Preparation of Imidazoline Corrosion Inhibitor by Catalytic Oxidation Based on Computer Aided Technology

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Abstract. Alkyl imidazoline corrosion inhibitor was prepared with Cocinic and diethylenetriamine (DTA) as reactant and xylene as water carrier. The relationship between the preparation process, molecular structure and the corrosion inhibition performance of boiler water system was studied by computer aided technology. The results showed that temperature, reaction time and reactant ratio were the key factors affecting the yield. Carbon steel corrosion inhibition rate of alkyl imidazoline derivatives in boiler water can reach more than 80%. The corrosion inhibitor has a strong inhibitory effect on the dissolution process of the corrosion anode and the depolarization process of the cathode, so it can be considered as a mixed corrosion inhibitor of carbon steel based on the anode. The reason of corrosion inhibition is that the corrosion inhibitor adsorbs on the surface of carbon steel and forms a thin film, effectively blocking the contact between the steel surface and water.

Keywords: Imidazoline, Corrosion Inhibitor, Preparation Process, Boiler Water, Computer Aided Technology

1. Introduction
Imidazoline, as an inhibitor, was first patented in the United States in 1949\cite{1,2}. At present, it has been widely used in oil fields, and its amount accounts for about 90% of the total amount of inhibitor\cite{3,4}. Almost no one involved in the application research of boiler pipeline under the water environment\cite{5,6}. In this paper, imidazoline corrosion inhibitors in the boiler water system were synthesized through the optimization of conditions, and the corrosion behaviors of alkylimidazoline derivatives of carbon steel in boiler water were studied.

2. Experimental Section

2.1. Reagents and experimental materials
Xylene, analytical pure, Beijing chemical plant; coconut acid, analytical pure, Tianjin Chemical Reagent Plant 1; diethylenetriamine, analytical pure, Tianjin Chemical Reagent Plant 1; sodium bicarbonate, analytical pure, Beijing Chemical Reagent Company; anhydrous calcium chloride,
analytical pure, Beijing Chemical Reagent Company; benzyl chloride, chemical pure, Beijing chemical plant; corrosion test piece, standard 20 × carbon steel, size 70mm × 13mm × 1.5mm, Jiangsu Huaiyin Medical Instrument Factory.

2.2. Preparation of imidazoline and derivatives
Cocinic acid, diethylenetriamine and a certain amount of xylene solvent are added into a three port bottle with a water separator, a thermometer, a stirrer and a condensing column, then zeolite is added, reflux at 140-160 °C for 2 h, and then reflux at 180-210 °C for 2 h, the reactant is cooled to 140 °C, and the xylene solvent and the unreacted diethylenetriamine are removed under reduced pressure to obtain imidazoline. The imidazoline was heated to 95-110 °C, and a certain amount of benzyl chloride was added slowly to the room temperature after holding for a period of time to obtain quaternized imidazoline.

2.3. Structural characterization
The structure of the product was characterized by nicolet605xbfi-ir.

2.4. Corrosion inhibition
Three standard 20 × carbon steel test pieces were roughed and finely ground successively with 120 × and 300 × sandpaper. Rinse with deionized water and blow dry. Then, degrease with anhydrous ethanol, blow dry, weigh the mass, and install it in the condensate system of the simulation boiler. The water feed to the simulated boiler is an aqueous solution containing 250mg/lcacl2 and 500mg/lnahco3. The boiler pressure is 0.1MPa, and the capacity is 1000ml. After 72h operation, the test specimen was removed, washed, dried, and weighed. The corrosion rate and inhibitor efficiency are calculated according to the mass change of the test piece.

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R = \frac{m_0 - m_1}{St} \quad (1)
\]

\[
I = \frac{R_0 - R_1}{R_0} \times 100\% \quad (2)
\]

Where R represents the corrosion rate, g/(M2 • h); M0 represents the pre corrosion mass of the test piece, G; M1 represents the post corrosion mass of the test piece, G; s represents the surface area of the test piece, m2; t represents the exposure time of the test piece, h; I represents the corrosion rate, R0 represents the corrosion rate without inhibitor, g/(M2 • h); R1 represents the corrosion rate with inhibitor, g/(M2 • h).

