Application of vegetable oil amide derivatives in oil field pipeline anticorrosion

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Abstract. Based on rapeseed oil and soybean oil, and diethylenetriamine and formaldehyde, a plant oil derived amide inhibitor was synthesized. The inhibition performance of plant oil derived amide inhibitor on A13 steel in 1 mol / L hydrochloric acid was studied by weight-loss experiment, electrochemical analysis and quantum chemical calculation. The adsorption behavior and mechanism of the inhibitor on A13 steel surface were revealed. The results of electrochemical experiments were consistent with the results of weight loss tests. The contact angle test results showed that the plant oil derived amide inhibitor can significantly enhance the hydrophobicity of A13 steel surface. The thermodynamic parameters show that the adsorption of plant oil derived amide inhibitor on A13 steel surface was self. The results of quantum chemical calculation showed that there are a lot of active sites in the structure of amide inhibitor derived from vegetable oil.

1. Introduction
With the development of social economy and urbanization, the demand for energy is increasing day by day, and the oil production is increasing year by year[1]. Oil is mainly transported by long-distance buried pipelines, which are susceptible to corrosion due to factors such as material, soil environment, microorganism, corrosion medium of produced liquid, etc., which will affect the quality of oil transportation, cause oil leakage, serious environmental pollution, even fire and explosion, and cause huge losses to enterprises and society[2]. It is necessary to improve the manufacturing and laying quality of oil pipelines, develop anti-corrosion technology of oil pipelines, ensure the stability of pipeline performance, and ensure the quality and safety of crude oil transportation. The material of petroleum pipeline is mainly steel, which is easily affected by ambient temperature, humidity, air, chemical and electrochemical corrosion, and also affected by the fluctuating stress of petroleum transportation, resulting in stress corrosion[3]. When the pipeline is laid in the soil, the soil quality, resistivity, pH, microorganism and other factors will cause corrosion to the pipeline[4]. In the oil and gas industry and other fields, acidizing is an important means to improve the oil recovery rate (EOR). Compared with other inorganic acids, hydrochloric acid is more economical and practical, so it becomes the most commonly used acid[5]. However, acidizing technology will seriously corrode pipelines and metal equipment, increase the maintenance cost and safety risks of the industrial sector. Especially in oil production, high water content crude oil will be produced. The most effective way to protect metals is to add corrosion inhibitors. Generally, the main corrosion inhibitors are organic compounds, and the structure often contains heteroatoms (N, S, O, P), heterocycles and unsaturated bonds[4-5].
2. Materials and methods

2.1. Experimental material
Rapeseed oil was purchased from Shaanxi Jianxing Agricultural Technology Co., Ltd.; soybean oil was purchased from Shaanxi Jianxing Agricultural Technology Co., Ltd.; Diethylenetriamine was purchased from Tianjin Fuchen chemical reagent plant; formaldehyde was purchased from Hubei University chemical plant; concentrated hydrochloric acid was purchased from Tianjin Chemical Reagent Co., Ltd.; petroleum ether, anhydrous ethanol, thiourea and hexamethylenetetramine are respectively purchased from Xi'an Chemical Reagent plant.

2.2. Synthesis of inhibitor
In this experiment, rapeseed oil, soybean oil and castor oil were reacted with two ethylene three amines, three ethylene four amines and four ethylene five amines to produce intermediate products, and then the intermediate products were reacted with formaldehyde to produce the final vegetable oil amide derivative inhibitor.

\[
\begin{align*}
    &\text{H}_2\text{N} - \text{N} - \text{R} & \text{O} \\
    &\text{O} & \text{O} \\
    &\text{O} & \text{O} \\
    &\text{O} & \text{O} \\
    &\text{H}_2\text{N} - \text{N} - \text{R} & \text{O} \\
    &\text{O} & \text{O} \\
    &\text{O} & \text{O} \\
    &\text{O} & \text{O} \\
\end{align*}
\]

Figure 1. Synthesis of rapeseed oil amide derivative inhibitor.

The reaction equation of the other soybean oil with diethylenetriamine is the same as that of rapeseed oil

2.3. Configuration of corrosion solution
We added a small amount of distilled water to the 150ml grinding bottle (to prevent the hydrochloric acid from volatilizing), then added 5% concentrated hydrochloric acid, and then added the concentrations of 70mg / L, 50mg / L, 20mg / L, 10mg / L, 5mg / L inhibitor solution, and blank inhibitor solution. We controlled the total volume of the solution to 120ml.

