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Gravimetric, electrochemical and surface studies on the anticorrosive properties of 1-(2-pyridyl)-2-thiourea and 2-(imidazol-2-yl)-pyridine for mild steel in hydrochloric acid

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Abstract: The 1-(2-pyridyl)-2-thiourea (TP) and 2-(imidazol-2-yl)-pyridine (IP) are described here for the first time as inhibitors for mild steel in acid medium based on investigations with weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The experimental results revealed that 1-(2-pyridyl)-2-thiourea and 2-(imidazol-2-yl)-pyridine are effective corrosion inhibitors for mild steel in acid medium, and their maximum corrosion inhibition efficiency at 4×10^4 M are 93.57% and 96.66%, respectively. TP and IP are determined as mixed-type inhibitors based on polarization studies, and their adsorption on mild steel surface follows Langmuir adsorption isotherm and physical adsorption is dominant. The formation and characteristic of protective layer on the steel surface were verified from their spectra of scanning electrochemical microscope (SECM), UV-visible, FT-IR and X-ray photoelectron spectroscopy (XPS) methods. Besides, the correlation between inhibition efficiency and molecular structure of inhibitor was theoretically studied via quantum chemical calculations.

Introduction

Mild steel is widely used in multitudinous industrial fields due to its excellent mechanical properties, easy availability and low price. As acidic solutions are widely used in various industrial processes, such as acid pickling, acid cleaning, acid descaling and oil well acidification, anticorrosion of mild steel in acid solutions is required.¹⁻³ Otherwise, the mild steel corrosion caused by acid solutions will induce huge economic losses and serious environmental pollution. Corrosion inhibitors are widely appreciated in the field of mild steel protection because of their excellent inhibition efficiency and considerable economic benefit. Accordingly, various corrosion inhibitors have been developed for the protection of mild steel in acid medium, which are usually organic heterocyclic compounds containing high electronegativity atoms, such as nitrogen, oxygen, sulfur and phosphorus, unsaturated bonds or a large conjugation system.⁴⁻⁷ For example, azoles,⁸ Schiff bases,⁹ quinolines,¹⁰ thiourea derivatives¹¹ and pyrimidines¹² have been reported as effective corrosion inhibitors for mild steel in hydrochloric acid solutions. Nevertheless, corrosion scientists are not very comfortable with corrosion inhibitors as they are usually not readily available, expensive, or water-insoluble. Recently, pyridine-type mild steel corrosion inhibitors have attracted increasing attention due to their properties of facile synthesis, water-soluble, low cost and high inhibition efficiency. Verma investigated the corrosion inhibition

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inhibitors a high priority.

behaviors of three chromenopyridines for mild steel in 1 M HCl solution and found that their inhibition ability was obviously enhanced with polar groups on the chromenopyridine ring, in which the inhibition efficiency of the functional groups in the preferential order of $-OH > -NO_2$.⁵ The result is in good agreement with reports in the literature that organic inhibitors with polar functional groups can be easily adsorbed on the metal surface and cause stronger corrosion inhibition capability.4,13 Elmsellem studied the corrosion inhibition performance of 2,6-bis-(hydroxy)-pyridine and diethyl 1,1'-(pyridine-2,6-diyl)bis(5-methyl-1H-pyrazol2-3-carboxylate for mild steel in 1 M HCl solution and found that corrosion inhibition occurs due to the adsorption of inhibitors on steel surface, and the differences in the inhibitive properties were attributed to the different molecular structures of inhibitors.⁷ Various researches on the use of corrosion inhibitors help to narrow the gap between anticorrosion experiments and practical mild steel protection. However, pursuing practical corrosion inhibitors is still at its early stages and further research is needed to fully understand the role that corrosion inhibitors play. Various different corrosion inhibitors are required to search for more practical corrosion inhibitors, which make the development of new mild steel corrosion

In this paper, 1-(2-pyridyl)-2-thiourea (TP) and 2-(imidazol-2-yl)-pyridine (IP) were smoothly synthesized from readily available starting materials, and their inhibition effect on the corrosion behavior of mild steel in 1 M HCl solution was investigated by means of weight loss test, potentiodynamic polarization measurement and electrochemical impedance spectroscopy (EIS). Surface analysis of scanning

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electrochemical microscope (SECM), UV–visible, FT-IR spectroscopy and X-ray photoelectron spectroscopy (XPS) were also used to confirm the formation and characteristic of protective film on steel surface in presence of inhibitor. Several quantum chemical calculations have been conducted to correlate the inhibition efficiency and mechanisms with the molecular properties of TP and IP compounds. Moreover, the mechanism of corrosion inhibition on mild steel surface in hydrochloric acid solution by TP and IP was proposed.

Experimental

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Inhibitor synthesis and characterization

As shown in Fig. 1, 1-(2-pyridyl)-2-thiourea (TP) inhibitor was synthesized in our laboratory and 2-(imidazol-2-yl)-pyridine (IP) was synthesized following the reported procedure in the literature (Fig. 1).¹⁴ The molecular structures of the inhibitors were confirmed by 1H NMR and FTIR spectroscopic, and the characterization data were shown as below:

TP, yield: 64%; mp: 146-148°C; ¹H NMR (400 MHz, d_6 -DMSO): δ /ppm = 10.56 (d, J=22.5Hz, 2H), 8.88 (s, 1H), 8.23 (d, J=4.0Hz, 1H), 7.76 (t, J=7.4Hz, 1H), 7.16 (d, J=8.3Hz, 1H), 7.03 (m, 1H); ¹³C NMR (100 MHz, d_6 -DMSO): δ /ppm =174.8, 158.6, 148.2, 138.3, 113.3, 109.9; IR (film) v_{max} : 3225, 3079, 1594, 1538, 1435, 1331, 1233, 1151, 1076, 1042, 995, 821, 767, 679 cm⁻¹. IP, yield: 92%; mp: 135-136°C; ¹H NMR (400 MHz, d_6 -DMSO): δ /ppm = 12.79 (s, 1H), 8.59 (d, J=4.8Hz, 1H), 8.04 (d, J=7.9Hz, 1H), 7.87 (t, J=7.7Hz, 1H), 7.35 (m, 1H), 7.16 (s, 2H); ¹³C NMR (100 MHz, d_6 -DMSO): δ /ppm =166.2, 155.1, 149.3, 137.2, 127.8, 124.2, 120.8; IR (film) v_{max} : 3314, 3048, 1598, 1483, 1462, 1418, 1386, 1142, 1113, 996, 957, 786, 736, 706 cm⁻¹.

Electrode and electrolytes

The experimental material for mild steel with chemical composition (wt.%): 0.047 C, 0.020 Si, 0.14 Mn, 0.025 P, 0.005 S and balance Fe. The dimensions of mild steel strips for electrochemical and surface analysis experiments were mechanically cut into $2.5 \times 0.5 \times 0.5$ cm and $0.5 \times 0.5 \times 0.05$ cm, respectively. For electrochemical experiment, the working electrode was embedded in epoxy resin with an exposed area of 0.25 cm². Prior to all the measurement, the strips were polished using SiC abrasive papers with different grades (400, 800, 1000 and 1200), degreased with acetone and washed with ethanol, then dried at room temperature. Analytical grade 37% HCl and ultrapure water were used for the



Figure 1 Synthetic route of the studied TP and IP

preparation of 1 M HCl corrosion test solutions. The concentration of 1-(2-pyridyl)-2-thiourea and 2-(imidazol-2-yl)-pyridine ranged from 1×10^{-4} M to 4×10^{-4} M in 1 M HCl solution. The solubility of TP and IP in 1 M HCl solution is 104 mg/ml and 241mg/ml, respectively.

