

Study on Syntheses and Properties of Sodium Monoitaconamic Carboxylate Surfactants With Amide Group

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Abstract. A series of novel surfactants, namely sodium monoitaconamic carboxylate anionic surfactants with amide group, were synthesized through amidation and neutralization reaction with itaconic anhydride (IAN) and long chain aliphatic amines (such as octadecylamine, hexadecylamine, tetradecylamine and laurylamine) and sodium hydroxide (NaOH) as raw materials. The chemical structures of the surfactants were characterized and determined by Nuclear Magnetic Resonance (¹H NMR) and Infrared Spectrometer(FT-IR). The synthesized surfactants had lower surface tension and critical micelle concentrations(CMC). Moreover, the productions had good solubilizing effects, wetting properties and foaming properties.

1. Introduction

As a class of long-chain organic compounds with amide groups, the most notable feature of amide surfactants compared to other kinds of surfactants is the intramolecular amide group, which makes the molecules easily hydrolyzed^[1]. The post-processing is simple, non-polluting and easily degradable, thus protecting the environment. As a result, amide surfactants have become a new focus of attention^[2]. The practical use of Amide surfactants has been more extensive^[3]. Prasath^[4] used itaconic anhydride and long-chain alcohol as raw materials to synthesize polymerizable surfactants and the surfactants were utilized for the preparation of nanosized PS latexes. Chen^[5] succeeded in synthesizing anionic oxalamide lauryl succinate sodium sulfonate gemini surfactant through amidation, esterification and sulfonation reactions under microwave irradiation conditions by using maleic anhydride, lauryl alcohol, sodium sulfite ethylenediamine as the starting materials. To reduce the destruction of chemical production to the environment by using biomass materials has become the primary focus of our experimental work^[6]. One of the raw materials of amide surfactants is itaconic anhydride, which is a derivative of itaconic acid. It is obtained by dehydration of itaconic acids produced by fermentation mostly^[7]. Itaconic anhydride is very active in chemical properties and is prone to be attacked by electrophilic reagents to carry out ring-opening reactions^[8].

2. Experimental

2.1. Materials

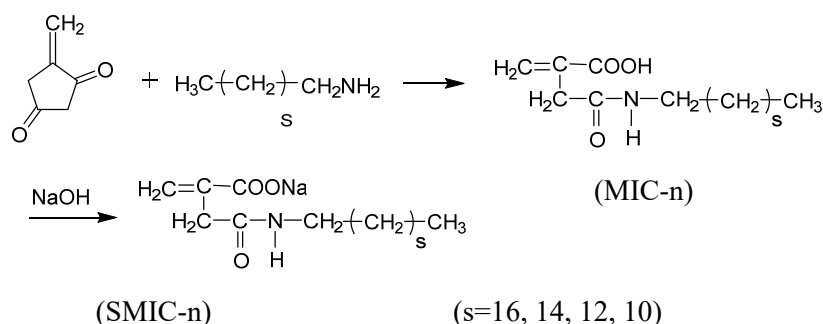
Itaconic anhydride (IAN, C.P. Grade, Qingdao HaiKe Biochemistry Co. Ltd, China); Octadecylamine, hexadecylamine, tetradecylamine and docanamine (A.R. Grade, Tokyo Chemical Industry (TCI)



company, Japan); Sodium hydroxide (A.R. Grade, Tianjin Bodi Chemical Reagent Factory, China); Dichloromethane (A.R. Grade, Laiyang Fine Chemical Works in Economic and Technological Development Zone China).

