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Inhibition Mechanism of the Imidazoline Derivate in H_2S Solution

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Abstract: Weight loss method and polarization curve measurement were employed to study the inhibition mechanism of imidazoline derivate for mild steel in acidic solution with H_2S. The results show that the derivate can retard the cathodic process, and belongs to the cathodic type inhibitor. The adsorption of the derivate on the surface of mild steel accords with the amended Langmuir adsorption isothermal equation, and higher temperature will facilitate its adsorption. The changes in the apparent activation energy (Ea) and the pre-exponential factor (A) of the corrosion reaction before and after the addition of inhibitor were also discussed.

Key words: mild steel; corrosion inhibitor; H_2S corrosion; Langmuir adsorption; imidazoline derivate
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1 Introduction

As a low-cost but excellent constructional material, carbon steel is widely applied to many industrial units. However, it suffers severe attack in service particularly in the oil refinery[1]. Under various actual environments, not only uniform corrosion but also localized corrosion can happen and the corrosion rate can range from practically zero corrosion to extremely serious corrosion[2]. The use of inhibitors is one of the most practical methods to control corrosion[3-5]. Most inhibitors are organic compounds containing nitrogen, sulfur and oxygen atoms. Among them, imidazoline derivates have many advantages such as high inhibition efficiency, low toxicity and easy production. Their inhibition is attributed primarily to the adsorption of the molecules of corrosion inhibitors, via their functional group, onto the metal surface[1]. There are many studies with regard to the relationship between adsorption and corrosion[6-10]. However, only a few researches on the adsorption of inhibitor in acidic solution with H_2S have been done[11-12]. In this paper, the inhibition efficiency of an imidazoline derivate was measured by weight loss method for mild steel in acidic solution with H_2S, and its inhibition mechanism was explained by polarization curves and Langmuir adsorption.

2 Experimental

2.1 Materials and Preparation

The material was mild steel Q235 in as-received condition with the following chemical compositions: 0.23% C, 0.47% Mn, 0.046% Si, 0.024% S, 0.012% P, 0.024% (by mass) Cu and remainder Fe.

The rectangular specimens with a dimension of 50mm × 10mm × 3mm were used for immersion test. The specimens were cut from Q235 steel plate, pol-

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ished with silicon carbide paper up to 800#, rinsed with distilled water and degreased with acetone before use.

The acidic solution containing 1000 mg/L H_2S was prepared in the following way: the distilled water was at first de-aerated by passing high purity nitrogen gas for 1h, and then suitable amount of $Na_2S \cdot 9H_2O$ was added to the distilled water; finally the solution acidity was adjusted to pH = 2 by adding diluted HCl to the solution in a sealed vessel to avoid H_2S escaping. All the reagents were AnalaR grade except the imidazoline inhibitor, which was synthesized in our lab by organic amine and organic fatty acid[13].

2.2 Immersion Test

Corrosion rates of the mild steel were measured by immersion experiment in the solution with and without imidazoline inhibitor respectively. Three parallel steel sheets were immersed in 500 mL bottle, which contained 500 mL solution. After immersed 6 hours, the sheets were taken out and put in an inhibited 10% HCl solution for 5min, then cleaned with water, acetone and weighed again. The test temperature was 40 ℃, 60 ℃ and 90 ℃ respectively.

2.3 Polarization Measurements

Potentiodynamic polarization tests were carried out using 273A Potentiostat/Galvanastat (EG&G Company, USA) in the test solution. A rod of mild steel Q235 mounted into epoxy resin was used as the working electrode with an exposed area of 0.785cm^2. After the electrode was immersed in solution for 0.5h, the potential was swept from −1.5 to 0.6V (vs. SCE) with a scan rate of 0.5mV/s. The reference electrode was a saturated calomel electrode (SCE), and the counter electrode was Pt plate. The polarization measurements were performed at 20 ± 1℃.

