Study on the compound of Imidazoline Corrosion Inhibitor

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Abstract: An imidazoline quaternary corrosion inhibitor suitable for oilfield was synthesized. Oleic acid, diethylene triamine, and quaternary ammonium reagents were used in the experiment. The dimethylbenzene was used as water carrying agent. Under the experimental conditions, the inhibition rate of the synthesized corrosion inhibitor in hydrochloric acid can reach to 99.113%. Infrared spectrometer was used for the imidazoline corrosion inhibitor intermediates and the quaternary ammonium and the structures were characterized. The complex with sodium sulfite, potassium iodide, sodium lauryl sulfate, potassium pyroantimonate, glycerol, OP-10, propargyl alcohol, isopropyl alcohol and thiourea were researched. The better mixtures with good synergy were selected and the best ratios were obtained.

1. Introduction

Corrosion inhibitors are needed to reduce the corrosion rates of metallic materials. Therefore, achieving the high inhibition efficiency is a key to project delivery and integrity risk management. Most studies in the literature considered the use of corrosion inhibitors as admixtures added during the mixing of concrete (1-6). The applicability of organic compounds as corrosion inhibitors for the metals in acidic medium has been recognized for a long time. Organic compounds employed as corrosion inhibitors can adsorb on the metal surface through heteroatoms such as nitrogen, oxygen, sulphur and phosphorus. They are transparent and can inhibit steel corrosion with very small concentrations (7–9). Imidazoline corrosion inhibitor as a novel, low toxicity and efficient water-based corrosion inhibitor can effectively inhibit metal corrosion and be used in the neutral medium environment, as well as the acid and alkaline conditions. At present, the largest amount of the oilfield corrosion inhibitors in the United States was the imidazoline corrosion inhibitor and its derivatives. Imidazoline is a kind of heterocyclic compounds with two nitrogen atom. The structures are as follows.

![Fig.1 The structures of imidazole, imidazoline and imidazoline corrosion inhibitor](image)

In this paper, the objective is to develop a kind of imidazolines quaternary corrosion inhibitor suitable for oilfield and obtain the best complex for improving the corrosion inhibition and the properties of temperature resistance.
2. Experiment

2.1 Preparation

Chemical reagents:
Oleic acid, diethylene triamine, dimethylbenzene, benzyl chloride, sodium sulfite, potassium iodide, sodium lauryl sulfate, coke antimony potassium, OP-10, propargyl alcohol, isopropyl alcohol and thiourea, hydrochloric acid and ethanol were purchased from Kelong chemical reagent factory (Chengdu, China). All of them were AR analytical reagent grade.

2.2 Principle

The acylation reaction and cyclization reaction mechanisms were as follows:

\[
\text{C}_2\text{H}_4\text{CH}_2\text{NH}_2 + \text{RX} \rightarrow \text{C}_2\text{H}_4\text{CH}_2\text{N}^+\text{C}_1\text{H}_3\text{N}^\text{R} + \text{X}^-
\]

The quaternization reaction mechanism in this experiment was as follows:

\[
2\text{C}_1\text{H}_3\text{COOH} + 2\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{CH}_2\text{NH}_2 + \text{C}_1\text{H}_3\text{C}^\text{O} \rightarrow 2\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_4\text{NH}_2 + \text{C}_2\text{H}_4\text{NH}_2 + \text{C}_1\text{H}_3\text{C}^\text{O} \rightarrow \text{C}_1\text{H}_3\text{C}^\text{O} \rightarrow \text{N} \rightarrow \text{C}_2\text{H}_4\text{NH}_2
\]

2.3 Synthesis of the corrosion inhibitor

A certain amount of oleic acid and 10mL dimethylbenzene as the water carrying agent were placed in a flask equipped with a mechanical stirrer and completely dissolved. Then add an appropriate amount of diethylene triamine under the stirring. In this process, water began to generate indicated the acylation reaction had begun. Then continue to be heated to 180°C to 220°C with the electric sets. The cyclization reaction kept about 4-8 hours. The imidazoline quaternary ammonium corrosion inhibitor was generated by adding a quaternizing agent reacting in a water bath for several hours. The molar ratio of the imidazoline intermediates and the quaternary ammonium reagent was 1:1. The product was a kind of yellow or brown viscous liquid.