2.2. Synthesis method

Take SMIC-18 as an example: Add the IAn and chloroform to a three-necked flask equipped with a condenser and a stirrer, and dissolve it after heating to 25°C. Octadecylamine dissolved in chloroform was then added dropwise to the system and reacted for 35-55 minutes. After the reaction, it was cooled and crystallized. The crystal system was filtered under reduced pressure to obtain the product, which was distilled under reduced pressure and recrystallized with chloroform, and then dried. Finally, a relatively pure product monoitaconamic carboxylate with amide group (MIC-18) was obtained. The intermediate product was then used as a raw material and neutralized by sodium hydroxide to obtain the series of surfactants. The synthetic route is shown in Scheme1. The acylation yield is calculated as follows:



Scheme 1. Synthetic route of SMIC-n

$$\text{Amidation yield} = \frac{\text{calculated value} - \text{experiment value}}{\text{calculated value}} \times 100 \% \quad (1)$$

2.3. Characterization of the prepared surfactants

2.3.1. Structural confirmation of the prepared surfactants

The synthesized surfactants were confirmed by Fourier Transform Infrared (FT-IR) spectra and ^1H NMR spectra. The Fourier Transform Infrared (FT-IR) spectra were collected on a Bruker VERTEX70 spectrometer using a KBr pellet, in the wavenumber range of 400 to 4000 cm^{-1} . ^1H NMR spectra were recorded on a Bruker 500 spectrometer with DMSO-d_6 as solvent.

2.3.2. Wetting property

This series of dried SMIC-n surfactants were tableted separately, and contact angles were determined by a JY-82C angle instrument at 25 ± 1 °C.

2.3.3. Surface tension and critical micelle concentration

The surface tension of the prepared surfactants was measured by a POWEREACH JK99C surface tensiometer by means of the Wilhelmy plate method at 25 ± 1 °C. Values were measured four times and then averaged. The concentration where there is a break in the curve of surface tension versus log concentration is taken as the critical micelle concentration^[9].

2.3.4. Foaming property

The foam heights of 1% solutions of the prepared surfactants were measured in cylinder equipped with a plug. This operation was repeated three times and the average value was determined^[10]. The Foam Properties was calculated from the equation (2) and equation(3):

$$\text{Foaming ability} = \frac{V_1}{V_0} \times 100\% \quad (2)$$

$$\text{Foaming stability} = \frac{V_2}{V_1} \times 100\% \quad (3)$$

where V_0 : the initial volume of surfactant solution (mL), V_1 : the initial foam height of surfactant solution (mL), V_2 : the final foam height of surfactant solution (mL).

3. Results and discussion

3.1. Optimum reaction conditions of MIC-n

Table 1. Synthesis conditions for amidation reaction

Sequence number	Molar ratio (IAN:ODA)	Reaction temperature(°C)	Reaction time (min)	Yield (%)
A1	1.05:1	25	35	84.13
A2	1.10:1	25	35	92.82
A3	1.15:1	25	35	91.55
A4	1.20:1	25	35	90.62
A5	1.25:1	25	35	80.53
B1	1.10:1	15	35	76.34
B2	1.10:1	20	35	76.28
B3	1.10:1	25	35	87.24
B4	1.10:1	30	35	83.99
B5	1.10:1	35	35	83.47
B6	1.10:1	40	35	76.98
C1	1.10:1	25	15	86.89
C2	1.10:1	25	25	88.70
C3	1.10:1	25	35	92.86
C4	1.10:1	25	45	91.67
C5	1.10:1	25	55	91.04

In order to find out the optimum reaction condition of amidation, the effects of the reaction molar ratio of itaconic anhydride and octadecylamine, reaction temperature and reaction time on the yield of amidation were investigated. As shown in Table 1 (A1~A5), it could be seen that the yield increased and then decreased with the increase of the molar ratio of itaconic anhydride and octadecylamine. When the molar ratio was 1.10:1, the yield reached 92.82%. As shown in Table 1 (B1~B6), the yield of amidation increased and then decreased with reaction temperature slowly increasing. When the reaction temperature was lower than 25°C, the yield was very low and less than 80%. When the reaction temperature was 25°C, the reaction yield was the highest at 88%. We can see the reaction yield was the highest at 35min from Table 1(C1~C5). Therefore, the optimum reaction conditions of MIC-n are as follows : n(IAn): n(ODA) = 1.10:1, reaction temperature is 25°C, and reaction time is 35 min. Under the optimum conditions for the synthesis of MIC-18, the yields of homologous surfactants MIC-16, MIC-14, and MIC-12 were almost the same as those of MIC-18, and they all reached 90 %, which could be demonstrated that the optimal synthesis process conditions for the synthesis of MIC-18 are also applicable to the synthesis of MIC-16, MIC-14 and MIC-12.

