Synthesis and performance of soybean oil derived amide inhibitor

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Abstract: In this paper, vegetable oil-derived amide corrosion inhibitor (SDLTF) was synthesized using soybean oil, diethylenetriamine and formaldehyde as raw materials. The effect of temperature and the amount of corrosion inhibitor on the corrosion inhibition effect was investigated by weightlessness test, and the inhibition performance, adsorption behavior and mechanism of SDLTF on A13 steel in 5% hydrochloric acid were studied by adsorption model and thermodynamic parameters. The results show that when the amount of corrosion inhibitor is 50mg / L, the corrosion inhibition efficiency is the highest, which can reach 91.20%. By simulating the isothermal curve, it was found that SDLTF conforms to the law of Langmuir isotherm adsorption.

1. Introduction
The level of national modernization is closely related to oil and natural gas, which is directly related to the stability and sustainability of economic development. Due to corrosion of pipelines and storage vessels, transportation and storage accidents of oil and gas often occur, which seriously affect production efficiency and economic conditions. What is important is that the damage to the environment is irreversible. The "first kilometre" (oil and gas extraction) and the "last kilometre" (oil and gas storage) are crucial to the oil extraction, production and transport routes. There are many acidic components in the oil (carbon dioxide, sulfur dioxide, nitrogen dioxide, etc.). These acidic gases have no corrosive effect on the oil pipeline in the dry environment, but there are some water molecules in the oil, which activate the acidic gas to corrode the pipeline. Corrosion inhibitor is generally considered to be the most effective and economical way to avoid or slow down pipeline corrosion during oil extraction and transportation. The vegetable oil amide derivative corrosion inhibitor has the characteristics of low dosage, low toxicity and no irritation, and has been rapidly developed in recent years. In this study, soybean oil was used as a raw material to react with diethylenetriamine and formaldehyde to produce a vegetable oil-derived amide corrosion inhibitor (SDLTF). The mechanism of corrosion inhibition in 5%HCl medium was explored.

2. Experiment part
2.1 Reagents and Instruments
Soybean oil (edible grade); Diethylenetriamine (analytical purity); Formaldehyde (analytical purity); Concentrated hydrochloric acid (37%, analytically pure); Petroleum ether (analytical purity);
2.2 Experimental methods

2.2.1 Synthesis of corrosion inhibitor
Weigh 1 part of soybean oil and 3 parts of diethylenetriamine, mix them into a 50ml round bottom flask, react for 4 hours at a constant temperature of 180 ℃, then mix the intermediate product and formaldehyde according to the ratio of 1:4 of the substance, continue to react for 4 hours at a constant temperature of 180 ℃, and obtain the final required vegetable oil amide derivative corrosion inhibitor (SDLTF). The reaction equation is as follows:

2.2.2 Corrosion weightlessness test
The A13 steel sheet used in the experiment was ground one by one with 300#, 600# and 1200# metallographic sandpaper before use, and then washed with distilled water. The alcohol and petroleum ether were greased and oil removed, then dried by cold wind, and then placed in a drying oven for drying and weighing. The treated A13 steel sheet was completely immersed in 5% HCl medium at a constant temperature of 30℃. After 4h of experiment, the test sheet was taken out, and the corroded product of A13 steel sheet was removed. After washing with distilled water, petroleum ether and ethanol, the product was dried until the weight was unchanged. Repeat the experiment above by changing the temperature to 40℃, 50℃ and 60℃. The corrosion inhibition rate (E_w) is calculated according to the following formula:

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

In the formula: \( E_w \) is the corrosion inhibition rate; \( W_0 \) is the loss mass of the test piece without SDLTF added, g; \( W_i \) is the loss mass of the test piece with SDLTF added, g.