The molar ratio of oleic acid and diethylenetriamine, reaction temperature, reaction time in the acylation stage and reaction temperature in the cyclization stage were selected for designing the four factors and three levels of orthogonal test analysis. The corrosion performance of the synthesis inhibitors (not separation and purification) under various reaction conditions (the amount of the mass fraction of 1.5%) were evaluated at atmospheric pressure and 80°C. The concentration of the hydrochloric acid solution is 15% (mass fraction). The tables of the factors and the data analysis were shown below.

| No. | A | B | C | D |
|-----|---|---|---|---|
| 1   | A1=1:1 | B1=150 | C1=180 | D1=2 |
| 2   | A2=1:1.1 | B2=160 | C2=200 | D2=3 |
| 3   | A3=1:1.2 | B3=170 | C3=220 | D3=4 |
The experimental results showed that the best reaction conditions is A3B2C3D2. The molar ratio of the reactants (oleic acid: diethylene triamine) was 1:1.2. The acylation time was 3h. The acylation temperature was 160°C. The cyclization temperature was 220°C. The optimal condition is D2>B2>A3>C3, which showed that the effect of the acylation time on the synthesis process is great. Under these conditions, the inhibition rate in hydrochloric acid (15%) can reach to 99.113%.

3. Results and Discussion

3.1 IR spectrum characterization of polymers

The imidazoline intermediate and the imidazolines quaternary corrosion inhibitor synthesized by the method in the experiment were analyzed with Fourier transform infrared spectrometer. The IR spectrums of the products were depicted in Figure 3-1 and Figure 3-2.

![Figure 3-1 The IR spectrum of the imidazoline intermediate](image1)

![Figure 3-2 The IR spectrum of the imidazolines quaternary corrosion inhibitor](image2)

In these two Figures, it could be seen that the absorption peak appeared at 1601 cm\(^{-1}\) in the spectrum clearly indicated the presence of C=N bond, and 1550 cm\(^{-1}\) was the stretching vibration peak of C-N bond which is the characteristic absorption peak of imidazoline ring. Absorption peaks observed at 1554 cm\(^{-1}\) and 3297 cm\(^{-1}\) in the Fig.3-1 were attributed to the stretching vibration of N-H bond. These results demonstrated that the typical structure of imidazoline was present in the polymer. Besides, the absorption peaks at 765 cm\(^{-1}\) and 1463 cm\(^{-1}\) were assigned to the stretching vibration peaks of benzyl group in the Fig.3-2. A sharp absorption peak at 2925 cm\(^{-1}\) showed the presence of \(-\text{CH}_2-\) group. Therefore, a conclusion could be that the structure of imidazoline quaternary was included in the polymer.

3.2 Performance of the imidazoline quaternary in the acid solution

3.2.1 The effect of different inhibitor concentrations on the corrosion inhibition

The synthetic inhibitor in the experiment was respectively added to the evaluation solution of 15% hydrochloric acid by mass fractions of 0.1%, 0.3%, 0.5%, 1%, 1.5%, 2%. Then the corrosion inhibition rate was calculated under the conditions of 80°C, four hours in the hydrochloric acid solution. The relationship between the corrosion inhibitor concentrations and the inhibition rate is shown in Figure 3-3.
Figure 3-3 the effect of different inhibitor concentrations on the corrosion inhibition

As shown in Figure 3-3, the inhibition rate first increased and then decreased with the increasing inhibitor concentration. Moreover, the inhibition rate of the corrosion inhibitor with 0.5% (wt) of the concentration reached maximums at 99.121%. Namely, within a certain range, as the concentration increased, the inhibition rate of the inhibitor was getting better. Because the surface of the steel sheet can be sufficiently covered with the increasing concentration of the inhibitor so that the inhibition efficiency is improved. But when the concentration of corrosion inhibitor is too high, it may causes the inhibitor shedding that makes the inhibition rate slows down.

