroxide, anhydrous magnesium sulfate were purchased from Sinopharm Chemical Reagent Co., Ltd. Palmitic acid, stearic acid, erucic acid, benzene, iminodiacetic acid, glycine, dl-glutamate, dimethyl sulfoxide were purchased from Shanghai Jingchun Biochemical Technology Co., Ltd.

0.5 mol fatty acid and 150 ml benzene were added into a 500 ml three-necked flask, stirred and dissolved in a water bath to 30°C. 1 mol thionyl dichloride was slowly added in by a constant pressure funnel in 30 minutes, then the condensation reflux reaction was carried out at 70~90°C for 3~4 hours. Then a vacuum distillation process was used to remove the excess thionyl dichloride and benzene to obtain the fatty acyl chloride. Add 1 mol amino acid to 500 ml flask, add 50 ml 20% sodium hydroxide solution, then add 100 ml anhydrous acetone, stirred thoroughly until the mixture was homogeneous. Then slowly adding fatty acyl chloride to a container.

During the process, the constant pressure funnel was used to add 20% sodium hydroxide water solution to control the pH value of the system in the range of 8~10. The system temperature was set at 0~10°C by an ice-water bath. After the reaction, the acetone was removed by spin-evaporation. A large number of white crystalline solid was precipitated after the pH value of the system was adjusted to 1~2 using a hydrochloric acid solution. Add the white crystal to the flask, dissolve in ethanol, heat to 40°C, and then add 20% sodium hydroxide. The precipitated crystal was dried to obtain the final product.

In section 3.3, the full and abbreviated names of the organic counterions are as follows: Octyltrimethylammonium chloride (OTAC), Decyltrimethylammonium chloride (DTAC), Decyltrimethylammonium bromide (DTAB), Dodecyltrimethylammonium chloride (LTAC), Didodecyldimethylammonium bromide (DDAB), Benzenemethanaminium (LBAC), Dodecyldimethylethylammonium bromide (DDAB), Dodecyl Trimethyl Ammonium Bromide (LTAB), Didodecyl dimethyl ammonium chloride (DDAC), Trimethyltetradecylaminium·bromide (MTAB), Trimethyltetradecylammonium chloride (MTAC), Tetradecyl dimethyl benzyl ammonium chloride (TDBAC), Hexadecyltrimethylammonium chloride (CTAC), Benzylhexadecyldimethylammonium chloride (BHDAC), Cetyltrimethylammonium bromide (CTAB), Dihexadecyldimethylammonium bromide (DDTAB), Cetethyldimonium bromide (HDEAB), Dimethyl distearyl ammonium chloride

(DTDAC), Trimethylstearylammmonium chloride (ODAC),
Dimethyldioctadecylammmonium bromide (DTDAB),
Stearyldimethylbenzylammmonium chloride (SDBAC) , Trimethylstearylammmonium
Bromide (TSAB).

2.2. Molecular structure verification

The molecular structure of the synthesized pH regulated surfactants were analyzed by liquid chromatography-mass spectrometry (Agilent 6510, USA) and ^1H NMR spectrum (Bruker III 400, Switzerland). The results are depicted in Supplementary Material.

2.3. Krafft point

The data of Krafft point (T_k) was obtained by cooling 1 wt% surfactant solution in an ice salt bath to -4°C . If the solution is clear, T_k of the surfactant was recorded as 0°C . If the solution is cloudy, slowly heating up and recording the temperature of the solution from cloudy to clear. The average value was obtained after repeated three times. During the measurements, the solutions were not buffered and the pH was around 9.

2.4. Surface tension test

The surface tension was measured by the surface tension meter (Dataphysics, China). A series of surfactant solutions were prepared and the surface tension was measured by the Wilhelmy plate method at 25°C . To eliminate the influence of metal ions on the results, self-made ultrapure water (PURELAB Option-Q, China) was used

to prepare samples, and resin-based storage bottles and test tubes were used to store samples. Besides, the average surface tension was measured three times at each concentration. During the measurements, the solutions were not buffered and the pH was around 9.

2.5. Rheological property test

The HAAKE MARS 60 rheometer was used to carry out the rheological experiment. The geometric fixture used as a parallel plate with a diameter of 50 mm. A bottom-mounted rheometer motor applies a strain on the sample through a lower plate, and a torque sensor was connected to the upper plate in contact with the sample to measure the resulting stress. By lowering the upper plate to extrude the sample, the sample can be uniformly distributed on the lower plate to form a regular cylindrical geometry with a slight expansion. The thickness of each sample was about 2 mm to ensure sufficient time for the sample to relax. The linear viscoelastic region was determined by a 1 Hz stress scan. The temperature was set at 70°C using an environmental control panel.