3 Results and Discussion

3.1 Polarization Curves of Mild Steel in H_2S Solution with and without Imidazoline Derivate

Fig. 1 shows the potentiodynamic polarization curves of mild steel immersed in the test solution containing different concentrations of imidazoline derivate. It can be seen that corrosion of the steel in acidic solution with H_2S is mainly controlled by cathodic reaction. Under the condition, the main cathodic reaction is the reduction of H^+, as shown by Stern[14]. The cathodic current decreases gradually with the concentration of inhibitor increasing while the anodic currents and the corrosion potential are affected slightly. Therefore, the addition of inhibitor can mainly retard the H^+ reduction and the derivate is a cathodic type inhibitor. Its inhibition mechanism belongs to "coverage effect" according to Cao's theory[15].

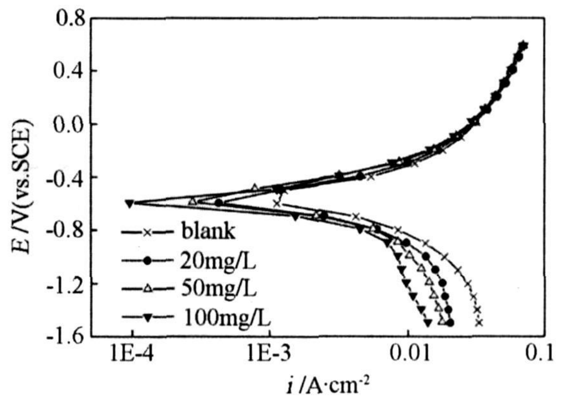

Fig. 1 Effect of inhibitor on the polarization curves of mild steel in solution containing 1000 mg/L H_2S with different concentrations of inhibitor

3.2 Adsorption Model of Imidazoline Derivate on Mild Steel Surface

Fig. 2 shows the inhibition efficiency of the derivate at different concentration at 60 ℃ and 90 ℃, respectively. It illustrates that the inhibition efficiency increases along with increasing the concentration of imidazoline inhibitor at each temperature, and keeps almost constant when its concentration is over 200 mg/L. This is in agreement with the result of polarization test. It is also seen that the higher the temperature is, the higher the inhibition efficiency is, which implies that higher temperature will facilitate the adsorption of inhibitor on the cathodic active sites of the steel surface.

The degree of surface coverage (θ) can be regarded as the area fraction of cathodic active sites covered by the corrosion inhibitor and can be calculated from Eq. (1)[16-18]:

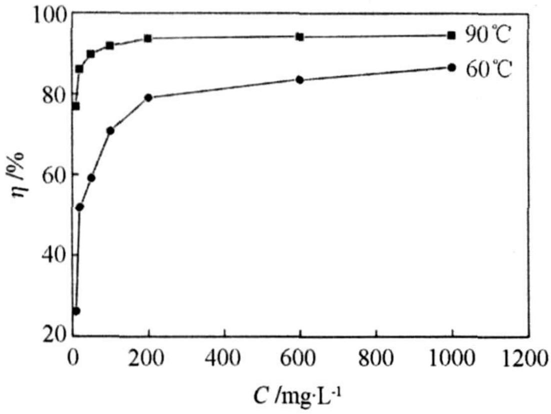

Fig 2 Effect of inhibitor concentration on inhibition efficiency at different temperatures

$$\theta = \frac{V_0 - V}{V_0} \quad (1)$$

Where V, V_0 represent the corrosion rate of specimens with and without the presence of inhibitor respectively. Assuming that the adsorption of inhibitor on mild steel surface follows the Langmuir adsorption isothermal equation[19-21]:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (2)$$

Where C is the inhibitor concentration, K is the adsorptive equilibrium constant. The figure about the relationships between C/θ and C at 60℃ and 90℃ is described in Fig 3 and the linear regression results are shown in Tab. 1.