2.4. Evaluation of corrosion inhibition by weight loss method
We put the previously prepared corrosion solution into a 60°C water bath for heating. When the temperature reaches the established temperature, hang the treated A3 steel sheet (2 pieces) with ropes into the bottle at one time (fast action). Pay attention that the A3 steel sheet does not touch the wall and bottom of the bottle. It should be completely immersed in the solution. After heating in the water bath for 2 hours, take out the A3 steel sheet. First, we washed it with distilled water, soaked it in A13 steel sheet and cleaned it in acetone solution. Then, we washed and removed the A13 steel sheet in ethanol solution, put it on quantitative filter paper, and dried it with a blower. After drying. Finally, we weighed the A13 steel sheet with an analytical balance and recorded the data. The corrosion inhibition rate is calculated according to the following formula:

\[
E_w = \frac{W_0 - W}{W} \times 100\%
\]

2.5. Adsorption model of amide derived from vegetable oil on steel surface
Assuming that the adsorption law of amide inhibitor derived from vegetable oil on steel surface conforms to Langmuir adsorption model, it should be [6-8]:

\[
\text{(1-1)}
\]
Formula:
\[
\frac{c}{\theta} = \frac{1}{K} + c
\]  \hspace{1cm} (1-2)

Formula:
\[
c - the inhibitor concentration; \\
K - the adsorption equilibrium constant; \\
\theta - the surface coverage, which is approximately replaced by the corrosion inhibition rate.
\]

2.6. Adsorption thermodynamic parameters
The adsorption thermodynamic parameters play an important role in studying the adsorption mechanism of inhibitors. The enthalpy of adsorption can be calculated by van’t Hoff equation:

\[
\ln K = \frac{-\Delta H^0}{RT} + \text{constant}
\]  \hspace{1cm} (1-3)

Where, \(\Delta H^0\) and \(K\) are the standard adsorption enthalpy and adsorption equilibrium constants, \(R\) is the gas (8.314J·k\(^{-1}\)·mol\(^{-1}\)), \(T\) is the absolute temperature (\(K\)), and constant is the integral constant. \(\Delta H^0\) can be directly calculated by the slope of the straight line. The standard adsorption free energy (\(\Delta G^0\)) can be calculated according to the following formula [6-8]:

\[
K = \frac{1}{55.5} \exp \left( \frac{-\Delta G^0}{RT} \right)
\]  \hspace{1cm} (1-4)

Where: 55.5 is the concentration of water in the solution, in mol/L. Finally, the standard adsorption entropy (\(\Delta S^0\)) can be calculated by the basic thermodynamic formula:

\[
\Delta S^0 = \left( \Delta H^0 - \Delta G^0 \right)/T
\]  \hspace{1cm} (1-5)

3. Results and Discussions

3.1. Evaluation of corrosion inhibition performance
It can be obtained from Figure 2, that in a 5% hydrochloric acid solution, the product of rapeseed oil and soybean oil reacting with diethylene triene and formaldehyde-derived vegetable oil-derived amide have a good corrosion inhibition effect on the steel sheet. As the concentration increased, the corrosion inhibition effect was continuously enhanced. After a certain concentration (about 20 mg/L), the corrosion inhibition rate \(E_w\) was basically unchanged with the increase of the concentration of the corrosion inhibitor. At four temperatures of 30 to 60\(^\circ\)C, the maximum corrosion inhibition rate exceeded 90\%, indicating that vegetable oil-derived amide corrosion inhibitors had a good corrosion inhibition effect on steel sheets in a 5% hydrochloric acid solution. Vegetable oil-derived amide corrosion inhibitors had the best effect on the corrosion inhibition rate of steel at 40\(^\circ\)C and 50\(^\circ\)C, and the effects of 30\(^\circ\)C and 60\(^\circ\)C were relatively poor. Due to the general solubility, the adsorption of the corrosion inhibitor on the steel surface was weakened, resulting in a poor corrosion inhibition effect at 30\(^\circ\)C. At the same time, as the temperature increases, the solubility of the corrosion inhibitor will increase, so the slow-release effect of 40 \(^\circ\)C and 50 \(^\circ\)C is relatively good. However, as the temperature increased, hydrochloric acid accelerated the corrosion rate of steel. The main reason is desorbed from the surface of the steel inhibitor molecule at higher temperatures, leads to undesirable corrosion results. However, On the other hand, high concentrations of inhibitors covered the steel surface better, and with increasing temperature, the corrosion rate (temperature coefficient) increased much lower than the absolute increase of the corrosion rate in the blank, so the corrosion inhibition rate varies with temperature, the trend of increasing and decreasing become gentle.
(a) Inhibition effect of amide inhibitor derived from soybean oil and (b) amide inhibitor derived from rapeseed oil.