2.6. Dynamic light scattering test

A NanoBrookOmni laser particle size analyzer was used to conduct a dynamic light scattering test. To ensure the stability of the test light system, it was necessary to preheat the instrument 30 minutes before the experiment. The sample was filtered by 0.04 μm filter and put into the test instrument. The observation grating was adjusted to 400, the wavelength is 532 nm and the scattering angle is 90°. The CONTIN

algorithm was used to process the experimental results. The temperature was set at 70°C.

2.7. Cryo-Transmission Electron Microscopy

Sample preparation shall be carried out in an environmental control system (T=25°C, humidity=90%). The copper net was clamped with tweezers and inserted into the chamber of the environmental control system. 5 µL sample was moved by a pipette gun and dropped on the copper net. The solution forms a thin film on the copper net, quickly insert the copper mesh into the liquid ethane to freeze the sample. The samples were observed in Jeol JEM-2100UHR by using Gatan 626. The image acquisition and storage system was Gatan 832 CCD camera.

3. Results and discussion.

3.1. Krafft point

T_k is the temperature at which the hydrated crystals, monomers, and micelles of ionic surfactants coexist. It is the lowest temperature at which ionic surfactants can be micellized, and is the lower limit of the temperature at which it can be applied. T_k of the pH regulated surfactant is shown in Table 1. As can be seen from Table 1, T_k decreases with the increase of carbon number in the hydrophobic alkyl chain of the surfactant molecule. That is consistent with the T_k of conventional ionic surfactants. Under the same length of hydrophobic tail chain, T_k of the Gly series surfactant is the highest, the Imi series surfactant is in the middle, and the Glu series surfactant is the lowest. It is generally believed that the ionic type, the head structure and the length of

the hydrophobic alkyl chain of the surfactant molecule all have an important effect on the solubility of the surfactant and T_k , among which the head structure is the main factor. The result shows that the existence of the amide group and dicarboxylic group lead to the highest strength of the non-covalent bond between the Glu series surfactant and water molecules, so that the lowest T_k can be obtained.

3.2. Surface activity

The variation curves of the surface tension of surfactant with concentration at 25°C are shown in Fig. 1 ~ Fig. 3. When the concentration of the surfactant is very low, the changing trend of surface tension is very tiny. With the concentration of surfactant increasing, the surface tension drops sharply. When the concentration of the surfactant continues to increase to a certain value, the surface tension reaches a stable platform. The concentration at the breakpoint of the curve is the critical micelle concentration (CMC), and the surface tension at this concentration is the critical surface tension (γ_{cmc}). Combining with Gibbs adsorption isotherm formula¹⁴, two physical quantities which can reflect the compactness of molecules on the gas-liquid interface can be calculated¹⁵: the max saturated adsorption (Γ_{max}) and the minimum molecular occupied area (A_{min}).

$$\Gamma_{max} = \frac{-1}{2.303nRT} \left(\frac{\partial \gamma}{\partial \log C} \right)_T \quad (1)$$

$$A_{min} = \frac{1}{N_A \cdot \Gamma_{max}} \quad (2)$$

Where R stands for gas constant (8.314 J·mol⁻¹·K⁻¹), T for absolute temperature.

A value of $n=3$ for the Gly and Imi series surfactants, and $n=2$ for Glu series surfactants¹⁶. Where N_A stands for Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$).

In general, the smaller the CMC, the higher the efficiency of reducing surface tension. The lower the γ_{cmc} , the stronger the ability to reduce the solvent surface tension. The surface activity parameters of the pH regulated surfactants are listed in Table 2. As can be seen, with the increase of the length of the hydrophobic tail chain, the value of CMC and γ_{cmc} of the pH regulated surfactants gradually decreased. That because with the increase of the length of the hydrophobic chain, the hydrophobic property of the surfactant is enhanced, and the self-aggregation occurs more efficiently at the gas-liquid interface, which leads to the gradual decrease the values of CMC and γ_{cmc} . As the length of hydrophobic tails increases, Γ_{max} increases and A_{min} decreases, which is caused by the enhancement of hydrophobic forces. The result is that the surfactant molecules are more tightly packed, and the packing density is increasing.

It is also clear from Table 2 that, the order of CMC and γ_{cmc} values is Glu>Imi>Gly when the hydrophobic tail chain length is the same. The possible explanation for this phenomenon is due to the combined effect of steric hindrance and electrostatic repulsion. From the point of view of steric hindrance, because the headgroup of the Gly series surfactant only contains one hydroxyl group, its headgroup has the least steric hindrance effect, so it has the most efficient and the strongest ability to reduce the surface tension. For both the Imi series and the Glu

series surfactant, it have the same number of the hydroxyl group on the headgroup of the surfactant. However the number of methylene groups on the headgroup of the Glu series surfactant is more than the Imi series surfactant, which leads to the maximum steric resistance among three, so the Glu series surfactant has the least efficient and the weakest ability to reduce the surface tension. From the point of view of electrostatic repulsion, due to the least charge on the head group of the Gly series surfactant, the electrostatic repulsion between the head group is also the least, which makes it easier to aggregate. When the length of the hydrophobic tail chain is the same but the molecular structure of the headgroup is different, for the Gly series surfactant, the value of Γ_{\max} is the largest and the value of A_{\min} is the smallest. This phenomenon can still be explained by the theory of the steric hindrance effect and electrostatic repulsion effect, which will not be repeated here. Due to the strongest surface activity, Gly-22 was chosen as the surfactant for constructing a pH-regulated wormlike micelles system.