Weight loss experiments

The steel specimens with a size of $1.0 \times 1.0 \times 0.1$ cm were immersed in glass beakers containing 100 ml 1 M HCl solution without and with different concentrations of TP and IP inhibitors at ambient temperature [(25±0.1) °C] for 24 h. After soaking, the specimens were removed from the test solutions, carefully rinsed the surface of the test piece with deionized water, dried under nitrogen and then re-weighed. Each group of samples was repeated three times under the same conditions, and the standard deviation values of weight loss results were less than 5% (Fig. 2), indicating that the reproducibility of the experiment is acceptable. The corrosion rate (v) and inhibition efficiency (η_w) were calculated by the average weight loss of three parallel specimens.^{13,15} In addition, weight loss tests were also carried out for mild steel in 1 M HCl in absence and presence of 4 \times 10 $^{\rm -4}$ M TP and IP at different temperatures from 25 °C to 55 °C.

Electrochemical measurement

Electrochemical tests were performed by CHI 760E electrochemical analyzer with a conventional three-electrode system including working electrode (0.25 cm² working area was exposed), auxiliary electrode (platinum plate with 1 cm² surface area) and reference electrode (saturated calomel electrode). All the potentials in this paper were referred to saturated calomel electrode (SCE). To obtain a stable working surface, the working electrode was immersed in test solution at open-circuit potential (OCP) for 0.5 h before measurement. The potentiodynamic polarization curves were measured in potential range from -550 to -150 mV (vs. SCE) with a scan rate of 1 mV s⁻¹. EIS measurement was performed at E_{OCP} in a frequency range from 100 kHz to 100 mHz and the amplitude was 5 mV. The corresponding EIS parameters and the appropriate equivalent circuit can be obtained by fitting the experimental results with ZSimpWin software. All the electrochemical tests were carried out under air atmosphere without stirring and the test temperature was controlled by thermostatic water bath.

Scanning electrochemical microscopy (SECM)

Scanning electrochemical microscope (CHI900C) uses a fourelectrode system: 25 μ m platinum ultra-microelectrode as the probe, working electrode (mild steel), Ag/AgCl/KCl (saturated) reference electrode and platinum counter electrode. The area of surface scanning was 600 μ m × 600 μ m, the distance between probe and substrate was 25 μ m. The probe tip potential was 0.6 V vs. the reference electrode. Before the test, the platinum probe was polished with Al₂O₃ powder with a particle size of 0.05 μ m and then washed with ultrapure water.

UV-visible and FT-IR spectroscopy analysis

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UV-vis Spectrophotometer (Perkin Elmer, Lambda 25) was employed to confirm the Inh-Fe complex formed between inhibitor molecules with mild steel. The absorption spectra of corrosion inhibitors before and after 24 h immersion in 1M HCI for steel were recorded and hydrochloric acid was used as blank control. FT-IR spectrum was performed with Nicolet 700 FT-IR spectrometer with ranging from 4000 to 400 cm⁻¹. The absorption spectrum was recorded from the mild steel surface without and with 4×10^{-4} M pyridine derivatives inhibitors after 24 h immersion in 1 M HCl solution at ambient temperature (~25 °C).

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) spectra were recorded by a Thermo VG Scientific ESCALAB 250 spectrometer with a monochromatic Mg K α X-ray source (1486.6 eV) and an X-ray beam of around 1 mm. The binding energy of the C 1s peak at 285.0 eV was used as internal reference.¹⁶ The XPS analyses were deconvolved using a nonlinear least squares curve-fitting program (XPSPEAK software, Version 4.1) with a Gaussian/Lorentzian product function. XPS spectra were practiced on protected mild steel surface with IP after 24 h of immersion in 1 M HCl solution at 25 °C.

Quantum chemical calculations

All the quantum chemical calculations were performed by density function theory (DFT) with B3LYP/6-31G(d, p) level within Gaussian 09 program package. The quantum chemical parameters of studied inhibitor molecules were calculated, including the lowest unoccupied molecular orbital energy (E_{LUMO}), the highest occupied molecular orbital energy (E_{LUMO}), the highest occupied molecular orbital energy (E_{LUMO}), the highest occupied molecular orbital energy (E_{LUMO}), energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$), fraction of electrons transferred (ΔN) and Mülliken charges. Besides, the condensed Fukui functions ($f(r)^-$: electrophilic attack, $f(r)^+$: nucleophilic attack) have been also computed using the natural population analysis on the system with N, N+1 and N-1 electrons.

Results and discussion

Weight loss study

Weight loss method was often used to evaluate the corrosion inhibition performance of organic corrosion inhibitors as the simple monitoring method and high reliability. Fig. 2 shows the corrosion rate (v) and inhibition efficiency (η_w) of steel in 1 M HCl in the presence of different concentrations of TP and IP at 25 °C. The v and η_w were obtained from the following equations:

$$v = \frac{W_1 - W_2}{s \times t} \tag{1}$$

$$\eta_w = \frac{v_o - v}{v_o} \times 100\% \qquad (2)$$

where v is corrosion rate, W_1 and W_2 (mg) are the steel sample weight before and after immersion, s (cm²) is the exposed area of steel specimens, t (h) is immersion time, v_0 and v indicate corrosion rate in absence and presence of inhibitors, respectively. It can be clearly seen from Fig. 2 that the v values





Figure 2 Variation of corrosion rate(a) and inhibition efficiency(b) with different concentrations of pyridine derivatives by weight loss. Error bars ($_{T}$) represent the standard deviations (%).

of mild steel decreased significantly and the η_w values increased with the addition of inhibitor. At 4 \times 10 $^{-4}$ M, the maximum η_w values of TP and IP were 93.57% and 96.66%, respectively, indicating that the presence of TP and IP inhibitor could effectively inhibit the corrosion of steel in 1 M HCl, and the η_w was related to the mount of inhibitor molecules adsorbed on metal surface. In addition, the values of v followed the order: v(TP) > v(IP) at any given inhibitor concentration, revealing that the molecular structure of inhibitor affected the adsorption property of organic molecules on steel surface. It could be explained that the strong conjugation between imidazolyl and pyridine ring significantly promotes the adsorption of imidazole group, so IP will have greater surface coverage and more adsorption active centers on steel surface, thereby increasing the η_w . The mechanism of the adsorption between the inhibitor molecules and the metal surface will be further elucidated in the following Section, Mechanism of corrosion inhibition.

Effect of temperature on inhibitive performances of TP and IP

Weight loss measurements at different temperature provide more detailed insights into the kinetics and thermodynamics of metal corrosion in aqueous solutions. Corrosion rate (v) and inhibition efficiency (η_w) obtained from weight loss measurements at different temperatures (25-55°C) are presented in Table 1. As showed in Table 1, the values of v increased with increase of temperature in both uninhibited and inhibited solutions, which is due to desorption of initially adsorbed inhibitor molecules, resulting in exposure of greater surface area of metal to corrosive medium leads to