3. Electrochemical test
The polarization curve of carbon steel was measured by potentiostat CT-2. The working electrode is A3 steel with an effective area of 1.00cm2. The auxiliary electrode is platinum electrode and the reference electrode is saturated calomel electrode. The corrosion medium is an aqueous solution containing 250mg/lcacl2 and 500mg/lnahco3, and the temperature is (40 ± 1) °C. The scanning speed is 30mV/min.

The AC impedance spectrum was measured by im6e type AC impedance spectrometer of ZAHNER Meßtechnik (Germany). The start frequency is 1 × 104hz, the end frequency is 1 × 10-3hz, and the signal amplitude is 1mV. The corrosion medium is aqueous solution containing CaCl2 (250mg/L) and NaHCO3 (500mg/L) at room temperature. The working electrode is A3 steel, the effective area is 1.00cm2, the auxiliary electrode is platinum electrode, and the reference electrode is saturated calomel electrode.
4. Results and discussion

(1) Preparation of Imidazoline

The factors that affect the yield of imidazoline include the molar ratio of acid/amine, reaction temperature, reaction time and the amount of xylene.

1) Acid/Amine Molar Ratio

In the preparation process, a series of imidazolines were prepared by changing the molar ratio of acid to amine and keeping other conditions unchanged. The yield was calculated by the water yield. The experimental results are shown in Table 1.

| N acid: n amine | Yield /% | N acid: n amine | Yield /% |
|----------------|----------|----------------|----------|
| 1 : 1          | 80.5     | 1 : 1.2        | 94.4     |
| 1 : 1.05       | 83.3     | 1 : 1.3        | 97.2     |
| 1 : 1.1        | 83.3     | 1 : 1.4        | 97.2     |

When amines are excessive, it can effectively inhibit the occurrence of side reactions. Table 1 shows that when the acid amine ratio should be 1:1.1-1:1.3, a slight excess of amine will not only help the synthesis of imidazoline, but also effectively inhibit the occurrence of side reactions. But amines should not be too much, because amines are too much, the increase of reaction yield is not obvious. Considering that the excess xylene and diethylenetriamine should be removed in the subsequent process, the molar ratio of fatty acid and diethylenetriamine was 1:1.3 in the experiment.

2) Reaction Temperature

The reaction temperature is one of the important factors in the reaction. The reaction consists of two steps: dehydration and cyclization. The control of reaction temperature is very important. In general, two temperature sections, i.e. addition dehydration section (140-160 °C) and cyclization dehydration section (180-210°C), need to be controlled to achieve the purpose of two-step dehydration. Hence, the temperature of the two temperature sections and the heating process between them have become important factors affecting the reaction. The ratio of N-acid to n-Amine was 1:1.3 and the reaction time was 8 h.

The more the water yield, the more thorough the reaction is. It can be seen from Figure 1 that increasing the maximum reaction temperature properly can provide high active ingredients and promote the synthesis reaction. The reason is that the temperature is too low, the reactants cannot form a homogeneous state, so that they cannot be fully contacted, thus affecting the content of active reactive species. However, when the maximum reaction temperature is further increased, the water yield does not increase correspondingly. The reason is that too high reaction temperature will cause side reaction, increase the possibility of imidazoline oxidation, and lead to excessive energy consumption of the whole reaction. Therefore, the maximum reaction temperature should not be too high. The experiment shows that the maximum temperature is between 210°C and 220°C.

![Figure 1](image-url)  
**Figure 1.** Relationship between reaction temperature and water yield
3) Reflux Reaction Time

The molar ratio of acid/amine is 1:1.3. It is found that when the heating temperature is below 140 °C, water is observed in the water separator after about 2 h. When the temperature is above 140 °C, water is observed in the water separator quickly. When the temperature is kept between 140 °C and 160 °C for 2 h, there will be little increase in the water yield, and gradually increase the temperature to 180 °C, there will be water in the water separator soon again. The results are shown in Table 2.