3.3. Effect of counterions on the apparent viscosity of the system

The viscosity of the mixed solution with a total mass concentration of 4 wt% (including 2 wt% of Gly-22 and 2 wt% of counter-ion) was measured by rheometer at 70°C and 170 s⁻¹ shear rate to determine the best counterion. The mixed solutions were not buffered and the pH was around 9.

Counterion can associate with pH regulated surfactants by hydrophobic and electrostatic interactions to form spherical, rod, wormlike and branched wormlike

micelles. The type of counter ion has a significant influence on the micelle morphology and then affects the viscosity increasing effect of the system. Fig. 4 and Fig. 5 show the effect of inorganic and organic counterions on the apparent viscosity of the system, respectively.

It can be seen from Fig. 4 and Fig. 5 that both inorganic and organic counterions can improve the viscosity of the system to some extent, but the viscosity-increasing ability of organic counterions is much higher than that of inorganic counterions¹⁷. A mean field treatment of the growth process for neutral or highly-screened micelles gives a prediction for the average contour length \bar{L} of the wormlike micelles¹⁸.

$$\bar{L} \sim \varphi^{1/2} \exp[E_c/k_B T] \quad (3)$$

In the above formula, φ is the surfactant volume fraction, T is the temperature, E_c is the end-cap energy required to form two hemispherical end-caps as a result of rod scission. The primary mechanism of increasing \bar{L} by adding inorganic salt is that inorganic counterion can screen the electrostatic repulsion between the charged headgroups of Gly-22, which results in a reduction of the optimal molecular area at the hydrocarbon–water interface, leading to an increase in E_c . Consequently, \bar{L} , which increases exponentially with E_c , increases dramatically. The mechanism of the micelle growth promoted by organic counterion can be clearly explained by the critical packing parameter P ¹⁹. According to $P=V/aL$, where V is the volume of the lipophilic chain having maximum effective length L , and a is the effective area per molecule at the surfactant–water interface. For $P < 1/3$, it is predicted that the

surfactants would assemble into spherical aggregates; for $1/3 < P < 1/2$, wormlike micelles are expected; whereas for $P > 1/2$, lamellar structures should form spontaneously.

On the one hand, when adding organic counterion with the opposite charge to Gly-22 aqueous solution, the hydrophilic head part of organic counterion neutralizes the head charge of Gly-22, which makes the electrostatic repulsion between the molecules of Gly-22 weaken and reduces the value of a . On the other hand, the hydrophobic tails of organic counterion were inserted into the hydrophobic barrier of micelles, which increased the value of V . The value of P increases with the two factors, which promotes the formation of wormlike micelles and explains why organic counterion is more effective than inorganic counterion in promoting viscosity increase. Also, as can be seen from Fig. 5, the viscosity of the mixed system increases with the increase of the hydrophobic tail chain length of organic counterion. As the hydrophobic tail chain of the organic counterion grows, the value of V increases. L is the maximum length of the hydrophobic chain, due to none of the hydrophobic tail chain of organic counterions is longer than that of Gly-22, L remains unchanged. Both of these factors contribute to an increase in the value of P . Therefore, ODAC was chosen as the counterion of the pH regulated wormlike micelles.

3.4. Rheological properties of pH regulated wormlike micelles

The steady-state shear viscosity of the Gly-22/ODAC mixed solution under different pH conditions varies with the shear rate is shown in Fig. 6. When $\text{pH} \leq 5$, the

apparent viscosity of the solution is minimal and does not change with the increase of shear rate. It shows the characteristic of Newton fluid, which indicates that the aggregates formed by surfactant in the system are mainly spherical micelles²⁰. As the pH increases, the solution begins to exhibit shear thinning and non-Newtonian fluid behavior, indicating the gradual formation of wormlike micelles in the system. Under the action of shear force, the wormlike micelle solution changes from the entangled network state to the directional parallel structure state, which leads to the gradual decrease of solution viscosity²¹.

The zero shear viscosity (η) of the mixed system can be obtained by extrapolation under different pH conditions. The results are shown in Fig. 7. When $\text{pH} \leq 5$, the zero shear viscosity of the system is very small. With pH value increases, the zero shear viscosity also increases. The zero shear viscosity of the system can reflect the strength of the network structure formed by the wormlike micelles, which indicates that the strength of the network structure formed by aggregates in the system increases with the increase of pH value. When $\text{pH} \geq 8$, the zero shear viscosity of the system is stable, which means that the network structure formed by aggregates in the system remains unchanged.