2.2.3. SDLTF adsorption model on steel surface
In the temperature range of 30℃ ~ 60℃, it is assumed that the adsorption of SDLTF molecules on the surface of A13 steel sheet is chemisorption, and its adsorption law conforms to the Langmuir adsorption model. The calculation formula is as follows:

\[ \frac{c}{\theta} = \frac{1}{K} + c \]  

In the formula: \( c \) is the concentration of SDLTF (mol/L); \( K \) is the adsorption equilibrium constant (L/mol); \( \theta \) is the surface coverage, and its value can be replaced by the corrosion inhibition rate.

2.2.4 SDLTF adsorption thermodynamic parameters
The thermodynamic parameters in chemisorption can be calculated by the Van’t Hoff equation:
In the formula: $\Delta H^0$ is the standard adsorption enthalpy (kJ/mol); $K$ is the adsorption equilibrium constant (L/mol); $R$ is the standard gas thermodynamic constant; $T$ is the absolute temperature (K); constant is the integral constant, that is, the linear fitting straight line The slope of is directly calculated as $\Delta H^0$. Standard adsorption free energy ($\Delta G^0$) and entropy change ($\Delta S$) can be calculated according to the following:

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

$$\Delta S^0 = \frac{(\Delta H^0 - \Delta G^0)}{T}$$  \hspace{1cm} (5)

In the formula: 55.5 is the quantity concentration of water substance in HCl solution, the unit is mol/L.

3. Results and discussion

3.1 Weightlessness test

It can be seen from Figure 1 that in the 5% concentration hydrochloric acid solution system, it has a good corrosion inhibition effect on the A13 steel sheet. At the same temperature, increasing the concentration of the corrosion inhibitor will change the corrosion inhibition rate of the solution. Proportionally, when the SDLTF reaches a certain concentration (50~80mg/L), the corrosion inhibition rate $E_w$ basically remains unchanged, that is, SDLTF reaches saturation adsorption on the surface of A13 steel; when the reaction temperature is 30℃, the concentration of the SDLTF solution It is 80mg/L, and the maximum corrosion inhibition rate is only 67.43%. Due to the general solubility of SDLTF, the corrosion inhibitor coverage on the steel surface is not good enough to effectively play the role of anticorrosion. The corrosion inhibition efficiency is not good; the concentration of SDLTF is 5 % Hydrochloric acid solution system has good corrosion inhibition effect on steel sheet. When the temperature is 40-60℃, the corrosion inhibition performance of SDLTF is better, and the maximum corrosion inhibition rate reaches 91.20%. With the increase of temperature, the moving speed of SDLTF molecules in hydrochloric acid solution increases, and the N And O atoms are usually easy to give electrons, and the Fe surface has empty electron orbits. The lowest empty orbit of the Fe-interface interacts with the active atoms of SDLTF, and electron movement occurs, resulting in chemical adsorption. Fe-interface. The active atoms of SDLTF are preferentially adsorbed on the surface of Fe, and the entire inhibitor molecule is driven to form a molecular self-assembly coverage effect on the surface of Fe, thereby achieving the purpose of corrosion inhibition.

![Figure 1. Corrosion inhibition rate ($E_w$) of SDLTF inhibitor solution at different concentrations with different temperatures](image-url)
3.2 SDLTF adsorption model on steel surface

It can be seen from Figure 2 that at a temperature of 30°C, the \((c/\theta)-c\) linear correlation coefficient (r) of SDLTF reaches 0.9985, which is highly correlated; at temperatures of 40°C, 50°C, and 60°C, respectively, \((c/\theta)-c\) linear correlation coefficient (r) reached 0.999, very close to 1, indicating that during this temperature period, from \((c/\theta)-c\) linear correlation coefficient (r), we can see that the SDLTF molecule on the surface of A13 steel plate adsorption method is mainly chemical adsorption, which is consistent with the Langmuir model. SDLTF covers the surface layer of the steel plate to form an adsorption film, which prevents the corrosion of HCl aqueous solution on the steel and plays a role in inhibiting corrosion. If the concentration of SDLTF reaches a certain value, saturation adsorption will be achieved on the surface of A13 steel. With the increase of SDLTF, the corrosion inhibition rate will not increase.