3.2. Structural Characterization of synthetic surfactants

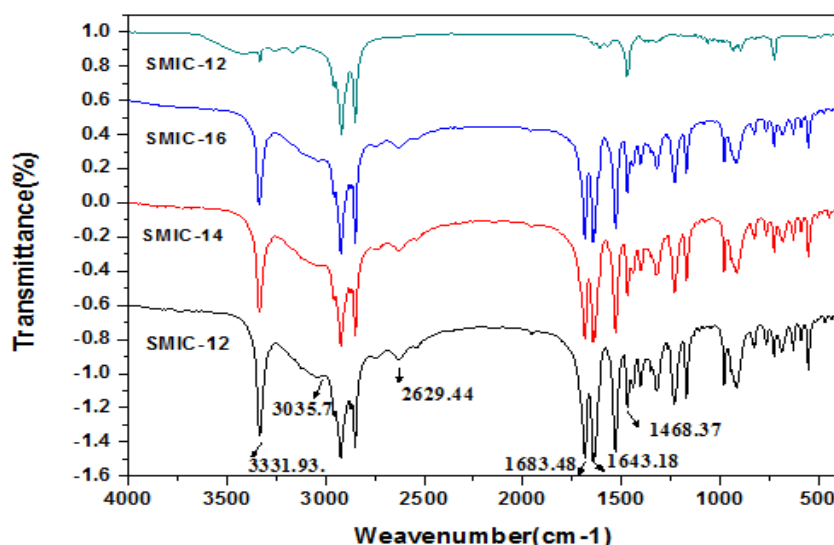


Figure 1. FT-IR spectra of SMIC-n

Table 2. The ^1H NMRs and relegation of MIC-n

Compds	^1H NMR, δ (ppm)
MIC-12	(500MHz, DMSO- d_6): δ 0.748~0.762(d, 3H, a-H); δ 1.145(s, 18H, b-H); δ 1.271(s, 2H, c-H); δ 2.966(s, 2H, d-H); δ 7.693(s, 1H, e-H); δ 2.892~2.905(d, 2H, f-H); δ 5.537(s, 1H, g-H); δ 5.994(s, 1H, g-H); δ 12.333(s, 1H, h-H);
MIC-14	(500MHz, DMSO- d_6): δ 0.747~0.760(d, 3H, a-H); δ 1.143(s, 22H, b-H); δ 1.269(s, 2H, c-H); δ 2.965(s, 2H, d-H); δ 7.693(s, 1H, e-H); δ 2.904~2.917(d, 2H, f-H); δ 5.537(s, 1H, g-H); δ 5.994(s, 1H, g-H); δ 12.345(s, 1H, h-H).
MIC-16	(500MHz, DMSO- d_6): δ 0.747~0.761(d, 3H, a-H); δ 1.143(s, 26H, b-H); δ 1.270(s, 2H, c-H); δ 2.965(s, 2H, d-H); δ 7.690(s, 1H, e-H); δ 2.905~2.917(d, 2H, f-H); δ 5.537(s, 1H, g-H); δ 5.994(s, 1H, g-H); δ 12.340(s, 1H, h-H).
MIC-18	(500MHz, DMSO- d_6): δ 0.745~0.759(d, 3H, a-H); δ 1.139(s, 30H, b-H); δ 1.265(s, 2H, c-H); δ 2.963(s, 2H, d-H); δ 7.708(s, 1H, e-H); δ 2.902~2.914(d, 2H, f-H); δ 5.537(s, 1H, g-H); δ 5.993(s, 1H, g-H); δ 12.356(s, 1H, h-H).