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and IP	at different to	emperatures.			
т	С	ТР		IP	
(°C)	(10 ⁻⁴ M)				
		v	η_w	ν η _w	
		(mg cm ⁻² h ⁻¹)	(%)	$(mg cm^{-2} h^{-1})$ (%)	
25	Blank	15.910±0.082	-	15.910±0.082 -	
	1	4.240±0.035	73.35	3.441±0.023 78.37	7
	2	2.231±0.037	85.98	1.542±0.015 90.31	L
	3	1.262±0.015	92.07	0.789±0.017 95.04	ŧ
	4	1.023±0.021	93.57	0.531±0.016 96.66	5
35	Blank	19.172±0.067	-	19.172±0.067 -	
	1	5.719±0.043	70.17	4.479±0.025 76.64	ŧ
	2	3.315±0.014	82.71	2.605±0.037 86.41	L
	3	2.410±0.056	87.43	1.576±0.019 91.78	3
	4	1.858±0.023	90.31	0.980±0.016 94.89)
45	Blank	25.810±0.045	-	25.810±0.045 -	
	1	8.479±0.032	67.15	6.804±0.021 73.64	ŧ
	2	5.415±0.012	79.02	4.210±0.032 83.69)
	3	3.985±0.062	84.56	3.002±0.041 88.37	7
	4	3.404±0.024	86.81	1.907±0.034 92.61	L
55	Blank	41.465±0.033	-	41.465±0.033 -	
	1	15.089±0.042	63.61	12.033±0.028 70.98	3
	2	9.313±0.011	77.54	8.231±0.019 80.15	5
	3	7.045±0.026	83.01	6.124±0.022 85.23	3
	4	6.282±0.022	84.85	3.782±0.013 90.88	3
					_

Table1 Weight loss results of mild steel in 1 M HCl with different concentrations of TP

decrease in efficiency of the inhibitors at high temperatures. That is to say, TP and IP are temperature-dependent corrosion inhibitors. In addition, it can be seen that the inhibition efficiency of IP is still higher than TP in the studied temperature range.

Kinetic parameters

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To gain a better understanding of the inhibition mechanism affected by temperature on corrosion inhibition, the kinetic analysis of mild steel in 1 M HCl in absence and presence of 4×10^{-4} M TP and IP at different temperatures from 25 °C to 55 °C was studied. The activation energy (E_a) of the corrosion process can be obtained by Arrhenius Eq. (3):

$$\ln v_{\rm corr} = \ln A - \frac{E_a}{RT}$$
(3)

where v_{corr} represents the rate of corrosion, *R* is the gas constant, *T* is the absolute temperature and *A* is the pre-exponential factor. Fig. 3 shows the Arrhenius plots for steel in 1 M HCl in the absence and



Figure 3 Arrhenius plots of Inv_{corr} vs. 1/T for steel in 1 M HCl in the absence and presence of inhibitors.



Figure 4 Arrhenius plots of $ln(v_{corr} /T)$ vs. 1/T for steel in 1 M HCl in the absence and presence of inhibitors.

presence of inhibitors. E_a values calculated from the slopes of straight lines are shown in Table 2. As depicted in Table 2, all the regression coefficients are almost close to unity, indicating that the corrosion of mild steel in 1 M HCl solution can be using the kinetic model. The values of E_a in presence of two inhibitors are higher than that for the uninhibited solution, it may be correlated with the existence of physical adsorption phenomenon by forming an adsorptive film of an electrostatic character on mild steel surface, which has been reported in the literatures.^{3,8}

The enthalpy and entropy of activation $(\Delta H^*, \Delta S^*)$ of the process was calculated from transition state Eq. (4) which listed in Table 2:

$$\frac{v_{\rm corr}}{T} = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right)$$
(4)

where *h* is Planck's constant and *N* is Avogadro's number. The plot of $\ln(v_{corr} /T)$ vs. 1/T for steel in 1 M HCl in the presence and absence of inhibitors at different temperatures, as shown in Fig. 4. As can be seen from Table 2, the values of ΔH^* were positive, which means that the activation process is an endothermic corrosion process. This has also been reported to be indicative of retarded dissolution of metal in inhibitor-containing solution.⁸ Therefore, the values of ΔH^* obtained in the present study (Table 2) indicate that mild steel dissolution is an endothermic process and was retarded by the inhibitors. The values of ΔS^* were lower for the uninhibited solution than that for the inhibited one. This might be attributed that the activated complex in the rate-determining step represents an association rather than dissociation step, meaning that decrease in disordering takes place on going from reactants to the activated complex, similar results have been reported elsewhere.^{3,8}

Adsorption isotherms

Adsorption isotherms can provide information on the adsorption behavior of inhibitor molecules on metal surface. Most organic

Table 2 Activation parameters for the steel dissolution in 1M HCl in the absence and the presence of inhibitors at 4×10^{-4} M.								
Inhibitors	R ²	E _a (kJ mol ⁻¹)	<i>∆H*</i> (kJ mol ⁻¹)	ΔS^* (J mol ⁻¹ K ⁻¹)				
Blank	0.997	44.99	42.40	-80.35				
TP	0.999	68.23	65.94	-23.73				
IP	0.998	72.59	70.00	-15.69				

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Figure 5 Langmuir adsorption isotherm of the inhibitors in 1 M HCl solution with different concentrations of TP and IP.

inhibitors act by adsorption on the metal surface, depending on the nature of the interaction between the inhibitor molecule and the metal surface, which contains two main modes: (a) electrostatic interaction between the charged molecules and the charged metal (physisorption) and (b) formation of coordinate bond between the molecules with unshared electron pairs and/or π -electrons and the iron with vacant d-orbital (chemisorption). Several adsorption isotherms including Frumkin, Langmuir, Temkin and Freundlich were deduced by fitting the surface coverage as a function of the concentration of two inhibitors at 25 °C. The Langmuir isotherm was found to be the most suitable model to fit the results of weight loss measurements, with linear regression coefficients and slopes close to 1 (Table 3), as shown in Fig. 5, indicating that the experimental data are well described by Langmuir isotherm and exhibit single-layer adsorption characteristic. This kind of isotherm involves the assumption of no interaction between the adsorbed species on the electrode surface.¹⁶ The Langmuir isotherm is given by Eq. (5):

$$\frac{c}{\theta} = \frac{1}{K_{ads}} + c \tag{5}$$

where *c* is inhibitor concentration, ϑ represents the surface coverage and K_{ads} is adsorption equilibrium constant. K_{ads} can be calculated from the intercepts of the straight lines, then the standard adsorption free energy (ΔG^0_{ads}) of the adsorption process associated with K_{ads} can be calculated by the following Eq. (6):

$$\Delta G_{ads}^0 = -RT \ln(55.5K_{ads}) \tag{6}$$

where ΔG^{0}_{ads} is free energy of adsorption, *T* is thermodynamic temperature and *R* represents the gas constant. The

Table 3 Thermodynamic parameters of inhibitors on mild steel surface in 1 M H	Cl
solution.	
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Inhibitors	<i>Т</i> (°С)	R ²	k	ΔG^{0}_{ads}	ΔH^{0}_{ads}	ΔS^{0}_{ads}
				(kJ mol ^{⁻¹})	(kJ mol⁻¹)	(J mol ⁻¹ K ⁻¹)
TP	25	0.999	0.967	-35.11	-6.88	94.73
	35	0.999	1.003	-36.09		94.84
	45	0.999	1.037	-37.08		94.97
	55	0.999	1.046	-37.93		94.66
IP	25	0.999	0.953	-35.64	-9.89	86.28
	35	0.999	0.969	-36.53		86.49
	45	0.999	0.989	-37.44		86.64
	55	0.997	1.001	-38.21		86.34

corresponding results are listed in Table 3. From Table 3, the ΔG^{0}_{ads} values of two inhibitors were -35.11 and -35.64 kJ/mol, respectively. Usually, the inhibitor molecules are mainly adsorbed on the surface of the metal substrate by electrostatic attraction when $|\Delta G^{0}_{ads}|$ is less than 20 kJ/mol, which belongs to physisorption. On the contrary, when $|\Delta G^0_{ads}|$ is above 40 kJ/mol, the absorption of organic molecules on the metal surface accompanied by charge sharing or transfer to form chemical bonds belongs to chemisorption.4,10 As mentioned above, the values of ΔG^0_{ads} for studied TP and IP inhibitor were -35.11 and -35.64 kJ/mol, respectively, denoting that the adsorption of inhibitor molecules on the surface of mild steel is not a single physical adsorption or chemical adsorption, which is the result of two kinds of adsorption interaction. Obviously, pyridine derivatives exist in the form of either neutral or cationic molecules in acidic media. In the form of neutral molecules, the TP and IP can adsorb on mild steel by the formation of coordinate bond between the molecules and Fe atoms. In the form of cationic molecules, the adsorption is predominantly related to the electrostatic interaction between the protonated compounds and mild steel surface negatively charged by the specific adsorption of Cl⁻ ions. Therefore, the adsorption of these compounds involves two modes of interaction. Besides, the absolute values of ΔG^0_{ads} for IP is higher than that of TP, further illustrating that IP has stronger adsorption capacity on the metal surface to produce better corrosion inhibition. However, it is difficult to distinguish between chemisorption and physisorption only based on these criteria, especially when charged species are adsorbed. The possibility of Coulomb interactions between adsorbed cations (protonated form) and specifically adsorbed anions (Cl⁻) can increase the Gibb's energy even if no chemical bond appears.^{16,17} The model of adsorption will be further discussed in the following Section, Adsorption thermodynamic parameters.

