A Study on the Comparison of Heterocyclic and Alkynol Compounds as Corrosion Inhibitors for Carbon Steel in the Pickling Process

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Corrosion inhibitor is a specialty chemical used in the pickling process to avoid the quality issue of carbon steel caused by acidic solution. In this study, two systems of carbon steel corrosion inhibitors (heterocyclic-based and alkynol-based formulas) were systematically studied in HCl solution. The inhibition performances were evaluated by the weight loss (WL) method, potentiodynamic polarization (PP), electrochemical impedance spectroscopy (EIS), and scanning electron microscopy (SEM). The inhibition efficiencies in the case of heterocyclic-based inhibitors at the pickling temperatures of 25 and 85ºC were 96 and 83%, respectively, while those in the presence of alkynol-based inhibitors were 95 and 88%. The worse inhibition performance was observed at a relatively high pickling temperature, which is because heterocyclic molecules are thermodynamically unfavorable to adsorb over the steel surfaces at high temperatures. Electrochemical measurements and surface analysis showed that both inhibitors could adsorb over the steel surfaces, slowing down the corrosion of steel sheets in HCl solution and resulting in relatively smooth morphologies, low roughness, and bright whiteness.

Keywords: Corrosion Inhibitors, Corrosion Inhibition, Electrochemical Analysis

1. INTRODUCTION

Carbon steels have been extensively used as the main alloy in many fields because of the overwhelming advantages such as low costs and excellent mechanical strength. However, scales will form while carbon steels are subject to the high-temperature production process, which not only remarkably affects the characteristics in the following applications but also imposes unexpected costs. To remove mineral oxides and mineral scales, a chemical treatment process like acid descaling (pickling) is a common cleaning process in the industry. There are many optional mineral acids for pickling reagents, such as hydrochloric acid (HCl), sulfuric acid (H_2SO_4), nitric acid (HNO_3), phosphoric acid (H_3PO_4), hydrofluoric acid (HF), and organic acids, among which HCl and H_2SO_4 are the most commonly used reagents for the pickling process. The composition of scales is FeO, Fe_3O_4, and Fe_2O_3 (from inside to outside) with different oxygen contents. In the HCl solution, FeO, Fe_3O_4, and Fe_2O_3 can all be dissolved, while only FeO can be dissolved in the H_2SO_4 solution. In addition, the present technology can effectively recycle the used HCl solution for regeneration. Therefore, for economic and environmental considerations, most steel products are pickled with HCl solution.

Although pickling can effectively remove scale, it also leads to problems including poor whiteness of the steel surface, increased roughness, hydrogen embrittlement, pitting corrosion, excessive corrosion of the metal, and so on. To deal with these problems, the corrosion of the base metal should be controlled by a protective method[1-2]. The addition of corrosion inhibitors can not only mitigate the above problems but also reduce the usage and mist of acid. Corrosion inhibitors are mainly organic compounds containing polar functional groups such as amine, aldehyde, ketone, aromatic ring, hydroxide, and so on, for the lone pair of uncoordinated electrons can adsorb on the empty 3d orbital of the metal[3]. By forming an inhibitory film, the inhibitor layer blocks the occurrence of electrochemical reactions, slowing down the possible corrosion reaction.

In terms of the formulation of commercial corrosion inhibitors, the heterocyclic or alkynol compounds are the most common ingredients in the corrosion inhibitor product[4-6]. In addition, nitrogen-included polymers are complementarily used for better inhibition efficiency and thermal stability. In this study, the inhibition performances of two commercial corrosion inhibitors, heterocyclic-based (CI_H) and alkynol-based (CI_A), on

carbon steel corrosion in an HCl solution were investigated. The performance of the corrosion inhibitor was evaluated by methods including weight loss (WL), potentiodynamic polarization (PP), electrochemical impedance spectroscopy (EIS) measurements, and scanning electron microscopy (SEM). To better understand corrosion inhibition under a variety of pickling conditions, the adsorption isotherms of these corrosion inhibitors on carbon steel surfaces in different picking temperatures were obtained based on the WL data.

2. EXPERIMENT METHOD

2.1. Materials

CI_H and CI_A are commercially available pickling inhibitors. The corrosion tests were done by using SPHC samples, which have the following composition: C 0.15%, Mn 0.58%, P 0.05%, S 0.05%, and the balance iron. The size of SPHC sheets goes to 40mm*30mm*2mm.