3.2.2 The effect of temperatures on the corrosion inhibition
The concentration of the synthetic inhibitor in the experiment was 0.5% (wt) and added into the evaluation solution of 15% hydrochloric acid. Then the corrosion inhibition rate was calculated under the conditions of 30°C, 50°C, 60°C, 70°C, 80°C, 90°C respectively and four hours in the hydrochloric acid solution. The relationship between the temperatures and the inhibition rate is shown in Figure 3-4.

Figure 3-4 the effect of temperatures on the corrosion inhibition

It could be seen from the Figure 4-2 that the inhibition rate of corrosion inhibitor is about 99.3% in the range of 30°C-80°C. And it reached the maximum at 50°C. Then it decreased with the rising temperature. When the temperature reached to 90°C, the inhibition reached to about 98.1%. The corrosion inhibitor was a kind of an adsorption inhibitor. Chemical absorption plays a major role in this process. The enhancement of the intermolecular interaction increased with the temperature rising. However, if the temperature continued to increase, the structure of the polymer chain will be changed (break, etc.).

3.2.3 The effect of different acid concentrations on the corrosion inhibition
The concentration of the synthetic inhibitor in the experiment was 0.5% (wt) and be added into the evaluation solution at 80°C for 4h. Then the corrosion inhibition rate was calculated under the hydrochloric acid concentrations of 5%, 10%, 15%, 20% respectively. The relationship between the different acid concentrations and the inhibition rate is shown in Figure 3-5.
It can be seen from Figure 3-5 that the corrosion rate declined when the concentration of hydrochloric acid solution was more than 15%. When the concentration of hydrochloric acid solution was less than 15%, the corrosion inhibition rates were all more than 99%. With the increase of the concentration of hydrochloric evaluation solution, corrosion will be increased dramatically. When the concentration to 20%, the reduction in corrosion rate showed that the concentration of hydrochloric acid has a greater effect on the corrosion of the electrode reaction.

3.3 Complex with the corrosion inhibitor
The synergistic corrosion inhibitor mixed with some substance can greatly improve the corrosion inhibiting efficiency and can relatively reduce the amount of corrosion inhibitor. So the complex with the corrosion inhibitor experiment was done in this paper. The corrosion inhibition rate of adding the synthesis imidazoline quaternary only was 99.113% (blank experiment in this chapter).

3.3.1 Complex with the sodium sulfite
The amount of the corrosion inhibitor is 0.5% (wt), the acidification temperature was 80°C, and the acidified time was 4 hours. The concentration of the hydrochloride evaluation solution was 15% (wt). The complex performance of the sodium sulfite and the imidazoline quaternary inhibitor was studied. The relationship between the amount of sodium sulfite and the corrosion rate was shown in Figure 3-6.

It can be seen from Figure 3-6 that the sodium sulfite could not improve the corrosion rate though it has some anti-corrosion performance. When the amount of the sodium sulfite was less, the maximum corrosion rate of the complex system can reach to 92.173%. When the amount was excessive, it may decompose by the impact of hydrochloric acid. So the result of the complex with sodium sulfite was not satisfied.

3.3.2 Complex with the potassium iodide
Synergistic effect on the organic and the halogen ions is studied as an Inhibition Synergistic Effect system. It is generally believed that the organic containing N, O, P, S in acid can occur the synergistic effect with halogen ions. The evaluation conditions were the same as above. The complex performance of the potassium iodide and the imidazoline quaternary inhibitor was studied. The relationship between the amount of potassium iodide and the corrosion rate was shown in Figure 3-7.
Figure 3-7 the effect of potassium iodide dosage on the corrosion inhibition

It can be seen from Figure 3-7 that the inhibition efficiency became better gradually with the increase in the amount of potassium iodide. The corrosion inhibition rate can reach to 99.369% when the amount of the corrosion inhibitor was 0.5% (wt). The corrosion inhibition rate would decline if the amount was excessive. This is because the inorganic anion added will increase the adsorption capacity of the organic cation inhibitor greatly. Found through the experiments, the steel surface will be black and the inhibition efficiency is poor when I⁻ ions acted on the steel separately. If I⁻ ions in the solution is excessive, the adsorption layer of I⁻ ions on the steel surface will not be covered by enough imidazoline which will result that the blank spots will generate by the adsorption of I⁻ ions but the imidazoline corrosion inhibitor. So the corrosion inhibition rate will decline.