Adsorption thermodynamic parameters

Thermodynamic parameters are important to further understand the adsorption process of inhibitor on steel/solution interface. The standard enthalpy (ΔH^0_{ads}) and entropy (ΔS^0_{ads}) of dissolution process could be calculated by Eqs. (7) and (8):

$$\ln K = \frac{\Delta H_{ads}^0}{RT} + B \tag{7}$$

$$\Delta S_{ads}^{0} = \frac{\Delta H_{ads}^{0} - \Delta G_{ads}^{0}}{T} \qquad (8)$$

where B is an integration constant. The fitted line of InK versus 1/T was show in Fig. 6. The values of ΔH^0_{ads} and ΔS^0_{ads} are listed in Table 3. As seen from Table 3, the ΔH^0_{ads} values are negative, which show that the adsorption is an exothermic process. Further, in the exothermic process the physisorption value ΔH^0_{ads} is around -40 kJ mol⁻¹ or less negative, while the value around -100 kJ mol⁻¹ or more negative is associated with chemisorption.² Therefore, the values of ΔH^0_{ads} obtained in this study for TP (-6.88 kJ/mol) and IP (-9.89 kJ/mol) suggest that can be considered physically adsorbed. The positive value of ΔS^0_{ads} can be attributed to the increased randomness at the

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Figure 6 InK vs. 1/T for the corrosion of mild steel in 1 M HCl in the absence and presence of different concentrations of inhibitors.

mild steel/solution interface during the adsorption of inhibitor molecules onto the mild steel surface.² This increase of disorder is due to more water molecules which can be desorbed from the mild steel surface by TP and IP molecules.

Open circuit potential (E_{OCP}) curves

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The variation of open circuit potential (E_{OCP}) of mild steel electrode with time in 1 M HCl solution in absence and presence of inhibitor at 25 °C was shown in Fig. 7. For all cases, the initial potential was









Figure 8 Potentiodynamic polarization curves of mild steel in 1 M HCl solution without and with different concentrations of inhibitors: (a) TP and (b) IP.

moved positive value by time and gradually remains constant, which is similar with the previous reported E_{OCP} -time curves of steel in 1 M HCl.¹² In the presence of inhibitor solutions, the open circuit potential values shifted towards more positive potentials during the immersion, which can be explained by the adsorption of inhibitor on the mild steel. By increasing the concentration of the inhibitor, the shift in E_{OCP} increases in the positive direction, indicating that inhibitor was more active for anodic reactions as compared to cathodic reactions. It took about 20 min to reach the steady state, so we chose the immersion time of 30 min for electrochemical measurements.

Potentiodynamic polarization curves

Fig. 8 shows the polarization curves of mild steel in 1M HCl solution without and with different concentrations of inhibitor TP and IP. The calculated electrochemical parameters such as corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (β_a , β_c), corrosion current density (i_{corr}) as well as inhibition efficiency (η) were summarized in Table 4. The calculation formula of inhibition efficiency was calculated as Eq. (9):

$$\eta(\%) = \frac{i_{\rm corr}^0 - i_{\rm corr}}{i_{\rm corr}^0} \times 100 \qquad (9)$$

where, i_{corr}^0 and i_{corr} represent the corrosion current densities of mild steel in the absence and presence of inhibitor solution,

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Table 4 Polarization curve parameters for the corrosion of mild steel in 1 M HCl	
solution without and with different concentrations of inhibitors.	

Inhibitors	с	Ecorr	i _{corr}	B a	6 c	η
	(mM)	(mV)	(µA cm⁻²)	(mV dec ⁻¹)	(mV dec⁻¹)	(%)
-	Blank	-349	450.9	116.2	-207.4	-
TP	0.10	-328	124.0	74.3	-241.1	72.50
	0.20	-324	75.6	63.2	-251.9	83.23
	0.30	-317	44.2	79.3	-239.1	90.19
	0.40	-314	39.3	70.6	-245.8	91.28
IP	0.10	-347	111.8	42.5	-200.4	75.21
	0.20	-342	57.1	33.2	-226.5	87.34
	0.30	-335	25.8	39.4	-215.1	94.28
	0.40	-323	19.1	34.1	-204.5	95.76

respectively. As can be seen from Fig. 8 that all of the curves shift towards low current density direction after TP and IP inhibitor were added, and the trend is more pronounced at higher inhibitor concentrations. In the presence of inhibitors, the icorr values shown in Table 4 are significantly reduced relative to the blank, and the values of $i_{\rm corr}$ gradually decreased with incremental concentrations, thus increasing the inhibition efficiency. Furthermore, all the cathodic polarization curves were almost parallel and have no significant changes with each other, which suggested the mechanism of hydrogen evolution reaction had not changed, still controlled by active site. The inhibitor molecules firstly absorbed on the electrode surface, merely hinder the active site of hydrogen evolution reaction on the metal surface, so that the available of H^{+} ions on the electrode surface was reduced, while the actual reaction mechanism had not effected. In the anodic domain, a transitional passivity region was observed after adding TP or IP inhibitor. And the current density decreased rapidly with the increase of potential after passing the peak of activity state, which could be due to the dissolution of iron on the electrode surface formed a layer of high resistance and corrosionresistant oxide film based on Fe (II). At higher potentials, the lowest peak of transition passivity followed by an increase in anodic current density, which may be due to the dissolution of the protective film to produce Fe(III) species or the discharge of oxygen by the water molecules.⁴

Simultaneously, it is worth noting that the values of η for two compounds follow the order: TP < IP, and maximum inhibition efficiency reached 91.28% and 95.76%, respectively. As seen in Table 4, the corrosion potential was also positive shift with the maximum displacement at 39 mV which was less than 85 mV compared with the blank, indicating that the investigated TP and IP belonged to mixed-type inhibitors which predominantly suppress the anodic reaction. The similar results of other N/S-heterocyclic compound inhibitors have been reported for the corrosion of mild steel in 1 M HCl solution.¹⁶⁻¹⁸ Another finding from Table 4 was that the values of θ_a and θ_c changed after addition of inhibitor, which indicates that inhibitors have the function of controlling the anodic and cathodic reactions in the corrosion process. In addition, the inhibition efficiency of IP is higher than that of TP at the same concentration, which is consistent with the results obtained by weight-loss method.