2.2. WL Experiments

Before doing WL experiments, Steel Plate Heat Commercial (SPHC) was descaled by 10% HCl solution. The cleaned and dried SPHC sheets were accurately weighted with a sensitivity of ±0.1 mg. For the different picking temperatures tests, the cleaned specimens were immersed in 10% HCl solution in the absence and presence of various concentrations of the inhibitors CI_H and CI_A for 30 minutes at 25, 45, 65, and 85°C. At the end of the WL tests, the specimens were taken out, cleaned with water, dried, and reweighted. The inhibition rate (η_1%) was determined by the following equation:

$$\eta_1\% = \frac{\Delta W_0 - \Delta W_1}{\Delta W_0} * 100\%$$

where ΔW_0 and ΔW_1 are the weight loss of SPHC sheets under the absence and presence of corrosion inhibitors pickling process, respectively.

2.3. Electrochemical Measurements

SPHC sheets were abraded by a series of emery papers (#400 to #2000) before electrochemical tests. Using a Gamry interface 1000 containing a frequency response analyzer in a conventional three-electrode system, which was assembled with carbon steel as the working electrode (WE), Pt wire as a counter electrode (CE), and an Ag/AgCl reference electrode (RE). The WE was immersed in 10% HCl solution for 30 minutes at 25°C to reach a relatively steady state and establish open circuit potential (Eocp). Polarization curves were recorded by scanning the potential between ±300 mV vs. Eocp at the scan rate of 1 mV/s. Electrochemical impedance spectroscopy (EIS) measurements were done

at Eocp by superimposing a disturbance sine wave of 5 mV amplitude. The frequency range of EIS measurements was 1.0×10^5 to 1.0×10^{-2} Hz. All the electrochemical experiments were done at 25°C.

Except for WL measurements, the results of polarization curves and EIS measurements can be used to calculate the inhibition rate (η_2%, η_3%) as well. With the following equation:

$$\eta_2\% = \frac{I_1 - I_0}{I_1} * 100\%$$

$$\eta_3\% = \frac{R_1 - R_0}{R_1} * 100\%$$

where I_0 and I_1 are the corrosion current densities without and with inhibitors, R_0 and R_1 are the polarization resistances of inhibited and uninhibited solutions, respectively.

2.4. Surface Analysis

The SPHC sheets after WL experiments (0.05% concentration of each corrosion inhibitor in 10% HCl solution at 85°C for 30 minutes) were used for surface analysis. The images were examined by a JSM-IT100 SEM (x1000, 15.0 kV), colorimeter for the whiteness, and probe-type surface roughness measuring instrument for the roughness.

3. RESULTS AND DISCUSSION

3.1 Pickling Temperature Effect

Table 1 shows the WL results of SPHC sheets in 10% HCl solution in the various concentrations of the inhibitors CI_H and CI_A from 25°C to 85°C. To elucidate the adsorption mode of CI_H and CI_A on the SPHC surface at a variety of pickling temperatures, the equilibrium constant of the adsorption process was calculated using the WL measurements data. To deduce the adsorption isotherm, the surface coverage values were fitted as a function of inhibitor concentration. Langmuir isotherm obeys the following equation:

$$\frac{C}{\theta} = \frac{1}{k} + C$$

where *C* is the inhibitor concentration (g/L), *k* is the adsorptive equilibrium constant (L/g) and θ is the surface coverage.
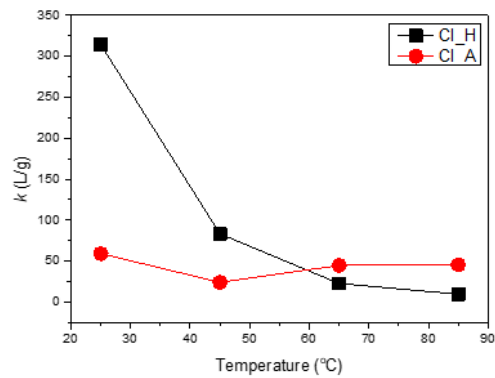
Figure 1 indicates Langmuir adsorption plots for the inhibitors CI_H and CI_A on SPHC sheets at pickling temperatures of 25, 45, 65, and 85°C. As shown in the figure, the values of linear correlation coefficients and slopes are very close to 1, approving the Langmuir mode of adsorption. The values of *k* were calculated from the intercepts of the straight lines and are displayed in Figure 2. The values of *k* for CI_H are higher than CI_A

Table 1 WL results of SPHC sheets in 10% HCl solution in the various concentrations of the inhibitors CI_H and CI_A at 25ºC to 85ºC.