From the steady-state shear analysis, with the pH value increases, the strength of the network structure formed by aggregates in the system increases. In order to verify the relationship between the strength of the network structure and the pH value, the dynamic viscoelasticity of the Gly-22/ODAC mixed system under different pH

conditions was measured. The experimental results are shown in Fig. 8. The plateau modulus G_0 represents the physical entanglement density between the wormlike micelles. The relaxation time τ represents the complexity of the three-dimensional network structure²². The effects of the pH value on plateau modulus G_0 and relaxation time τ of the mixed system are shown in Fig. 9 and Fig. 10. As can be seen from the diagram, both G_0 and τ of the mixed system show a monotonous increasing trend with the pH value increases, which indicates that the density of the physical entanglement points between the wormlike micelles in the system increases. At the same time, the strength of the spatial three-dimensional network structure increases²³. The results above consistent with the steady state shear analysis.

3.5. Morphological characteristics of pH regulated wormlike micelles

The dynamic light scattering works like this: large, slow-moving particles exhibit a slower pattern of light, while small, fast-moving particles exhibit a faster pattern of light²⁴. Therefore, the particle size and its distribution can be calculated by the fluctuation and the light intensity correlation function. In order to verify the changes in the internal structure of the Gly-22/ODAC system, the aggregate structure of the mixed system was characterized by the dynamic light scattering, and the experimental results are shown in Fig. 11.

The average fluid mechanics radius of aggregates with different structures is significantly different in the dynamic light scattering results. By analyzing the results of the mixed system under different pH conditions, it is found that the average fluid

mechanics radius of the system is about 2~5 nm at pH=5, which indicates that the aggregates in the Gly-22/ODAC system were mainly in the form of spherical micelles. At pH=8, the average fluid mechanics radius of the system is about 30~40 nm, which indicates that the aggregates existed mainly in the form of wormlike micelles²⁵. The results show that the aggregation could change from spherical micelles to wormlike micelles by changing pH conditions.

To verify that pH value can regulate the aggregates morphology from spherical micelles to wormlike micelles, the microscopic morphology of aggregates under different pH value conditions was observed employing Cryo-TEM. As shown in Fig. 12, no wormlike micelles is observed at pH=5. When pH=8, a dense entangled network formed by wormlike micelles can be observed in the picture. When the pH value of the solution is greater than 8, the carboxyl group on the molecular structure of Gly-22 is entirely ionized, so the electrostatic attraction between the negatively charged Gly-22 and the positively charged ODAC is strongest. By reducing the value of a and increasing the value of V , the formation of a large number of wormlike micelles can be explained. When the pH value of the solution decreases from 8, the ionization of Gly-22 decreases gradually, so the electrostatic attraction between Gly-22 and ODAC decreases gradually, resulting in the transition from wormlike micelles to spherical micelles.

If the viscosity of the Gly-22/ODAC system is reversible, the system can be reused, which can significantly reduce fracturing, stimulation and other applications

in the oilfield or other industrial fields. In order to study the pH cycling performance of the 2% Gly-22/2% ODAC system, we repeatedly adjust the pH value of the system between 5 and 8 and measure the viscosity. The experimental results are shown in Fig. 13. As can be seen from Fig. 13, when pH=5, the viscosity of the system is approximately equal to 2 mPa·s. When the pH value increases to 8, the viscosity increases by 3 orders of magnitude. When the pH value drops to 5, the viscosity of the system drops back to 2 mPa·s. We repeated the experiment 3 times, and the change of viscosity is within 1 order of magnitude, and the change trend remained unchanged. The experimental results show that the Gly-22/ODAC system has excellent pH cycle regulation performance, which can greatly reduce the application cost of the system in oil field chemistry and other industrial fields.

4. Conclusion

In this article, the results of the surface activity test show that pH regulated surfactants have lower surface tension, which indicates that it is easier to adsorb directionally at the gas-liquid interface and to aggregate in solution. On the one hand, the hydrophilic head part of organic counterion neutralizes the head charge of Gly-22, which makes the electrostatic repulsion between the molecules of Gly-22 weaken and reduces the value of a . On the other hand, the hydrophobic tails of organic counterion were inserted into the hydrophobic barrier of micelles, which increased the value of V . The value of P increases with the two factors, which promotes the formation of wormlike micelles and explains why organic counterion is more effective than

inorganic counterion in promoting viscosity increase. The results of rheology and dynamic light scattering show the transition from spherical micelles to wormlike micelles was observed when the pH value increased from 5 to 8. The results of Cryo-transmission electron microscopy verify the result directly. Besides, the experimental results show that the Gly-22/ODAC system has excellent pH cycle regulation performance, which can significantly reduce the application cost of the system. It is hoped that the results will be helpful to the application of regulated surfactants in oil field chemistry and other industrial fields.