The FT-IR spectra of SMIC-n were represented in Fig. 1. The vibration absorption peak and the deformation vibration absorption peak of -NH in the amide group was at 3331.93 cm^{-1} and 1468.37 cm^{-1} respectively. The stretching vibration absorption peak of C=O in the amide was at 1643.18 cm^{-1} . The functional groups preliminarily prove that there was an amide bond (-CONH) in the product from the above three characteristic peaks; There was a C=O absorption peak in the carboxyl group at 1683.48 cm^{-1} , and 3035.7 cm^{-1} and 2649.44 cm^{-1} were stretching vibrational absorption peaks of -OH in the carboxyl group. There was a C=O absorption peak in the carboxyl group at 1683.48 cm^{-1} , and 3035.7 cm^{-1} and 2649.44 cm^{-1} were stretching vibrational absorption peaks of -OH in the carboxyl group. It could be preliminarily proved the itaconic anhydride had conducted ring-opening reaction during the reaction, producing carboxyl groups. The ^1H NMR spectrum analysis of MIC-n were shown in Table 2. The analysis confirmed that the structure of the prepared products were the target compounds.

3.3. Physicochemical properties of synthetic surfactants

3.3.1. Wetting property

As shown in Fig. 2, the four surfactants synthesized had better wetting properties, particularly SMIC-12, the contact angle of SMIC-12 surfactant turned out to be the smallest, which was 44.5°, while SMIC-18 was the largest, which was 71.5°. The results were related to the solubility of

surfactants, which was decreased when carbon atoms increased.

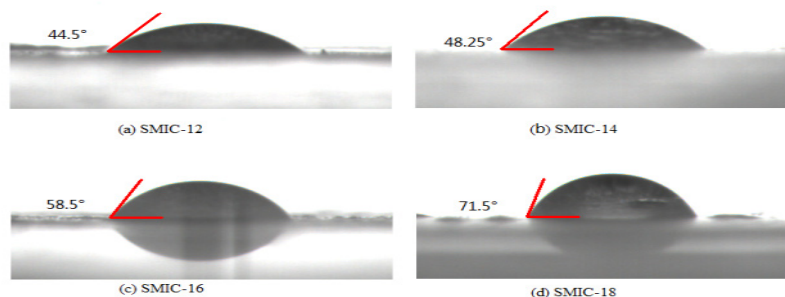


Figure 2. Contact angle of SMIC-n

3.3.2. Surface tension and critical micelle concentration

In Fig. 3, the surface tension of the surfactant decreased to an equilibrium gradually with the increase of the concentration of surfactant SMIC-n. According to the turning point in the γ lgc curve, the critical micelle concentration (CMC) of the four amide-type carboxylate SMIC-n surfactants could be obtained. The CMC value decreased with hydrophobic carbon atoms increasing. SMIC-18 had the smallest CMC value of 4.418×10^{-4} mol / L and had the smallest surface tension of 35.176 mN/m. The amide carboxylate surfactants had excellent ability to reduce surface tension, which may be due to the series surfactants contained both two hydrophilic polar groups, amide bonds and $-\text{COONa}$.

3.3.3. Foaming property

From Fig. 4, it can be seen that the foaming performance of the series of SMIC-n surfactants gradually decreased with the increase of the number of carbon atoms in the hydrophobic chains. SMIC-12 had the best foam performance and SMIC-18 had the worst foam performance. This may be due to the fact that as the number of carbon atoms in the hydrophobic chain increases, the surfactant will have poorer water solubility, and the surface tension will increase. The best foam stabilization performance was SMIC-16. The size of liquid surface tension is an important condition for foam production and the stabilizing foam performance is closely related to the nature of liquid film.