Inhibitor	Concentration (%)	25 ºC	45 ºC	65 ºC	85 ºC
			η (%)		
CI_H	0.05	96.46	94.34	92.69	82.99
	0.1	96.48	94.77	93.27	85.72
	0.25	96.78	95.71	97.15	92.93
CI_A	0.05	95.18	88.35	91.38	88.15
	0.1	95.82	91.91	92.62	89.59
	0.25	97.17	93.97	94.08	90.8
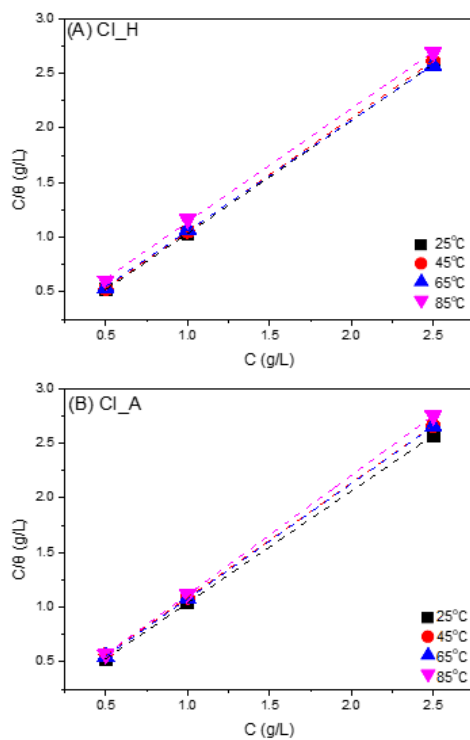
Fig.1. Langmuir adsorption isotherm linear regression for (A) CI_M and (B) CI_A on SPHC surface in 10% HCl solution at 25ºC to 85ºC.

Fig.2. Adsorptive equilibrium constant (k) calculation results of CI_M and CI_A at 25ºC to 85ºC.

hand, since the alkynol molecule has stronger adsorption on metal surfaces, the adsorptive equilibrium constant shows relatively stable at a wide range of pickling temperatures.

3.2 Electrochemical Measurements

Figure 3 shows the obtained Tafel plots for the SPHC electrode at 25ºC in the absence (BK) and the presence of the inhibitors CI_H and CI_A at the concentrations of 0.05% and 0.1%. The corrosion potentials (E_{corr}) and corrosion current densities (I_{corr}) were derived from Tafel curves using the Tafel extrapolation method. The figure shows that the addition of both inhibitors to the acidic solution causes the Tafel curve to shift to more anodic potentials and lower current densities. The calculated inhibition efficiencies (η_2) and the electrochemical parameters are listed in Table 2. The data in Table 2 shows that with the first addition of CI_H and CI_A, the value of I_{corr} decreases from 6.31 to 0.38 and 0.45 mA*cm^{-2}, respectively. The decrease in I_{corr} value is continued regularly with the addition of the inhibitors. The results also show that in all inhibitor concentrations, the values of η_2% for CI_H are larger than those of CI_A, indicating that CI_H is a more efficient corrosion inhibitor for carbon steel in 10% HCl solution at 25ºC.