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Conflict of interest

The authors declare that they have no conflict of interest.

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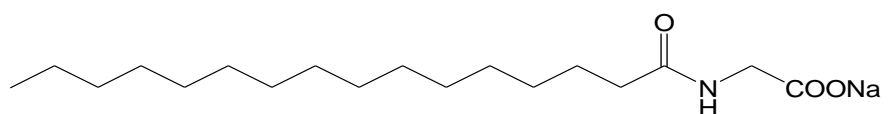
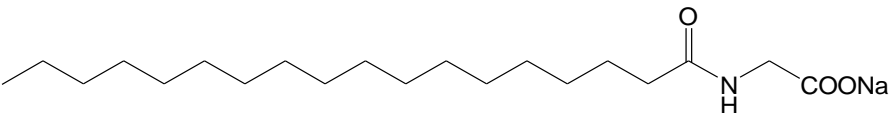
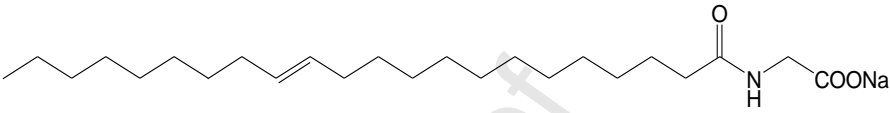
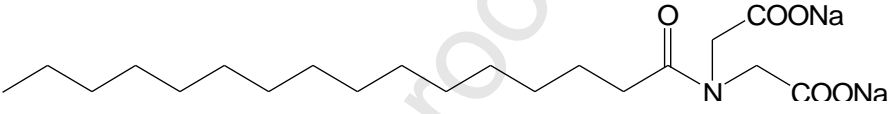
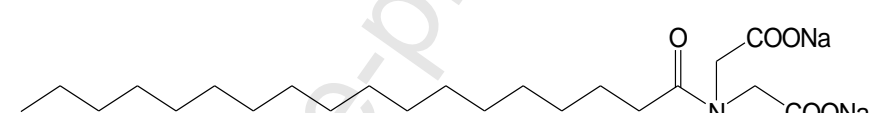


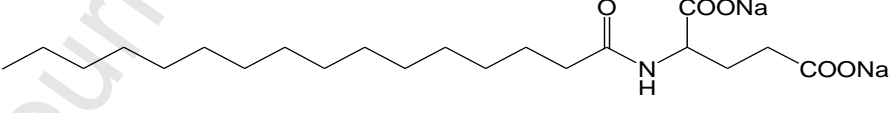
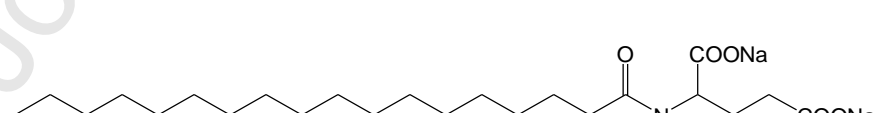
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Scheme 1. Molecular structure and code of pH regulated surfactants.

Number	Abbv.	Molecular structure
1	Gly-16	
2	Gly-18	
3	Gly-22	
4	Imi-16	
5	Imi-18	
6	Imi-22	
7	Glu-16	
8	Glu-18	
9	Glu-22	

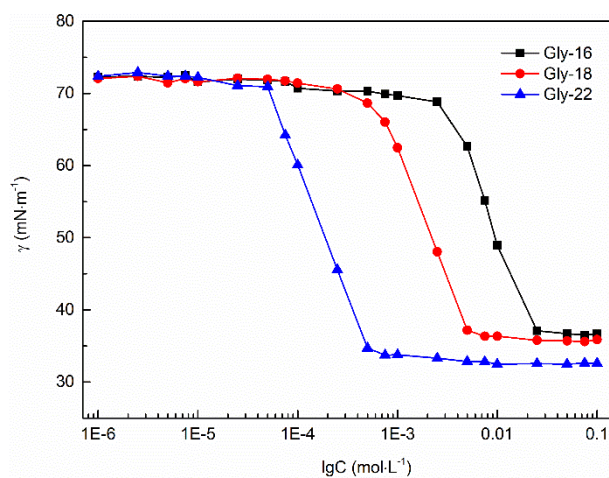


Fig. 1. The surface tension of the Gly series surfactant.