3.3.3 Complex with SDS
The evaluation conditions were the same as above. The complex performance of the SDS and the imidazoline quaternary inhibitor was studied. The relationship between the amount of SDS and the corrosion rate was shown in Figure 3-8.

Figure 3-8 the effect of SDS dosage on the corrosion inhibition

It can be seen from Figure 3-8 that the inhibition rate of the corrosion inhibitor system can reach to above 99% when the amount of SDS was 0.03%. However, with the increase in the amount of SDS, the inhibition efficiency decreased. The corrosion inhibition rate also fell to below 90% with the same amount of the corrosion inhibitor and the SDS. The reason may be due to the strong electric effect between the positive ion surfactant and anion surfactant that made the solubility of the corrosion inhibitor decline.

3.3.4 Complex with the potassium pyroantimonate
For the potassium pyroantimonate can be used as the synergist and have the property of temperature resistance, the complex performance of the potassium pyroantimonate and the imidazoline quaternary inhibitor was studied. The evaluation conditions were the same as above. The relationship between the amount of potassium pyroantimonate and the corrosion rate was shown in Figure 3-9.
Figure 3-9 the effect of potassium pyroantimonate dosage on the corrosion inhibition

It can be seen from Figure 3-9 that the corrosion inhibition rate was 99.364% when the amount of the potassium pyroantimonate was 0.03%. Compared to the imidazoline corrosion inhibitor separately used, the inhibition efficiency was improved about 0.2%. However, the corrosion inhibition rate decreases with the increase of the amount of potassium pyroantimonate. Therefore, complex ratio of the potassium pyroantimonate and the imidazoline inhibitors was 3:50.

3.3.5 Complex with the glycerol

Under the condition of the presence of the colloidal particles of the surface active agent, the process of increasing the solubility of poorly soluble drugs and forming a clear solution is called solubilization. The solubilizing surfactant called solubilizers. The surface active agent is able to form micelles in water so it can increase the solubility of poorly soluble drugs. Micelles are tiny colloid particles and the dispersion system is a colloidal solution. Then the insoluble drugs can be occluded or adsorbed to increase the amount of dissolution. Alcohols are selected as solubilizers mainly taking into account of the performance, a wide variety of sources and comply with the advantage of the solubilizer. The complex performance of the glycerol and the imidazoline quaternary inhibitor was studied. The evaluation conditions were the same as above. The relationship between the amount of glycerol and the corrosion rate was shown in Figure 3-10.

Figure 3-10 the effect of glycerol dosage on the corrosion inhibition

It can be seen from Figure 3-10 that the corrosion inhibition rate was above 99% when the amount of the glycerol was about 0.1%. Glycerol can improve the solubility of the corrosion inhibitor. However, the corrosion rate will be some decline with the increase of the amount of glycerol. So the efficiency of the complex was not very good.

3.3.6 Complex with the isopropyl alcohol

Isopropyl alcohol also can be seen as a kind of solubilizers. The complex performance of the isopropyl alcohol and the imidazoline quaternary inhibitor was studied. The evaluation conditions were the same as above. The relationship between the amount of isopropyl alcohol and the corrosion rate was shown in Figure 3-11.
Figure 3-11 the effect of isopropyl alcohol dosage on the corrosion inhibition

It can be seen from Figure 3-11 that the corrosion inhibition rate could not be improved effectively by the isopropyl alcohol added. Especially when the added amount was more than 0.5%, there was a substantial decline on the corrosion inhibition rate of the corrosion inhibitor system. It shows that the complex effect of isopropyl alcohol and the corrosion inhibitor compound was not ideal.