Fig 3 indicates that C/θ and C obey linear correlativity at 60 ℃ and 90 ℃. However, the slopes of two lines deviate from the theoretical value, 1, to some extent. Therefore, the adsorption of inhibitor on mild steel surface conforms to the amended Langmuir adsorption isothermal equation, as shown in Eq. (3)[22]:

$$\frac{C}{\varepsilon\theta} = \frac{1}{K} + C \quad (3)$$

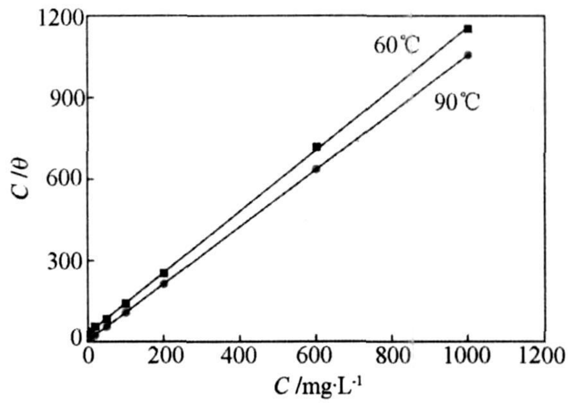

Fig 3 Relationship between C/θ and C at different temperatures

The adsorption equilibrium constant (K) can be calculated in terms of Eq. (3). Other thermodynamic parameters were calculated approximately according to Eqs (4), (5) and (6)[21-23]:

$$\Delta H^{\ominus} = \frac{RT_2T_1}{T_2 - T_1}\ln\left(\frac{K_2}{K_1}\right) \quad (4)$$

$$K = \frac{1}{55.5}\exp\left(\frac{-\Delta G^{\ominus}}{RT}\right) \quad (5)$$

$$\Delta S^{\ominus} = \frac{\Delta H^{\ominus} - \Delta G^{\ominus}}{T} \quad (6)$$

The results are listed in Tab. 2.

Tab. 1 Linear regression results between C/θ and C at different temperatures

Temperature/℃	Linear regression coefficient /r	Slope	Intercept /K^{-1}	Adsorptive equilibrium constant/K
60	1.000	1.12	29.894	0.033
90	1.000	1.05	2.781	0.360

Tab. 2 Thermodynamic parameters of adsorption on material surface using Eqs (3) ~ (6)

Temperature/℃	Correction factor/ε	Adsorptive equilibrium constant/K	$\Delta H^{\ominus}$ /kJ·mol^{-1}	$\Delta G^{\ominus}$ /kJ·mol^{-1}	$\Delta S^{\ominus}$ /J·K·mol^{-1}
60	1.129	0.038	77.322	-2.049	238.244
90	1.054	0.379	77.322	-9.197	238.246

It can be seen from Tab. 2 that the value of K increases with the temperature going up, which indicates the adsorption process will be enhanced when the temperature rises. The positive values of the adsorption heat ($\triangle H^{\Theta}$) mean that the adsorption of inhibitor molecules onto mild steel surface is an endothermal process, which also proves that the higher temperature will be helpful to the adsorption of inhibitor. The negative values of the adsorption free energy ($\triangle G^{\Theta}$) mean that the adsorption is a spontaneous process. The positive values of the adsorption entropy ($\triangle S^{\Theta}$) suggest that the process of adsorption is accompanied by the increasing of entropy. It might be interpreted in the following way: the adsorption of inhibitor onto mild steel surface results in the desorption of H_2O molecules. The decrease in entropy resulted from the former process is smaller than the increment in entropy in the latter process, as a result, the systemic entropy increases. It is a driving force for the displacement of H_2O molecules by inhibitor on mild steel surface[10].