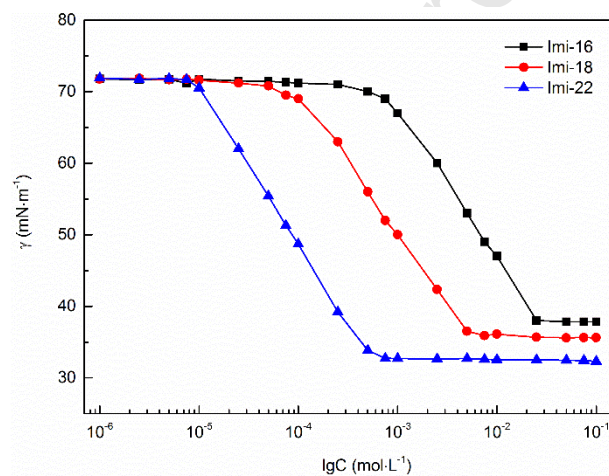


Fig. 2. The surface tension of the Imi series surfactant.

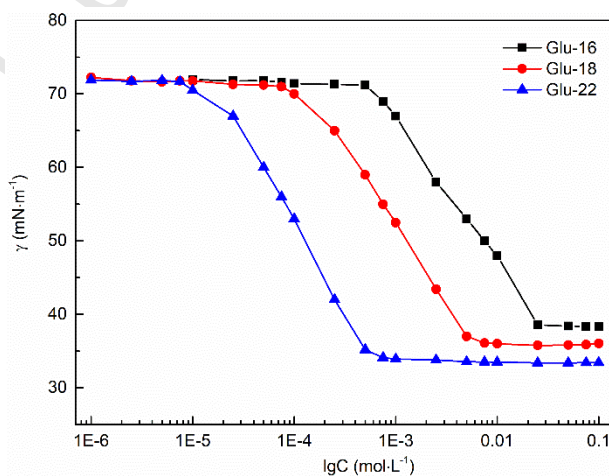


Fig. 3. The surface tension of the Glu series surfactant.

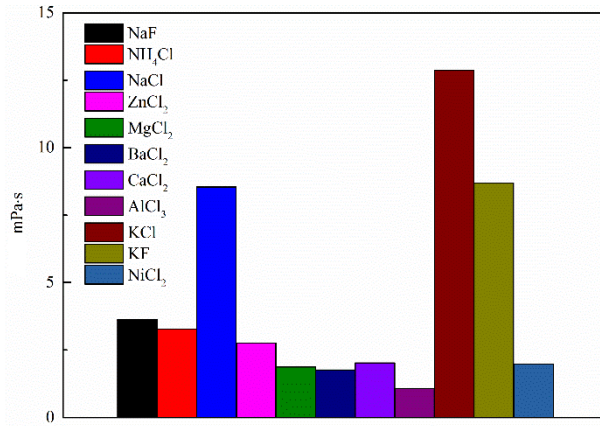


Fig. 4. Apparent viscosity of 2 wt% Gly-22/2 wt% inorganic counterion mixed system.

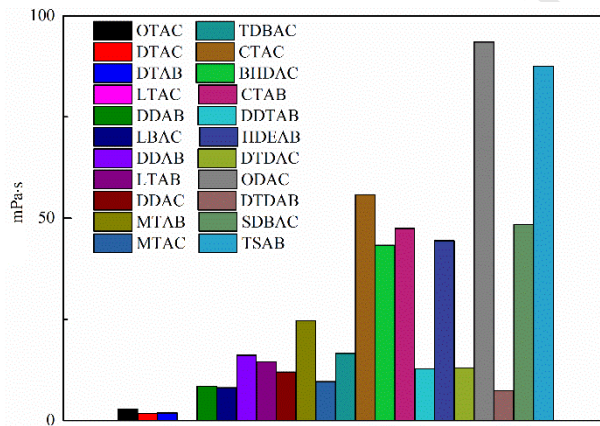


Fig. 5. Apparent viscosity of 2 wt% Gly-22/2 wt% organic counterion mixed system.

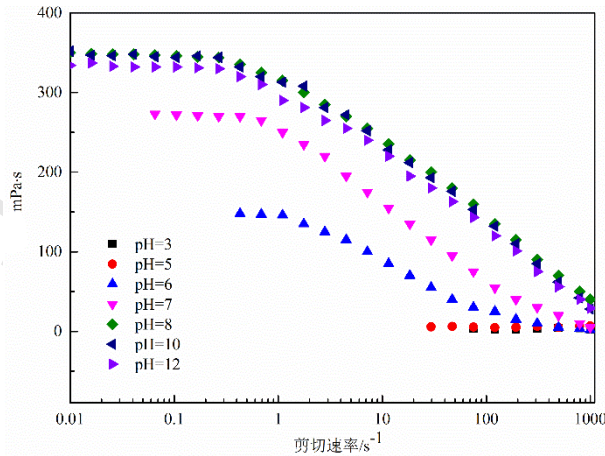


Fig. 6. The steady-shear viscosity of the 2 wt% Gly-22/2 wt% ODAC mixed system under different pH conditions.