3.3.7 Complex with OP-10
Emulsifier OP-10 is a kind of non-ionic surface-active agent with the excellent performance of emulsifying, wetting and diffusion. The complex performance of the OP-10 and the imidazoline quaternary inhibitor was studied. The evaluation conditions were the same as above. The relationship between the amount of OP-10 and the corrosion rate was shown in Figure 3-12.

Figure 3-12 The effect of OP-10 dosage on the corrosion inhibition

It can be seen from Figure 3-12 that the corrosion inhibition rate was 99.464% when the amount of OP-10 was 0.1%. Compared with the imidazoline quaternary corrosion inhibitor used alone, the corrosion inhibition rate can be increased by about 0.3%. So OP-10 and imidazoline quaternary corrosion inhibitor can play a very good synergy. The best complex ratio of OP-10 and imidazoline quaternary corrosion inhibitor was 1:5.

3.3.8 Complex with propargyl alcohol
The propargyl alcohol and imidazoline quaternary inhibitor have good synergies. Multilayer polymer adsorption films were formed on the surface of the steel by propargyl alcohol. When complex with the organic nitrogen compound, the polycondensation reaction occurred at the surface of the metal. The polymer film will be more dense to play a better physical shielding effect. The complex performance of the propargyl alcohol and the imidazoline quaternary inhibitor was studied. The evaluation conditions were the same as above. The relationship between the amount of propargyl alcohol and the corrosion rate was shown in Figure 3-13.
Figure 3-13 the effect of propargyl alcohol dosage on the corrosion inhibition

It can be seen from Figure 3-13 that the efficiency of the imidazoline quaternary inhibitor can be improved significantly with the added propargyl alcohol. A tightly adsorbed film can be formed on the metal surface to inhibit the corrosion occurs. The corrosion inhibition rate of the system was 99.339% when the amount of propargyl alcohol was 1%. Therefore, the best complex rate of propargyl alcohol and the imidazoline inhibitor was 2:1.

3.3.9 Complex with thiourea

The complex performance of the thiourea and the imidazoline quaternary inhibitor was studied. The evaluation conditions were the same as above. The relationship between the amount of thiourea and the corrosion rate was shown in Figure 3-14.

Figure 3-14 The effect of thiourea dosage on the corrosion inhibition

It can be seen from Figure 3-14 that the improvement of corrosion inhibition rate of the corrosion inhibitor system with the addition of thiourea was not obvious though it was reported that there is a better corrosion synergies between thiourea and imidazoline corrosion inhibitor in the literature. But in this experiment, the synergies between thiourea and the imidazoling quaternary inhibitor was not obvious.

4. Conclusions

In this paper, imidazoling quaternary inhibitor was synthesized. And the experimental results showed that the best molar ratio of the reactants (oleic acid: diethylene triamine) was 1:1.2. The acylation time was 3h. The acylation temperature was 160°C. The temperature of the cyclization was 220°C. Under these conditions, the inhibition rate in hydrochloric acid can reach to 99.113%.

Reference to the “Experimental methods and evaluation for acidification inhibitor performance”, each factor of the corrosion inhibition performance was evaluated. The relationships of the concentrations of the corrosion inhibitor, acidification temperature, acidification time, acid concentrations with the imidazoline quaternary corrosion were obtained in the evaluation solution of hydrochloric. When the amount of corrosion inhibitor was 0.5% (wt), acidification temperature was 80 °C, acidification time was 4 hours and the hydrochloric acid concentration was 15%, the corrosion inhibition rate can reach to 99.1%. The corrosion inhibition rate can reach to 90% when the acid concentration was 20%. The experiment illustrates that the corrosion inhibitor has good heat resistance and acid resistance.

The complex with sodium sulfite, potassium iodide, sodium lauryl sulfate, potassium
pyroantimonate, glycerol, OP-10, propargyl alcohol, isopropyl alcohol and thiourea were researched. The better mixtures with good synergy were selected, and the best ratios are as follows: the ratio of potassium iodide and the corrosion inhibitor is 1:1. The ratio of potassium pyroantimonate and the corrosion inhibitor is 3:50. The ratio of OP-10 and the corrosion inhibitor is 1:5. The ratio of propargyl alcohol and the corrosion inhibitor is 2:1.

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