Figure 9 Nyquist plots for mild steel in 1 M HCl solution without and with different concentrations of inhibitors: (a) TP and (b) IP

.22 Hz

800 Zr / Ωcm

1000

1200

600

Electrochemical impedance spectroscopy (EIS)

400

200

To further study the steel surface interface changes in presence and absence of corrosion inhibitor, electrochemical impedance measurements were conducted. The Nyquist plots of mild steel in 1 M HCl solution with different concentrations of TP and IP were displayed in Fig. 9. As can be seen from Fig. 9 that in presence of inhibitor the diameter of the capacitive loop increased with increasing TP or IP concentration demonstrate an improvement in charge transfer resistances and inhibition efficiencies. In addition, the imperfect and approximately compressed semi-circle capacitive loops were shown in Nyquist diagram was generally believed to be "dispersion effect" caused.¹⁹⁻²¹ Ordinarily, such phenomenon can be traceable in the roughness of the metal electrode surface and other in-homogeneities of the metal electrode surface. In addition, the diameter of the capacitive loop in presence of inhibitor is larger than that in the uninhibited acidic solution and the diameter of the high frequency loop increases notably with increasing the concentration of inhibitor, which indicates that the corrosion of mild steel in 1 M HCl is retarded by the inhibitor. The corresponding Bode plots are exhibited in Fig. 10. It is apparently seen from Fig.10 that the phase angle of TP and IP have two maximum peaks within the studied frequency range, which means the double-

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Figure 11 Equivalent circuit used to fit the EIS experiment data: (a) without inhibitor and (b) the presence of inhibitor.

layer impedance does not performance ideal capacitive behavior due to the dispersing effect. Besides, the absolute







Figure 13 Equivalent circuit fit for mild steel in the presence of IP at 2×10^{-4} M.

impedance increased significantly as inhibitor concentration increased at low frequency. This is due to the fact that more molecules were adsorbed on the surface of the steel with increasing concentration, and the thicker the adsorption film was, more difficult the charge transport process become. Since

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Table 5 EIS parameters for the corrosion of mild steel in 1 M HCI solution without and with different concentrations of inhibitors.

Inhibitors	с	Rs	C _d	n _d	R _{ct}	C _f	n _f	R _f	ηz
	(10 ⁻⁴ M)	(Ω cm²)	(µF cm ⁻²)		(Ω cm ²)	(µF cm ⁻²)		(Ω cm²)	(%)
-	Blank	0.91±0.03	595±2.32	0.89±0.05	52.4±1.61	-	-	-	-
TP	1	0.73±0.05	318±3.06	0.91±0.07	182.9±3.58	47±1.21	0.87±0.03	26.1±1.92	74.93
	2	1.26±0.04	192±3.21	0.84±0.03	356.9±6.13	34±0.81	0.86±0.02	33.2±1.79	86.57
	3	1.39±0.03	85±1.89	0.87±0.02	593.2±4.52	31±1.02	0.84±0.02	42.9±1.57	91.76
	4	1.84±0.05	84±1.94	0.88±0.02	719.4±7.25	27±0.98	0.83±0.05	45.0±2.21	93.14
IP	1	1.21±0.04	191±2.44	0.89±0.04	228.8±4.48	40±1.13	0.91±0.07	34.8±2.48	80.12
	2	0.76±0.03	125±2.46	0.91±0.06	497.2±3.61	33±1.69	0.88±0.02	43.1±1.63	90.30
	3	0.84±0.05	70±1.71	0.85±0.03	1010.1±7.12	19±0.91	0.88±0.04	57.8±1.49	95.09
	4	0.96±0.04	65±1.36	0.87±0.02	1286.3±8.36	14±0.61	0.86±0.03	40.5±1.42	96.05

Table 6 Comparison of the inhibition efficiency of TP and IP with the literature data as corrosion inhibitors for mild steel in 1 M HCl solution.

Inhibitor	10 ⁻⁴ c (M)	η (%)	Ref.
1-(2-pyridyl)-2-thiourea	4	93.14	This paper
2-(imidazol-2-yl)-pyridine	4	96.05	This paper
3-pyridinecarboxaldehyde thiosemicarbazone	5	90	[28]
3-pyridinecarboxaldehyde-4-phenyl thiosemicarbazide	5	91	[29]
4-pyridinecarboxaldehyde-4-phenylthiosemicarbazide	5	90	[29]
2-hydroxybenzaldehyde-thiosemicarbazone	4	94	[30]
methylthiourea	10	92.4	[31]
phenylthiourea	10	96.8	[31]
thiourea	10	87	[32]
(5-methyl-1-pyridin-2-yl-1H-pyrazol-3-yl)methanol	5	83	[33]
5-methyl-1-pyridin-2-yl-1H-pyrazol-3-carboxylate	5	70	[33]
2-phenylimidazo[1,2-a]pyridine	10	89.0	[22]
2-(mmethoxyphenyl) imidazo[1,2-a]pyrimidine	10	90.8	[22]
2-(3-methyl-1H-pyrazol-5-yl) pyridine	10	86	[34]
2,5-bis(4-pyridyl)-1,3,4-thiadiazole	4	79.2	[35]

the adsorption properties of corrosion inhibitor molecules have profound influence on charge transfer process, constant phase element (CPE) was usually used to optimize the electric double layer capacitance for obtaining more accurate experimental data.^{15,22} The impedance of the CPE (Z_{CPE}) can be calculated by Eq. (10):

$$Z_{\rm CPE} = [Y_0(jw)^n]^{-1}$$
(10)

where Y_0 is the magnitude of the CPE, *j* the imaginary number, ω the angular frequency, and n the phase shift. The CPE_d element was considered to be a double layer capacitance (C_d) model which contained H₂O and other ions adsorbed on steel surface, and CPE_f served as a model for the inhibitor membrane (C_f).^{23,24} The values of C_d and C_f are calculated from Y_0 and n as follows:

$$C = \frac{Y_0(w)^{n-1}}{\sin(n(\pi/2))}$$
(11)

where $w_{max} = 2\pi f_{max}$, and f_{max} is the frequency at the maximum value of the imaginary component of the impedance spectrum.

For the purpose of better analysis of electrochemical impedance characteristics, ZSimpWin software had been utilized to fit the data and the EIS results are simulated by an equivalent circuit revealed in Fig. 11 obtained in accordance with the data fitting curve illustrated in Figs. 12 and 13. The small values of χ^2 (2.42/8.24 × 10⁻⁵) indicates a better fit. The electrochemical parameter R_s is electrolyte resistance, R_{ct} is charge transfer resistance, R_f is membrane resistance, C_d represents double-layer capacitance on the electrochemical impedance parameters obtained by equivalent circuit were listed in Table 5. The inhibition efficiency (η_z) can be calculated by the ac polarization resistance R_g ($R_g = R_f + R_{ct}$) in Eq. (12):

$$\eta_z(\%) = \frac{\left(R_{\rm p} - R_{\rm p}^0\right)}{R_{\rm p}} \times 100$$
 (12)

where R_p^0 and R_p are the ac polarization resistance of steel electrode in the uninhibited and inhibited solutions, respectively. As can be seen from Table 5, the values of R_{ct} rose sharply with increasing the concentration of inhibitor, indicating the corrosion inhibitor TP and IP could effectively inhibit the charge transfer reaction in the protective film.

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Meanwhile, with the increasing concentration of studied inhibitors, the values of $C_{\rm f}$ and $C_{\rm dl}$ were gradually decreased due to the decrease in exposed electrode surface area, local dielectric constant and/or an increase in the thickness of the electric double layer capacitor.²⁵⁻²⁷ It expressed that the corrosion inhibitor molecules instead of water molecules adsorbed on the surface of steel, forming a layer of adsorption film which could prevent the metal matrix and corrosive media contact, then slowing down the corrosion. Furthermore, another diverting discovery we could find in Table 5 was that the value of n were close to unit and didn't show significant fluctuations, which revealed the interface behavior was nearly capacitive and the charge transfer controlled the dissolution mechanism of the steel. Finally, it is worth pointing out that the value of η_{z} calculated by EIS increased with the addition of inhibitor and the maximum $\eta_{\rm w}$ reached 93.14% (TP) and 96.05% (IP) at 4×10^{-4} M, coinciding with that obtained by weight loss and polarization curves studies.