at low pickling temperatures (25 and 45ºC), indicating that CI_H can be better adsorbed on the SPHC surface and therefore, better inhibit the corrosion reaction. The inhibition efficiencies of CI_H were significantly reduced at high pickling temperatures (65 and 85ºC), as well as the adsorptive equilibrium constant. Discussion from the composition of the inhibitor, CI_H is composed of heterocyclic. The kinetic energy of the molecules increases with the rising temperature, and heterocyclic molecules in solution turn to interact with metal-adsorbed heterocyclic molecules, the desorption leads to the worse inhibitory at high pickling temperature. On the other
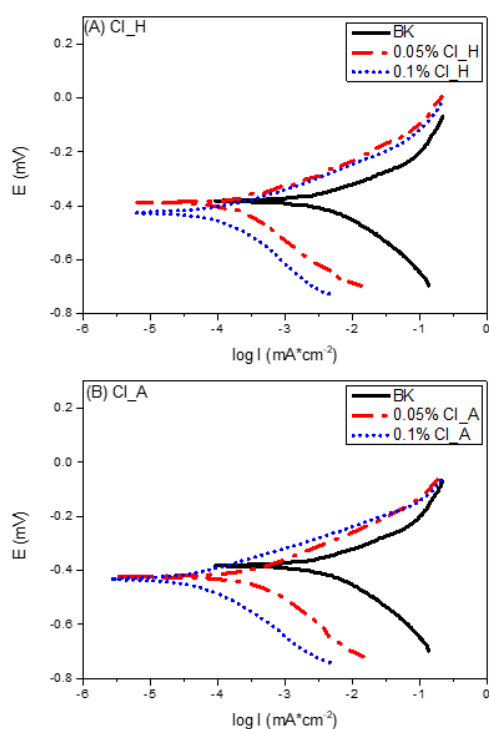
Fig.3. Polarization curves for SPHC sheets electrode in 10% HCl solution without inhibitor (BK) and with different concentrations of (A) CI_M and (B) CI_A with a scan rate of 1 mV/s.

Figure 4 shows the obtained EIS data as Nyquist plots. As seen in Figure 4(A) and (B), the shape of the Nyquist plots was not changed after the inhibitors' addition, indicating that the inhibitors do not alter the mechanism of the corrosion reaction. The figure also shows that with the addition of both inhibitors to the acidic solution, the impedances (Rct) get larger compared to no inhibitor-added acidic solution (BK), this observation can be attributed to the adsorption of inhibitors on the SPHC surface and hindrance of the charge transfer reaction. The inhibition efficiencies (η_3%) and the electrochemical parameters are listed in Table 2 as well. From Table 2, Rct displays an insignificant difference at low concentrations (0.05%) within the two inhibitors. EIS measurements exhibit poorer detection acuity than WL and PP. When the concentration rises to 0.1%, CI_H shows better inhibition efficiency than CI_A, the same trend with WL measurements and polarization curves.
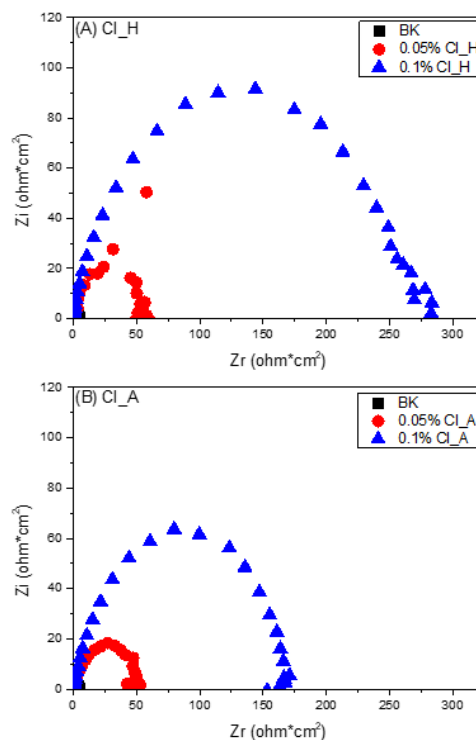

Fig.4. Nyquist plots recorded for SPHC sheets electrode in 10% HCl solution without inhibitor (BK) and with different concentrations of (A) CI_M and (B) CI_A.

Table2 Potentiodynamic polarization, Electrochemical impedance parameters, and WL measurements with the corresponding η% values derived from SPHC sheets in 10% HCl solution at 25ºC in the absence inhibitor (BK) and presence of various concentrations of the inhibitors CI_H and CI_A.

