Synthesis and Characterization of Novel Mixed Aliphatic Imidazolinium Salts

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Abstract: With the mixed fatty acid obtained by hydrolysis of refined gutter oil, and triethylenetetramine as raw materials, mixed aliphatic imidazoline fatty amine intermediate was synthesized by acylation-cyclization, which was then reacted with cyanamide to synthesize a novel mixed aliphatic imidazoline guanidinium corrosion inhibitors. The optimal synthesis conditions were determined through orthogonal tests: raw materials mass ratio (intermediate: cyanamide) of 8:1.3, reaction temperature of 120° C, reaction time of 4 h, and ethylene glycol monomethyl ether as solvent. The characterization of the product structure by infrared spectroscopy, ultraviolet (UV) spectrum and nuclear magnetic resonance (NMR) were carried out.

1. Introduction
Imidazoline compounds are widely used in the field of industrial corrosion inhibitors due to their good thermal stability and good biodegradability [1-3]. Gutter oil is a kind of inedible oil whose peroxide value and acid price index exceed the standard limits seriously. Its main ingredient is mixed fatty acid glyceride, and its comprehensive utilization has been highly concerned by researchers in various countries.

In this paper, the refined gutter oil recycled from industry, as raw material was hydrolyzed to fatty acid and then reacted with triethylenetetramine, followed by synthesis of a mixed aliphatic imidazoline fatty amine intermediate, which was then reacted with cyanamide to synthesize a novel mixed aliphatic imidazolinium guanidinium compound. The intermediate and target molecule had not been reported in literatures before, and their synthesis reactions are as follows:

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\begin{align*}
\text{RmCOOH} + \text{NH}_2\text{H}_3\text{NH}_2 \xrightarrow{140-200 \degree C} \text{R}_n\text{NH}_2\text{H}_3\text{NH}_2 \\
\text{N} & \xrightarrow{\text{solvent type/Δ}} H_3\text{NH}_2\text{Cl}^{-}
\end{align*}
\]

Scheme1. Synthetic routes of mixed fatty imidazoline guanidinium

Orthogonal experimental method was used to optimize the optimal reaction conditions for product synthesis; The structure of the synthesized product was characterized by infrared spectroscopy, ultraviolet (UV) spectrum, and nuclear magnetic resonance (NMR).

2. Experiment
2.1 Materials and Instruments
The refined gutter oil was obtained from a chemical plant in Guangzhou. Cyanamide was Macklin agent, and xylene, ethanol, acetone, sodium hydroxide and hydrochloric acid were all of analytical grade and purchased from Guangzhou Chemical Reagent Factory. Mixed fatty acids were made according to the literature [5]; Nicolet380 Fourier infrared spectrometer was manufactured in the United States Thermo Fisher company; Cary 100 UV-Vi spectrophotometer was made in Malaysia; Bruker AVANCE III 600M NMR instrument was produced in Switzerland.

2.2 Preparation of mixed aliphatic imidazoline fatty amine
The mixed fatty acids were placed in a three-necked flask, as well as a certain proportion of triethylenetetramine and 30 mL xylene, and heated to micro-boiling (130-132 °C.) for 6 h under N₂ protection. During the process, a water separator was used to continuously separate the by-product water. Then the flask was heated to 190~200 °C and the cyclization reaction was continued for 6 h, followed by pressure reduction to distill the excessive triethylenetetramine and other low-boiling liquids. The crude product was successively dissolved with ether, extracted twice with 5% sodium chloride deionized water, dried by sodium sulphate and filtered. After the rotary evaporation of the filtrate, brown and viscous mixed aliphatic imidazoline fatty amine was obtained.

2.3 Synthesis of Mixed Aliphatic Imidazolinium Guanidinium
8 g mixed aliphatic imidazoline fatty amine intermediate was added into a three-necked flask, in addition with a certain weight of 50% cyanamide and 30 mL solvent according to the orthogonal test table. The mixture was heated to a certain temperature, and cooled down after a certain period of action, neutralized with concentrated hydrochloric acid, adjusting the pH value to 6-7. The impurities were removed through rotary evaporation, and the crude product was obtained. After recrystallization with anhydrous ethanol, filtration and sedimentation, and vacuum drying, the target product, mixed aliphatic imidazolinium guanidinium, was obtained.