Compared with the earlier studied pyridine and/or thiourea base corrosion inhibitors by EIS method in 1 M HCI was shown in Table 6 (Ref. 22,28-35), TP and IP exhibited better corrosion inhibition behaviour. This phenomenon is related to the steric hindrance effect and the number of heteroatoms in the structure.

SECM experiments

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SECM technique was used to obtain the change of Faraday current distribution on the surface of the substrate by micro-probe to scan at various positions on the substrate surface, thus directly characterizing the morphology and electrochemical activity of the matrix surface. The distance from the tip above the sample is determined by approach curves.^{36,37} When a mild steel electrode was under open circuit potential, the substrate undergoes selfcorrosion reaction resulting in the release of Fe²⁺ ions. The probe potential of 0.60 V can oxidize ferrous ions to Fe³⁺ and be detected at the UME in the generator-collector mode, as shown in Fig. 14.³⁷ The SECM area scans images of mild steel specimens surface in 1 M HCl solution without and with 4 \times 10⁻⁴ M of TP and IP were displayed in Fig. 15. As can be seen from Fig. 15a, multiple current peaks appear in the SECM surface scanning map in acid solution with a maximum value of 5100 nA, indicating faster metal corrosion at these active sites. In addition, the current fluctuations were caused by anodic dissolution on the surface of steel sample. Howbeit, in the presence of corrosion inhibitors (Fig. 15b and c), the current density of the entire scanning surface was distributed uniformly. The current maximum value for TP and IP inhibitors were23 and 11 nA, respectively, which again shows that IP has better inhibitive performance than IP. This is due to the obstacles encountered in the diffusion field around tip to reduce the tip current, indicating that the addition of inhibitor reduced the acid dissolution of mild steel and formed uniform adsorption film. Thus, the above analysis reveals that the adsorption film of pyridine derivatives molecules have formed on metal surface.

UV–Visible and FTIR spectroscopy analysis

To confirm the formation of Inh-Fe complex on steel surface, UV-vis absorption spectra of 1 M HCl solution containing 4 $\times 10^{-4}$ M of



Figure 14 Schematic diagram of SECM tip working in the generator-collector mode.



(b)

(c)

(a)





Figure 15 SECM images of mild steel after immersion in 1 M HCl solution for 1h: (a) Blank, (b) 4×10^{-4} M TP, (c) 4×10^{-4} M IP.

inhibitors (TP and IP) before and after the steel immersion for 24 h were shown in Fig. 16. The absorption spectra of TP and IP before the mild steel immersion display shorter wavelength absorption bands at 226 nm, 263 nm and 251 nm, respectively, attributable to the $\pi \rightarrow \pi^*$ transition of aromatic ring in compounds. And the broadband at around 311 and 283 nm was $n \rightarrow \pi^*$ electron transition duo to the lone pair electrons of N and/or S atom.^{38,39}

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Figure 16 UV-visible spectra of pure inhibitor and pyridine derivatives inhibitors adsorbed on MS surface: (a) TP and (b) IP.

After immersion in a solution containing mild steel for 24 h, it is clearly seen from Fig. 16 that the band at 263 nm has completely disappeared and the maximum band shift of $n \rightarrow \pi^*$ transition was red shifted, which was probably the chargetransfer process from ligand to metal, indicating that N and/or S interacted with Fe to form a complex. At the same time, the absorbance at short wavelength absorption band becomes larger and the absorbance at long wavelength absorption band becomes smaller. Generally speaking, changes in the position of absorbance maximum and/or changes in absorbance values indicated that a complex was formed between two substances in solution, as reported in the literature.^{40,41} Compelling evidence was provided for the possibility of Fe²⁺ and inhibitor forming complex in 1 M HCl solution by these experimental results.

In order to support the complex formation between corrosion inhibitor and steel surface, we analyzed the pure inhibitor and the sample scratched from steel surface by FTIR, the related spectrum was shown in Fig. 17a and b, respectively. It can be seen from Fig. 17 that the FTIR of the protective film formed on steel surface showed all characteristic peaks of thepure inhibitor, as the molecular vibrations moved towards higher or lower wave numbers, possibly due to the formation of inhibitor and Fe^{2+} complex on steel surface. Comparing the FTIR spectrum of pure inhibitor with





Figure 17 FTIR spectrum of pure inhibitor and pyridine derivatives inhibitors adsorbed on MS surface: (a) TP and (b) IP.

adsorptive membrane on steel surface, it can be found that the peaks of stretching vibration at N-H (TP: from 3225 cm⁻¹ to 3266 cm⁻¹; IP: from 3314 cm⁻¹ to 3222 cm⁻¹), C=N (TP: from 1594 cm⁻¹ to 1551 cm⁻¹; IP: from 1598 cm⁻¹ to 1572 cm⁻¹) and C=S (TP: from 1233 cm^{-1} to 1206 cm^{-1}) were shifted significantly, which shows that they were mostly involved in the adsorption process to form coordination bond with Fe atoms.⁴²⁻⁴⁴ In addition, the C = C peaks at 1435 cm⁻¹ and 1479 cm⁻¹ for TP were merged into a broad peak at 1443 cm⁻¹ and the IP peaks at 1462 cm⁻¹ and 1483 cm⁻¹ were merged at 1469 cm⁻¹, suggesting that π electrons of pyridine ring were involved in the inhibitor adsorption process. The above findings clearly illustrated that the functional group of 1-(2-pyridyl)-2-thiourea and 2-(imidazol-2-yl)-pyridine were involved in formation a coordination bond with iron metal, using a solitary pair of electrons on N/S atoms and aromatic π -electrons.

Surface analysis by XPS

In order to confirm the nature of the organic film adsorbed on the steel surface and the adsorption mode of the inhibitor, XPS test was used to investigate the composition of the organic adsorbed layer on the steel surface in 1 M HCl solution in presence of best inhibitor (IP). As shown in Fig. 18a, the XPS spectra with three elements (C 1s, N 1s and Fe 2p) were detected, which give evidence for the

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adsorption of the inhibitor on the mild steel surface. Fig. 18(b-d) shows the high-resolution XPS spectra of the major elements (C 1s, N 1s and Fe 2p3/2) on the protected steel surface. The deconvoluted C 1s spectrum was fitted into three peaks (Fig. 18b). The first peak located at 285.0 eV can be attributed to the C-C, C=C and C-H aromatic bonds, the second peak at 286.3 eV may be associated with the presence of C-N and C=N bonds in the heterocyclic ring. The last peak at higher binding energy (288.6 eV) may be ascribed to C=N⁺ structures, resulting probably from the protonation of the =N- structure in the imidazole ring.^{17,19} As shown in Fig. 18(c), the N 1s spectrum consists of three peaks located at 399.4 eV, 400.7 eV and 401.5 eV, respectively. The first component is attributed to the bonds of C-N and the unprotonated N atoms (=N- structure) in the heterocyclic ring, 10,16 while the second component is mainly ascribed to N-Fe bond due to the coordination of nitrogen in IP ring with the steel surface. Indeed, the N-Fe bond complex can make the peak shift to higher binding energy compared to uncoordinated =N- structure.¹⁰ The last peak at 401.4 eV is probably due to the oxidized nitrogen originating from the protonation of nitrogen in the pyridine and/or imidazole ring, which leads to a positive polarization of the nitrogen atom, and therefore the binding energy is increased.¹⁰ The Fe $2p_{3/2}$ spectrum exhibits three peaks as displayed in Fig. 18(d). The first peak at about 710.9 eV is assigned to ferric compounds, such as Fe₂O₃ (i.e., Fe³⁺ oxide) and FeOOH (i.e., oxyhydroxide). The second peak located at around 713.4 eV indicates the presence of a small concentration of FeCl₃ on the steel surface due to the hydrochloric acid medium, while that appeared at 714.6 eV may be ascribed to the satellite of Fe(III).¹⁶

The results obtained by XPS analysis supports the adsorption of inhibitors on mild surface. Especially, the presence of the nitrogen species on the steel surface indicates that the IP compound can adsorb on steel by physisorption simultaneously accompanied by chemisorption in 1 M HCl, and corroborates the thermodynamic study. Furthermore, the Fe 2p_{3/2} XPS results show that the formation of a stable and insoluble layer (Fe₂O₃, FeOOH) can reduce ions diffusion, and therefore improves the corrosion resistance of mild steel in 1 M HCl medium.