Inhibitor	Concentration (%)	E_{corr} (V)	I_{corr} (mA*cm^{-2})	η^2 (%)	R_{ct} (ohm*cm^2)	η^3 (%)	η^1 (%)
				Electrochemical		**WL**	
BK	-	-0.38	6.31	-	5.00	-	-
CI_H	0.05	-0.38	0.38	93.97	55.00	91.00	96.46
	0.1	-0.43	0.06	99.09	275.00	98.18	96.78
CI_A	0.05	-0.42	0.45	92.92	55.00	91.00	95.18
	0.1	-0.42	0.13	97.96	165.00	96.97	95.82

3.3 Surface Analysis

SEM micrographs of SPHC sheets surface after 30 minutes of immersion in 10% HCl solution at 85ºC without (BK) and with 0.05% CI_H and CI_A are shown in Figure 5. The thoroughly rough surface of SPHC in Figure 5 (A) shows that due to the corrosive attack from the HCl solution, the steel surface is harshly damaged and covered with corrosion products. However, by adding CI_H and CI_A to the corrosive medium, as shown in Figure 5 (B) and (C), the steel surface remained smoother and had fewer holes. Except for the imagined observation, the roughness and whiteness of the surface are also measured, the data shown in Table 3. The surface treated with inhibitor-added acidic solution has the excellent characteristics of low roughness and high whiteness. These observations prove that CI_H and CI_A inhibit the corrosion reaction of steel in HCl solution.

4. CONCLUSIONS

Two different systems of commercial corrosion inhibitors, CI_H (heterocyclic-based) and CI_A (alkynol-based), perform well as inhibitors for SPHC sheets corrosion in 10% HCl solution. CI_H shows better inhibition efficiencies than CI_A at low pickling temperature but worse at high temperature, due to the heterocyclic molecules desorb at the latter easily. The corrosion behavior was inspected by the electrochemical method. The results showed that, compared with the inhibitor-free pickling process, the corrosion current density gets smaller and impedance gets larger with inhibitor-added treatment. At the same time, the surface of SPHC sheets gets smoother morphologies, lower roughness, and better whiteness after the presence of inhibitors CI_H and CI_A. Although both inhibitors can effectively adsorb on the steel surface for corrosion inhibition, the efficiency remains different during the pickling condition. By clarifying these characteristics, we could select the suitable chemicals more precisely for production.
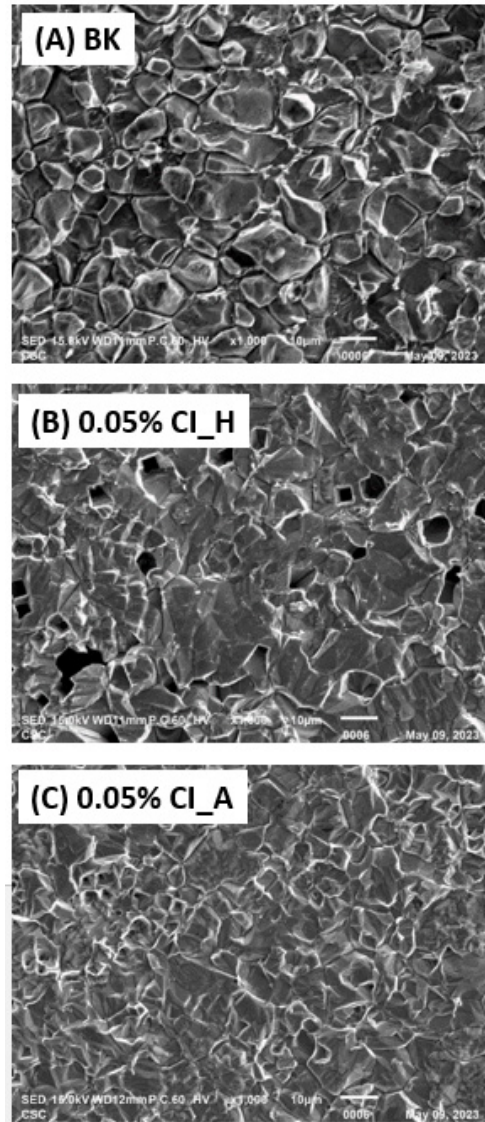

Fig.5. SEM micrographs of SPHC sheets after 30 minutes immersion in 10% HCl solution at 85ºC (A) without inhibitors (BK) and with 0.05% of (B) CI_M and (C) CI_A.

Table 3 Roughness and whiteness results of SPHC sheets in 10% HCl solution at 85ºC in the absence of inhibitor (BK) and presence of 0.05% inhibitors CI_H and CI_A.

Inhibitor	Roughness		whiteness
	Ra (μm)	Rz (μm)	L
BK	0.47	2.45	53.15
0.05% CI_H	0.26	1.40	62.39
0.05% CI_A	0.23	1.36	63.46

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