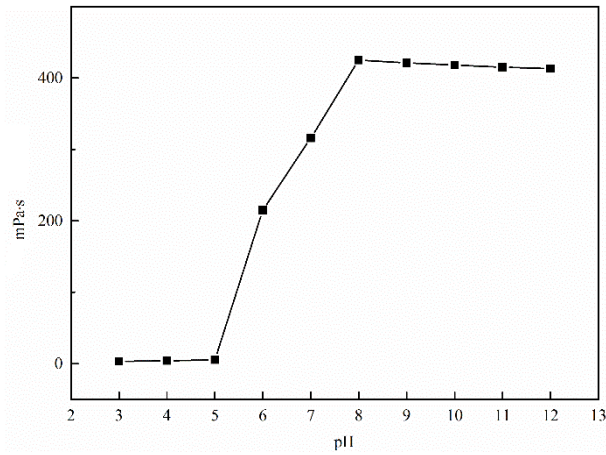


Fig. 7. Zero-shear viscosity of the 2 wt% Gly-22/2 wt% ODAC mixed system under different pH conditions at 70°C.

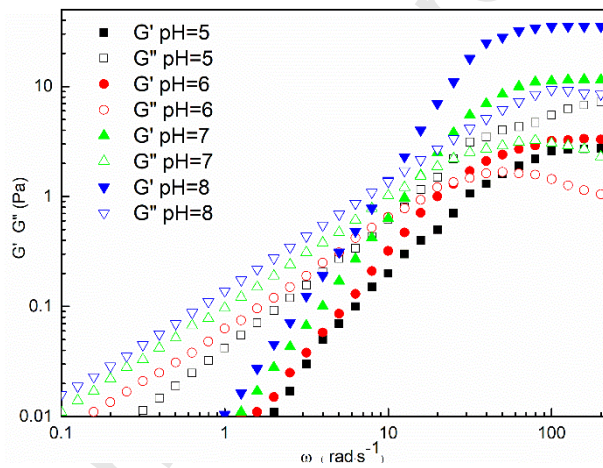


Fig. 8. Dynamic viscoelasticity of the 2 wt% Gly-22/2 wt% ODAC mixed system under different pH conditions at 70°C.

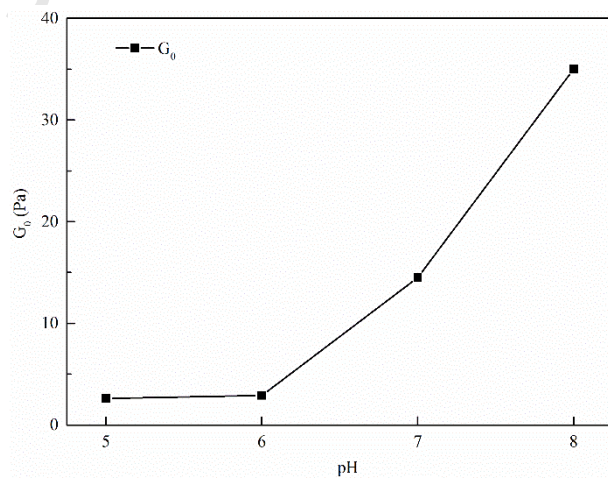


Fig. 9. The G_0 of the 2 wt% Gly-22/2 wt% ODAC mixed system under different pH conditions at

70°C.

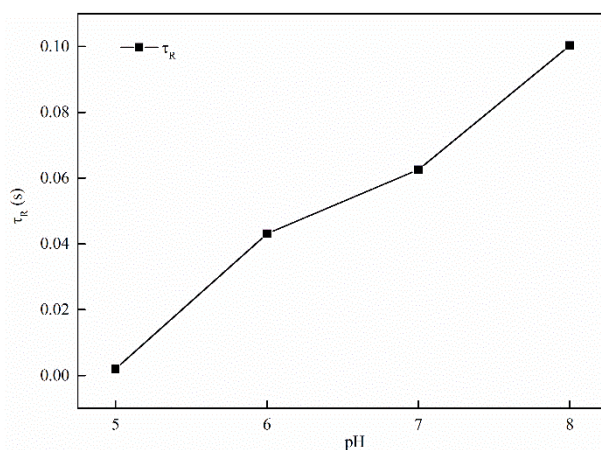


Fig. 10. The τ of the 2 wt% Gly-22/2 wt% ODAC mixed system under different pH conditions at

70°C.