Ouantum chemical calculations

To further study the correlation between the molecular structures of investigated inhibitors and inhibitive effect, quantum chemical calculations are carried out in this work. The donor-acceptor interactions between the inhibitor molecules and iron atoms can be analyzed by Mülliken charges and Fukui indices. Fig.19 shows the strictly optimized molecular structures of TP and IP. Zhang et al. reported that Mülliken charges distribution can be used to analyze the adsorption of inhibitor molecules on the metal surface, and an atom with a large negative charge is easily adsorbed on the metal surface.⁴ In this study, the Mülliken charges of the selected C, N and S atoms for studied inhibitors were calculated with the dates listed in Table 7. As can be clearly found in Table 7, the larger negative atoms are N6, N11, N13 and S17 for TP, N6, N16 and N17 for IP, these atoms are active adsorptive atoms and will donate electrons to the empty d-orbital of Fe atom to form coordination bonds. Thus, the pyridine, imidazole rings and thiourea group act mainly as the adsorption centers of TP and IP molecules on mild steel. In addition, Fukui function was employed to predicting the local site selectivity,

(a)



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(b)

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Figure 19 Optimized structures of TP (a) and IP (b).

and the Fukui function $f(r)^+$ and $f(r)^-$ were related to nucleophilic

Table 7 Mulliken charge, $f(r)^{+}$ and $f(r)^{-}$ for TP and IP.							
Compounds	Atoms	Mulliken	$f(\mathbf{r})^{+}$	<i>f</i> (r) ⁻			
TP	C1	0.486503	0.08802	-0.02451			
	C2	-0.120076	0.00541	0.0295			
	C3	-0.054153	0.08291	0.0324			
	C4	-0.102592	0.10743	0.05906			
	C5	0.09872	0.00488	0.00788			
	N6	-0.443916	0.07626	0.04606			
	N11	-0.577954	-0.01597	0.05354			
	N13	-0.588564	0.05001	0.04721			
	C16	0.32548	0.09242	-0.00801			
	S17	-0.239796	0.23223	0.533			
IP	C1	0.250797	0.13638	-0.00157			
	C2	-0.114908	0.01501	0.07591			
	C3	-0.058391	0.07631	0.00399			
	C4	-0.10043	0.14426	0.11717			
	C5	0.100965	0.00869	0.03314			
	N6	-0.460309	0.09406	0.03659			
	C11	0.072061	0.08403	0.18846			
	C12	0.031937	0.02004	0.0949			
	C15	0.454113	0.00919	0.09647			
	N16	-0.466019	0.08639	0.15996			
	N17	-0.545989	0.04051	0.0815			





(b)

(a)

(b)



Figure 20 HOMOs of two studied inhibitors of TP (a) and IP(b).



Figure 21 LUMOs of two studied inhibitors of TP (a) and IP(b).

attack and electrophilic attack, respectively, which can be calculated by Eqs. (13) and (14): 4

$$f_i(r)^+ = q_i(N+1) - q_i(N)$$
 (13)

$$f_i(r)^- = q_i(N) - q_i(N-1)$$
 (14)

where q_i (N+1), q_i (N) and q_i (N-1) are the charge of atom *i* in cationic, neutral and anionic, respectively. The calculated Fukui indices for the inhibitor are displayed in Table 7. As an extensively

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accepted point of view, the higher the values of $f(r)^+$ and $f(r)^-$ are, the stronger the ability of atom to gain and lose electron, respectively. It can be seen from Table 7, the larger $f(r)^+$ values are found on C4, C16 and S17 atoms for TP, and C1, C4 and N6 for IP, which can accept electrons from steel surface to form backdonating bond. While, the preferred sites for an electrophilic attack are C4, N11 and S17 for TP, and C4, C11 and N16 for IP, which can form coordination bonds by donating electrons to steel surface. Consequently, from the above calculated results, it can be inferable that the most active reaction region in the studied inhibitors should be the pyridine, imidazole ring and thiourea which can both donate and accept electrons to form back-donating bonds and coordinate bonds to realize the adsorption of these inhibitors on steel surface.

The frontier molecular orbitals were useful to study the adsorption activity of inhibitor molecules by electrons distribution. HOMO is often associated with the capacity of a molecule to donate electrons, whereas LUMO represents the ability of the molecule to accept electrons.⁴ Figs. 20 and 21 show the electron density distribution of HOMO and LUMO for TP and IP inhibitor molecules, respectively. For IP the densities of both HOMO and LUMO are on the pyridine and imidazole ring, which means that they could be both the acceptor of the electron and the donor of the electron. That is, the electron transfer occurs when inhibitor molecules interact with the metal surface. For TP, LUMO is located on the pyridine ring and thiourea group, but HOMO absent on the pyridine ring except nitrogen atom, which reveals that the pyridine ring of TP could be mainly accepting electrons instead of donating electrons. Thereby, comparing with TP, it is reasonable to assume that the pyridine ring of IP has additional ability to donate electrons to the empty *d*-orbital of Fe atom to form coordination bonds, which may be the main reason of the inhibition efficiency of IP is higher than that of TP. The values of quantum chemical parameters (E_{HOMO} , E_{LUMO} and ΔE) were calculated and listed in Table 8. Where, E_{HOMO} and E_{LUMO} are related to the capability of inhibitor molecules to donate electrons and accept electrons, respectively.³² As reported previously, the higher the values of E_{HOMO} are, the more likely of the molecule to donate electrons. On the contrary, the lower the values of E_{LUMO} are, the stronger the abilities of inhibitor molecule to accept electrons.^{4,32} It is clear in Table 8 that the E_{HOMO} values obey the order of $E_{HOMO,IP} > E_{HOMO,TP} >$, which is consistent with the inhibition efficiency order of η (IP) > η (TP). Thus, there is a good correlation between the η and E_{HOMO} . However, the E_{LUMO} values obey the order of $E_{LUMO,TP} < E_{LUMO,IP}$, which disagree with the inhibition efficiency obtained from experimental results. This result is usually interpreted as having complex interactions that may play a crucial role in the adsorption process. Another important parameter in Table 8 is the separation energy ($\Delta E = E_{LUMO} - E_{HOMO}$), that usually varies with the reactivity of the inhibitor molecule towards its adsorption on metallic surface. Usually, if ΔE decreases, the reactivity of inhibitor molecules is enhanced, and more easily adsorbed on steel surface. As showed in Table 8, the ΔE values follow the order of $\Delta E_{TP} > \Delta E_{IP}$, which indicated that the adsorption of IP on steel surface is the most stable and has a higher corrosion inhibition performance, and corroborates the experiment results.