![Figure 2. Langmuir adsorption model of SDLTF corrosion in hibitorin 5% hydrochloric acid with different temperatures](image)

It can be seen from Table 1 that the change value of the adsorption equilibrium constant decreases inversely with the temperature. The chemical adsorption is exothermic, and the temperature of the inhibitor molecules increases with temperature. The adsorption capacity on the surface layer of the steel plate decreases, and the coverage and corrosion resistance decrease. That is, the molecular diffusion speed is accelerated, resulting in enhanced interaction between SDLTF molecules on the surface of the A13 steel plate, making it difficult for the SDLTF molecules to be completely adsorbed on the surface of the A13 steel plate, forming a closed protective film.
Table 1. (c/θ) - c linear regression parameters of SDLTF corrosion inhibitor in 5% hydrochloric acid with different temperatures

| Temperature/℃ | Correlation coefficient/ r | slope | Adsorption equilibrium constant \( K \), L/mol |
|---------------|---------------------------|-------|-------------------------------|
| 30            | 0.9985                    | 1.2271| 2.86×10^5                     |
| 40            | 0.9996                    | 1.0677| 2.50×10^5                     |
| 50            | 0.9995                    | 1.0483| 2.22×10^5                     |
| 60            | 0.9993                    | 1.0433| 1.89×10^5                     |

3.3 SDLTF adsorption thermodynamic parameters

It can be seen from Figure 3 that through the linear regression fitting of the data, the value of the adsorption enthalpy \( \Delta H^0 \) is obtained, and the adsorption thermodynamic parameters at each temperature are calculated (see Table 2). The coverage on the surface of the A13 steel has a weakening effect; \( \Delta G^0 < 0 \), indicating that the SDLTF molecule is a spontaneous adsorption behavior process on the surface of the A13 steel sheet [12]; \( \Delta S^0 > 0 \), which shows that the total entropy of the SDLTF solution system increases, indicating this The increase of the total entropy of the system is an important driving force for the adsorption process of SDLTF on the surface of A13 steel sheet. It can be known from the adsorption thermodynamic parameters that the low temperature is conducive to the adsorption of SDLTF on the surface of A13 steel sheet, thereby playing the role of corrosion inhibition and anticorrosion.

![Figure 3. lnK-(1/RT) linear regression equation of SDLTF inhibitor solution](image)

Table 2. Adsorption thermodynamic parameters of SDLTF corrosion inhibitor on the surface of A13 steel sheet in 5% hydrochloric acid

| Temperature/℃ | \( \Delta G^0 \), kJ/mol | \( \Delta H^0 \), kJ/mol | \( \Delta S^0 \), J/(mol·K) |
|---------------|-------------------------|------------------------|------------------------|
| 30            | -41.77                  | -11.4                  | 104.75                 |
| 40            | -42.80                  | -11.4                  | 104.69                 |
| 50            | -43.84                  | -11.4                  | 104.70                 |
| 60            | -44.76                  | -11.4                  | 104.29                 |
4. Conclusion
(1) The vegetable oil-derived amide corrosion inhibitor (SDLTF) was synthesized from soybean oil, diethylenetriamine and formaldehyde as raw materials, which significantly inhibited the corrosion of A13 steel sheet in 5% HCl solution. Corrosion inhibition performance. The efficiency of corrosion reduction gradually increases with the increase of the concentration of the corrosion inhibitor. When the concentration of the corrosion inhibitor reaches 50mg/L, the effect of corrosion reduction tends to be stable;

(2) The simulation results of thermodynamic adsorption isotherm equation show that vegetable oil-derived amide corrosion inhibitor (SDLTF) follows Langmuir isotherm adsorption on the surface of A13 steel sheet.

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