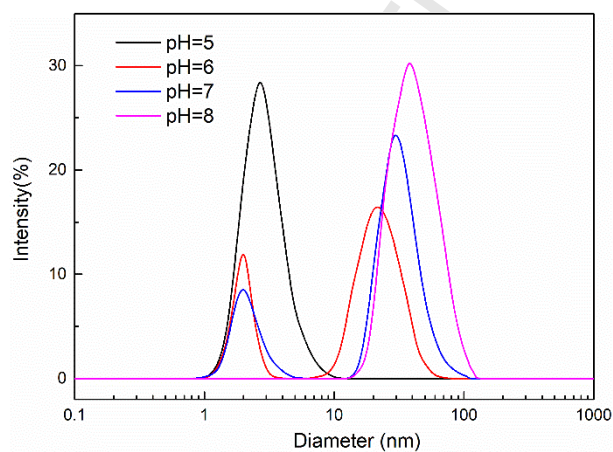


Fig. 11. DLS result of the 2 wt% Gly-22/2 wt% ODAC mixed system under different pH

conditions at 70°C.

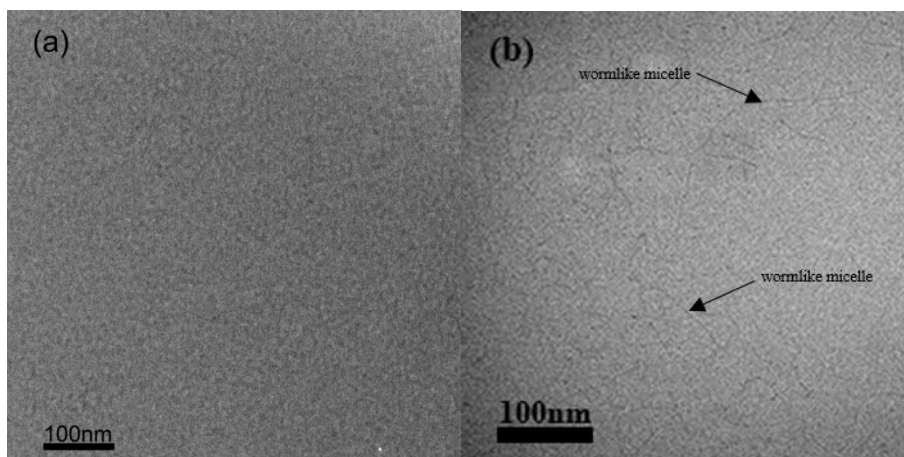


Fig. 12. The morphology of micelle formed in the 2 wt% Gly-22/2 wt% ODAC mixed system at different conditions (a. pH=5, b. pH=8).

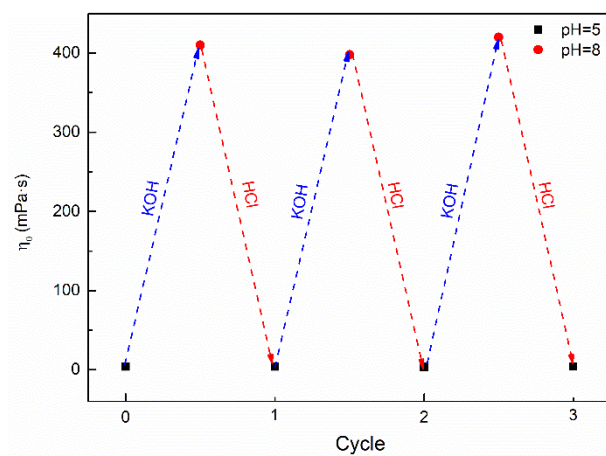


Fig. 13. Different cycles of zero-shear viscosity of the 2 wt% Gly-22/2 wt% ODAC mixed system at 70°C

Table 1. Krafft point of the pH regulated surfactants.

	Gly-16	Gly-18	Gly-22	Imi-16	Imi-18	Imi-22	Glu-16	Glu-18	Glu-22
T_K	8.3	17.9	22.3	2.8	15.7	20.5	<0	11.6	15.5

Table 2. The surface active parameters of the pH regulated surfactants.

Abbreviations	cmc (mmol·L ⁻¹)	γ_{cmc} (mM·m ⁻¹)	Γ_{max} ($\mu\text{mol}/\text{m}^2$)	A_{min} (\AA^2)
Gly-16	20.11	38.49	0.71	233
Gly-18	5.82	35.72	0.78	212
Gly-22	0.53	32.53	0.83	201
Imi-16	23.08	38.65	0.48	349
Imi-18	6.27	35.95	0.50	333
Imi-22	0.57	32.97	0.54	305
Glu-16	25.04	38.88	0.48	344
Glu-18	6.13	36.04	0.51	328
Glu-22	0.59	33.46	0.55	301

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

The authors declare that they have no conflict of interest.

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Zhihu Yan: Conceptualization, Writing - Original Draft, Writing - Review &

Editing

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Xia Lu: Resources

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Haibin Lv: Resources

Caili Dai: Supervision

Minglian Jiao: Supervision

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Highlights

- A series of pH regulated surfactant with different hydrophobic chain and carboxyl position were synthesized.
- The results of rheology, DLS and Cyro-TEM show the transition from spherical micelles to wormlike micelles was realized when pH varied.
- The Gly-22/ODAC system has excellent pH cycle regulation performance.

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