3. Results and discussion
3.1 Optimization of target molecule synthesis conditions
The results of orthogonal tests for target molecule synthesis are shown in Table 1.

| Number | Intermediate: cyanamide (w/w) | Cyclization temperature (°C) | Aciylation time (h) | Solvent type      | Yield (%) |
|--------|-------------------------------|-----------------------------|--------------------|-------------------|-----------|
| 1      | 8: 1                          | 70                          | 4                  | 2-Methoxyethanol  | 63.21     |
| 2      | 8: 1.3                        | 70                          | 2                  | DMF               | 58.42     |
| 3      | 8: 1.6                        | 70                          | 3                  | Cyclohexanone     | 59.65     |
| 4      | 8: 1                          | 95                          | 3                  | DMF               | 60.53     |
| 5      | 8: 1.3                        | 95                          | 4                  | Cyclohexanone     | 65.91     |
| 6      | 8: 1.6                        | 95                          | 2                  | 2-Methoxyethanol  | 61.73     |
| 7      | 8: 1                          | 120                         | 2                  | Cyclohexanone     | 63.38     |
| 8      | 8: 1.3                        | 120                         | 3                  | 2-Methoxyethanol  | 65.26     |
| 9      | 8: 1.6                        | 120                         | 4                  | DMF               | 67.98     |
| K1     | 62.37                         | 60.42                       | 61.18              | 63.40             |
| K2     | 63.20                         | 62.72                       | 61.81              | 62.31             |
| K3     | 63.12                         | 65.54                       | 65.70              | 62.98             |
| R      | 0.83                          | 5.12                        | 4.52               | 1.09              |

As can be seen from Table 1, the order of the factors affecting the synthesis is: reaction temperature>
reaction time > solvent type > amount of cyanamide. The optimal synthesis conditions of the target molecule were: raw materials mass ratio (intermediate: cyanamide) of 8:1.3, reaction temperature of 120° C, reaction time of 4 h, and ethylene glycol monomethyl ether as solvent.

3.2 Infrared spectrogram analysis
The middle product and the target molecule were measured with KBr pellet by infrared spectrometer, and their infrared spectrogram are displayed in Figure 1.

![Infrared spectrogram of the middle and target molecule](image1.png)

Shown as Fig. 1, in the spectrogram of the middle product, NH and NH$_2$ stretching vibration absorption peaks appear at 3291.3 cm$^{-1}$, CH$_2$ and CH$_3$ stretching vibration absorption peaks at 2925 and 2854 cm$^{-1}$, and C=N stretching vibration absorption peak at 1661.2 cm$^{-1}$. As for the target molecule, NH and NH$_2$ stretching vibration absorption peaks emerge at 3442.8 cm$^{-1}$ in the spectrogram, CH$_2$ and CH$_3$ stretching vibration absorption peak at 2927.8 and 2855.7 cm$^{-1}$, C=N stretching vibration absorption peak at 1665.6 cm$^{-1}$. The information of these functional groups is completely conformed to the theoretically predicted results of the intermediate and target molecular functional groups.

3.3 UV spectrogram analysis
With anhydrous ethanol as the solvent, UV spectra of the target products of 10mg/L and 5mg/L were determined, presented in Fig.2.

![UV spectrogram of the target product](image2.png)

As can be seen in Fig. 2, UV absorption characteristic peaks of imidazoline ring of two different concentrations were appeared at 203 nm and 226 nm, which is in agreement with the literatures [6], proving the imidazoline ring in the target product has been successfully synthesized.

3.4 NMR spectrogram analysis
With DMSO-d6 as the solvent, the target molecule was subjected to NMR scanning and $^1$HNMR and $^{13}$CNMR spectrograms were show in Fig. 3 and Fig. 4.

![Fig. 3 $^1$HNMR spectra of the target product](image1)

![Fig. 4 $^{13}$CNMR spectra of the target product](image2)

In Fig. 3 and Fig. 4, it can be found that the absorption peak positions measured by hydrogen and carbon NMR of the target molecule, are consistent with those produced by the theoretically assumed molecular structure, demonstrating the successful synthesis of the target product.

4. Conclusions

(1) The optimal reaction conditions of mixed aliphatic imidazolinium guanidinium corrosion inhibitors were: raw materials mass ratio ($m_{\text{intermediate}}$ : $m_{\text{cyanamide}}$) of 8:1.3, reaction temperature of 95°C, reaction time of 4 h, and ethylene glycol monomethyl ether as solvent.

(2) The analysis results of infrared, UV and NMR spectrograms were consistent with the structural information of the target molecule, demonstrating the successful synthesis of the target product.

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