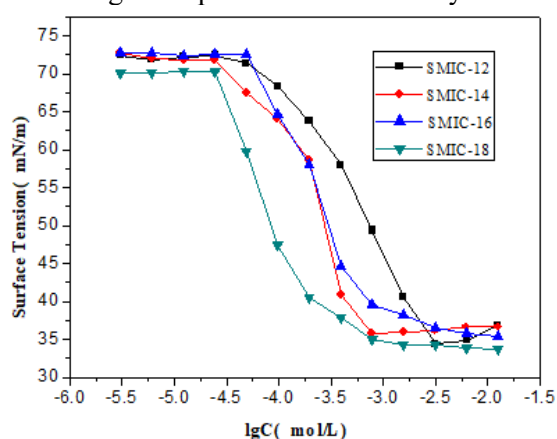


Figure 3. Surface tensions of aqueous SMIC-n solutions at different concentrations

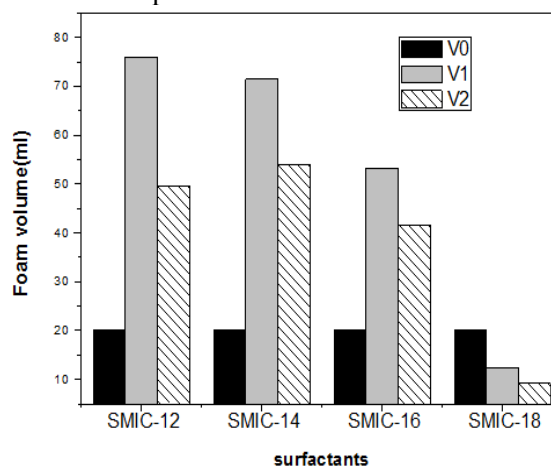


Figure 4. Foaming behavior of SMIC-n Surfactant

4. Conclusions

Biomass raw material IAn and long-chain aliphatic amines (octadecylamine, hexadecylamine, tetradecylamine and dodecylamine) were used as the main reaction materials. A series of intermediates, monoacylamide carboxylic acid (MIC-n), were synthesized through amidation reaction. After neutralization reaction, a series of sodium monoitaconamic carboxylate anionic surfactants with amide group SMIC-n (n=12, 14, 16, 18), were obtained. The surface tension of the series of surfactants were in the range of 33.891~35.176mN/m and the CMC were in the range of $4.418 \times 10^{-4} \sim 3.894 \times 10^{-3}$ mol/L. The series of surfactants exhibited good solubilizing effects, wetting properties and foaming properties. So we can deepen the research on its application value.

Acknowledgements

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References

- [1] Zhou Y, Chen Y, Han C, Lai J, Sui L and Luo G 2015 *J. Surfact. Deterg.* 17 727-732.
- [2] Masyithah Z, Sembiring S B, Alfian Z and T Herawan 2011 *Indo . J. Chem.* 11 223-228.
- [3] Akbaş H, Kocaoğlu S, Bozl M and Dikmen A 2016 *Colloid. Polym. Sci.* 294 1439-51.
- [4] Prasath RA and Ramakrishnan S 2005 *J. Polym. Sci. Pol. Chem.* 43 3257-67.
- [5] Chen H and Zhu B 2014 *J. Surfact. Deterg.* 17 937-942.
- [6] Li P, Xu H, Xie H, Zhang H, Du Lei and Xu J 2017 *Chem. Ind. & Eng. Pro.* 36 3047-52.
- [7] Kassi E, Loizou E, Porcar L and Patrickios CS 2011 *Eur. Polym. J* 47 816-822.
- [8] Malferrari D, Armenise N , Decesari S, Galletti P and Tagliavini E 2015 *Acs .Sustain. Chem. Eng.* 3 1579-88.
- [9] Hu D, Guo X and Li J 2013 *J. Surfact. Deterg.* 16 913-919.
- [10] Xu J, F C, T Li, Zhang S, Gao C and Wu Y 2016 *J. Surfact. Deterg.* 19 373-379.