Calculating electrons fraction transferred from inhibitor molecule to a metal surface can also analyze the relationship between corrosion inhibition and molecular structure, to determine

Table 8 The calculated quantum chemical parameters for TP and IP.								
Compounds	Е _{номо} (eV)	E _{LUMO} (eV)	<i>ΔΕ</i> (eV)	ΔN	μ(D)			
TP	-5.84	-1.02	4.82	0.74	5.31			
IP	-5.42	-0.91	4.51	0.85	4.92			

the adsorption capacity on the metal surface. According to Pearson theory, the fraction of electrons transferred to the metal surface is calculated as Eq. (15):⁴

$$\Delta N = \frac{\chi_{\rm Fe} - \chi_{\rm inh}}{2(\eta_{\rm Fe} + \eta_{\rm inh})}$$
(15)

where χ is absolute electronegativity and η is global hardness, which are given by Eqs. (16) and (17):

$$\chi = \frac{-E_{HOMO} - E_{LUMO}}{2} \tag{16}$$

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2} \tag{17}$$

For Fe, the theoretical values of $\chi_{\rm Fe}$ and $\eta_{\rm Fe}$ are 7 and 0 eV mol⁻¹, respectively. According to previous reports, if $\Delta N < 3.6$, the inhibition efficiency increases with the increase in electron-donating ability to the metal surface.³² In the present study, it can be clearly found in Table 8 that the ability to donate electrons to the metal surface follows the order of $\Delta N_{\rm IP} > \Delta N_{\rm TP}$, which is also in agreement with the experimental results of weightlessness and electrochemical studies (see Tables 1 and 4).

Besides, there's another calculated parameter in Table 8, μ , which has been considered as a significant index to associate with the inhibition efficiency. The large value of dipole moment probably increases the inhibitor adsorption through electronic force.⁴⁵ In Table 8, μ (TP) > μ (IP), while η (TP) < η (IP), which indicates that the better inhibitive performance of IP would not be arisen from intermolecular electrostatic force.

Mechanism of corrosion inhibition

The corrosion inhibition mechanism of organic inhibitor on metal surface has received extensive attention in the literature.^{10,42} It's generally believed that these compounds are adsorbed on metal surface, suppressing anode and cathode reactions to avoid further corrosion of the metal. Therefore, the corrosion mechanism of steel in HCl solution can be explained by adsorption theory, and a plausible mechanism of adsorption model was proposed in Fig. 22.

In hydrochloric acid solution, the steel will form several tiny corrosive batteries that cause electrochemical corrosion. The dissolution of iron at the anode was given as:

$$Fe + Cl^- \rightleftharpoons (FeCl^-)_{ads}$$
 (18)

$$(\text{FeCl}^-)_{ads} \rightleftharpoons (\text{FeCl})_{ads} + e^-$$
 (19)

$$(\text{FeCl})_{\text{ads}} \rightarrow (\text{FeCl}^+) + e^-$$
 (20)

$$\operatorname{FeCl}^+ \rightleftharpoons \operatorname{Fe}^{2+} + \operatorname{Cl}^-$$
 (21)

Generally, chloride ions in the corrosive medium should be preferentially adsorbed on the positively charged metal

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Figure 22 Schematic illustration of the adsorption mechanism of inhibitor on mild steel surface in 1 M HCI solution.

surface in virtue of its hydration degree.^{46,47} Besides, the TP and IP molecules can form cationic species in acidic medium, which will be in equilibrium with the corresponding neutral form by the following equation:

Inł

$$h + xH^+ \leftrightarrow (InhH)^{x+}$$
 (22)

Therefore, the protonated inhibitor can be electrostatically adsorbed on the surface of negatively charged mild steel due to the specific adsorption of Cl⁻ anions (physical adsorption) and formed a protective layer (FeCl⁻InhH⁺)_{ads}, namely, protonated organic compounds have produced synergistic effect with Cl⁻, then the anodic dissolution reaction of iron is prevented. Thus, it can be concluded that the reaction pathway in the presence of inhibitor appears to form a protective layer (FeCl⁻InhH⁺)_{ads} by electrostatic action rather than steps 18-21. The hydrogen evolution reaction occurs at the cathode could be shown as follows:

$$Fe + H^+ \rightleftharpoons (FeH^+)_{ads}$$
 (23)

$$(\text{FeH}^+)_{ads} + e^- \rightarrow (\text{FeH})_{ads}$$
 (24)

 $(FeH)_{ads} + H^+ + e^- \rightarrow Fe + H_2$ (25)

In hydrochloric acid solution, the protonated inhibitors are also adsorbed at the cathodic sites of mild steel, competing with H^{\star} for electrons to reduce the evolution of H_2 without affecting the hydrogen evolution mechanism.

Apart from physisorption, chemisorption process can occur through the displacement of water molecules from the metal/solution interface and the free electron pairs of N, S heteroatoms and/or π electrons of inhibitor molecule with the unoccupied d-orbital of iron atoms will form coordination bonds. Also, the excess negative charge accumulated on metal surface can be transferred from the d-orbit of Fe to the empty π^* orbital of inhibitor molecules (retro-donation), thus enhancing the adsorption of inhibitor molecule on steel surface.⁴⁸ In addition, the non-polar groups in the molecule may be tiled on metal surface to form a relatively complete hydrophobic protective layer. Thus, a barrier between acid solution and metal was formed to prevent the diffusion of iron from the corrosion product into solution and the solution of H^{+} shift to the metal corrosion reaction process, then reducing the rate of metal corrosion process. Besides the above reaction, TP and IP may undergo chelation reaction with Fe²⁴ generated by the dissolution of steel in acid solution (Fig. 22). It can be reasonably speculated, the N and S atoms in inhibitor molecule can coordinate with Fe(II) species to form stable chelates that were deposited on the active sites of steel

surface, and the N and/or S atoms in inhibitor molecule that have been adsorbed on the metal surface were not coordinate with iron atoms can also chelated with Fe(II) species.^{16,33} Thus, the stability and compactness of the adsorption film on the metal surface were improved and the corrosion of steel was effectively prevented from acid solution. Based on above analysis, it can be concluded that the adsorption process first occurs physical adsorption, followed by chemical adsorption, and the large negative values of ΔG_{ads} also indicate that the adsorption of TP and IP molecules were mainly chemically adsorbed in the present study.

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Conclusions

1-(2-Pyridyl)-2-thiourea (TP) and 2-(imidazol-2-yl)-pyridine (IP) have been synthesized and their corrosion inhibitions for mild steel in 1 M HCl solution have been investigated. The main conclusions can be drawn as follows:

- (1) TP and IP were effective corrosion inhibitors for mild steel corrosion in 1 M HCl. Their inhibition efficiency increased with the increase of inhibitor concentration, in which the corrosion inhibition performance of IP was better than that of TP.
- (2) Tafel polarization data showed that TP and IP belonged to mixed-type inhibitors, which predominantly suppressed the anodic reaction. EIS measurements revealed that the values of R_{ct} increased in presence of pyridine derivatives due to the adsorption of inhibitors at the electrode/solution interface.
- (3) The adsorption of TP and IP on mild steel surface follows Langmuir adsorption isotherm and the calculated thermodynamic parameters suggest the adsorption is mainly the physisorption.
- (4) The SECM, UV-visible, FT-IR and XPS analysis showed that the adsorption film of TP and IP was formed on metal surface.
- (5) Quantum chemistry calculation results showed that the pyridine, imidazole rings and thiourea group in the studied inhibitors will play an important role in donating and/or accepting electrons to form back-donating bonds and coordination bonds for the adsorption of these inhibitors on mild steel surface. There is a good correlation between inhibition efficiency and the quantum parameters of E_{HOMO} , ΔE and ΔN .

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Table of contents entry



The 1-(2-pyridyl)-2-thiourea and 2-(imidazol-2-yl)-pyridine is described here for the first time as an inhibitor for mild steel in acid medium.