3.2. Adsorption constant of amide inhibitor derived from vegetable oil

The data in Table 1 and Figure 3, both illustrated that the correlation coefficient (r) of the (c/θ) - c line was very close to 1, that under this condition, the adsorption of vegetable oil-derived amide corrosion inhibitors on the steel surface met Langmuir adsorption equation. In addition, as the temperature increased, the adsorption equilibrium constant (K) tended to decreased in the range of 30 to 60 °C, and it was difficult for the corrosion inhibitor to form a single adsorption layer on the surface of the steel. The main reason was that the movement speed of the inhibitor molecules increased at high temperature, which enhanced the interaction between the adsorption inhibitors.

| Temperature °C | r     | Slope L/mol | K/L/mol     |
|----------------|-------|-------------|-------------|
| Rapeseed oil   |       |             |             |
| 30             | 0.9968| 1.4009      | 2.00×10^5  |
| 40             | 0.9992| 1.0543      | 1.41×10^5  |
| 50             | 0.9963| 1.0323      | 9.80×10^4  |
| 60             | 0.9989| 1.0461      | 7.20×10^4  |
| Soybean oil    |       |             |             |
| 40             | 0.9998| 1.0677      | 2.50×10^5  |
| 50             | 0.9997| 1.0483      | 2.22×10^5  |
| 60             | 0.9977| 1.0823      | 1.89×10^5  |
3.3. Adsorption thermodynamic parameters of amide inhibitor derived from vegetable oil

All can be obtained directly ΔH° adsorption thermodynamics parameter calculated by the slope of the line of Figure 4. The negative adsorption enthalpy in Table 2 indicated that the adsorption process of vegetable oil-derived amide corrosion inhibitors on the steel surface was an exothermic process, that is, temperature rise was not conducive to the adsorption of corrosion inhibitors. ΔG° <0 indicates that the adsorption of corrosion inhibitors in steel was spontaneous, and the absolute value was in the range of 20-40 kJ/mol, which further indicated that the adsorption of vegetable oil-derived amide corrosion inhibitors on steel belonged to physical adsorption and chemical adsorption [7]; ΔS°>0, which meant that the inhibitor molecules were adsorbed on the steel surface and squeezed out many water molecules. The increase in entropy caused by water desorption was much greater than the decrease in entropy caused by the inhibitor adsorption, so it leaded to an increase in the total entropy of the system. In this process, the increase in total entropy was an important driving force for the generation of adsorption[8].

![Figure 4. lnK- (1/RT) of vegetable oil derived amide inhibitor](image)

**Table 2.** Adsorption thermodynamic parameters of amide inhibitor derived from vegetable oil on steel surface with different temperatures

| T/K  | ΔG°/kJ/mol | ΔH°/kJ/mol | ΔS°/(J/(mol·K)) |
|------|------------|------------|-----------------|
|      |            |            |                 |
| Rapeseed oil derived amides |          |            |                 |
| 20   | -40.88     | -28.77     | 39.97           |
| 30   | -41.29     | -28.77     | 40.00           |
| 40   | -41.65     | -28.77     | 39.88           |
| 50   | -44.93     | -28.77     | 48.53           |
| Soybean oil derived amides |          |            |                 |
| 20   | -41.77     | -11.4      | 104.75          |
| 30   | -42.80     | -11.4      | 104.69          |
| 40   | -43.84     | -11.4      | 104.70          |
| 50   | -44.76     | -11.4      | 104.29          |

4. Conclusions

In this paper, two kinds of plant oil derived amide inhibitors were designed and synthesized, and the inhibition performance of plant oil derived amide inhibitors on A13 steel in 5% (V/V) hydrochloric acid was systematically studied. At the same time, the inhibition mechanism and adsorption behavior of plant oil derived amide inhibitors were studied and discussed at 30 °C, when the concentration of plant oil derived amide inhibitor was 70 mg / L, the inhibition rate of A13 steel can reach more than 90%; the inhibition rate of plant oil derived amide inhibitor was less affected by temperature, and showed good inhibition effect in the temperature range of 30-60°C. The adsorption isotherm of Langmuir was satisfied, and chemical adsorption was the main method. A dense hydrophobic film is formed on the surface of A13 steel, which can effectively isolate the contact between steel surface and H+. The results of quantum chemical calculation showed that the adsorption active sites of the inhibitor were distributed.
in the whole molecular structure, and the molecule of the inhibitor was distributed in the whole molecular structure. The results show that the ability of electron and Fe interaction was stronger than that of electron and Fe interaction. The plant oil derived amide inhibitor has the characteristics of green environmental protection, high thermal stability and strong adsorption capacity, and its preparation method is simple and easy. It has a good application prospect in oil and gas industry, water treatment, acid pickling and other fields.

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