**Table 2. Relationship between reflux time and water yield**

| t/h | V/mL | t/h | V/mL |
|-----|------|-----|------|
| 0.5 | 0.3  | 6   | 3.4  |
| 2   | 2.6  | 8   | 3.5  |
| 4   | 3.3  | 10  | 3.5  |

4) Dosage of Water Carrying Agent

On the one hand, the water carrying agent (xylene) can make the reactant have good solubility, which is convenient for reaction; on the other hand, the water carrying agent can be azeotropic with the water generated by reaction, so as to play the role of timely drainage, and make the reaction proceed in the direction of the product generated. When the ratio of N-acid to n-Amine is 1:1.3 and the reaction time is 8h, the relationship between different amount of water carrying agent and water yield is obtained. The results are set out in Table 3.

**Table 3. Relationship between water carrying capacity and water yield**

| φ xylene: φ acid/amine | V/mL | φ xylene: φ acid/amine | V/mL |
|------------------------|------|------------------------|------|
| 0.10                   | 1.5  | 0.25                   | 3.5  |
| 0.15                   | 2.3  | 0.30                   | 3.5  |
| 0.20                   | 3.1  |                        |      |

Table 3 shows that when the amount of water carrying agent is not enough, it will affect the final conversion rate of the reaction. The water yield is very small. The water carrying agent can achieve good water yield effect when the total volume is about 25%. Too much water carrying agent cannot obviously promote the reaction process. Given the subsequent experiments need to reduce the pressure to steam the water carrying agent, the amount of water carrying agent should be 25%.

Alkylimidazoline derivatives were synthesized from cocinic acid and diethylenetriamine. The relationship between the structure and the corrosion inhibition in boiler water system was studied by mass method and infrared spectroscopy. The infrared spectrum of imidazoline derivatives with outstanding corrosion inhibition is shown in Figure 3. At 1544cm-1, a strong characteristic absorption peak of N-H bending vibration occurs. At 1608cm-1, a characteristic absorption peak of C = n stretching vibration of azoline ring occurs. At 1653cm-1, a characteristic absorption peak of C = C in cocooilec acid occurs, suggesting that the product is imidazoline derivative. It can also be seen from the above data that there is nitrogen in the imidazoline derivative which does not share the electron pair. The atom can coordinate with the metal element to form a strong chemical adsorption layer, and the double bond can also chemically adsorb on the metal surface through the action of π bond.

Meanwhile, another capacitive arc appears in the low frequency region of the impedance complex plane with inhibitor, which indicates another time constant. The results show that in the presence of inhibitor, in addition to the surface charge transfer caused by the inhibitor adsorption layer connected to the metal surface, there is an additional electrochemical process, that is, the inhibitor and the iron ion dissolved in the solution and on the surface of carbon steel generate chelates, which are adsorbed on the surface of carbon steel. For the inhibitor with strong adsorption, its impedance spectrum shows twice time constant pattern, suggesting that the inhibitor has formed a measurable strong and tough adsorption film on the metal surface. Therefore, it can be known that imidazoline corrosion inhibitor can form a strong adsorption film on the surface of carbon steel to prevent corrosion.
5. Conclusions
Optimal conditions for alkylimidazole synthesis: 1:1.3 N-acid/n-Amine, 25% of the total volume of the reactant, refluxed at about 140 °C, gradually rise to 210 °C, refluxed for 8 h, product yield above 90%. The corrosion inhibition of alkyimidazoline derivatives is closely related to its molecular structure, which can reach above 80% on carbon steel in the boiler water. Alkyimidazoline derivatives can strongly inhibit the anodic dissolution process and cathodic depolarization process and are considered as anode-based mixed inhibitors of carbon steel. According to the characteristics of polarization curve and its shift with the increasing inhibitor concentration, the inhibitor can also be regarded as an anode inhibiting passivator of carbon steel. The reason that alkyimidazoline derivatives can inhibit the corrosion process is that the film formed by strong adsorption on the carbon steel surface effectively blocks the contact between the carbon steel surface and water.

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