3.3 Effect of Imidazoline Derivate on the Apparent Activation Energy and Pre exponential Factor of Corrosion Reaction

It has been reported by a number of researchers that the relationship between the logarithm of the corrosion rate and the reciprocal of temperature is linear approximately for the acid corrosion of mild steel and follows Eq. (7)[19,20].

$$\ln V = \frac{-Ea}{RT} + \ln A \quad (7)$$

Where V is the corrosion rate, Ea is the apparent activation energy, R is the gas constant, T is the temperature, and A is the pre exponential factor.

Fig. 4 is the relationship between lnV and 1/T. It is found that all the regression coefficients (r) are very close to 1, which means that the linear relationship between them is good. The values of Ea and A were calculated through the slope and intercept of the lines, and the results are shown in Tab. 3. It betrays that Ea and A decrease when the concentration of inhibitor goes up. A represents the collision frequency of the reactive particles, its fall will bring on a drop in the corrosion rate. On the contrary, the decrease of Ea will accelerate the corrosion reaction, and the value of the corrosion rate depends on them. In the present study, the variance of A is more remarkable than that of Ea, i.e. the value of A might be the dominant factor to decide the corrosion rate. Therefore, the lower A and Ea in the presence of inhibitor will ultimately lead to the lower corrosion rate, which is consistent with the results of the gravimetric and polarization measurements.

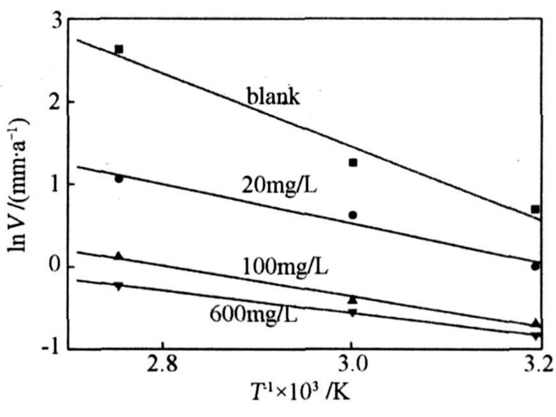

Fig. 4　Relationship between lnV and 1/T in solutions containing different concentrations of inhibitor

Tab. 3　Parameters of the regression between lnV and 1/T

Concentration of inhibitor /mg·L^{-1}	Linear regression coefficient/r	Slope/(−Ea/R)	Intercept/lnA	Ea /kJ·mol^{-1}	A
0	0.987	−4.460	14.83	37.08	2.76×10^6
20	0.985	−2.381	7.66	19.80	2.31×10^3
100	0.995	−1.850	5.19	15.38	1.79×10^2
600	0.999	−1.367	3.53	11.36	3.44×10^1

4 Conclusions

1) The imidazoline derivate can mainly retard the H^+ reduction of mild steel in acidic solution with H_2S and belongs to the cathodic type inhibitor.

2) The adsorption of inhibitor on the cathodic active sites of the steel surface accords with the amended Langmuir adsorption isothermal equation.

3) The adsorption process will be increased at higher temperature. Better corrosion inhibition can be obtained at higher temperature.

4) With the increasing of inhibitor concentration, both the pre exponential factor and the apparent activation energy decrease in the present study. The value of A is the dominant factor to decide the corrosion rate so that the corrosion rate reduces due to the addition of inhibitor.

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咪唑啉衍生物在 H_2S水溶液中的腐蚀抑制机理

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摘要: 使用失重法和电化学极化技术研究了咪唑啉衍生物在 H_2S水溶液中对碳钢腐蚀的抑制机理.结果表明:咪唑啉衍生物能有效抑制 H_2S的腐蚀,属于阴极型缓蚀剂.咪唑啉衍生物在金属表面上的吸附符合Langmuir等温吸附,温度越高,越有利于吸附.加入缓蚀剂后,降低了腐蚀反应的活化能和指前因子,而指前因子是腐蚀反应的决定因素,因此缓蚀剂的加入能降低腐蚀速率.

关键词: 低碳钢; 缓蚀剂; H_2S腐蚀; Langmuir吸附; 咪唑啉衍生物