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One derivate of Thiadiazole（MTYDBH）as Corrosion Inhibitors for Copper in 3.5% NaCl Solution Under Various Conditions

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Corrosion of copper in 3.5% NaCl solutions and its inhibition by MTYDBH have been studied using weight loss test and various electrochemical techniques. Weight loss measurement gave an inhibition efficiency of about 99.07% with 100mg/L MTYDBH present. Potentiodynamic polarzation measurements showed that the present of MTYDBH in 3.5%NaCl solutions decrease corrosion currents and slightly shifts the corrosion potional in a positive direction. EIS measyrements were used to investigate the mechanism of corrosion inhibition. The corrosion resistance of copper with inhibitors under alkaline conditions is better than that under near neutral or conditions acidic and the order is alkaline > neutral > acidic. The electronic properties such as the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) energy levels, and molecular orbital densities were computed.

Keywords: Copper corrosion; Corrosion inhibitors; electrochemical techniques; 3.5%NaCl solution

1. INTRODUCTION

Due to its high electrical and thermal conductivity, good mechanical workability and relatively noble properties, copper has been one of the most important materials in industry. It is used as substitute of carbon steel widely used in indutry such as pipelines for domestic and industrial water utilities including sea water, heat conductors, heat exchangers[1]. However, due to the vast amount of chemical substance especially the high concentration of Cl^-, corrosion issues of Cu are unavoidable.

Hence, corrosion of copper and its protection in a wide variety of media, particularly when they contain chloride ions, have attracted the attention of many investigators [2-11].

One of the most important methods in the protection of copper against corrosion is the use of inhibitors such as natural materials, mineral salts, organic compounds and so on. Particularly, the most widely used inhibitors are organic compounds[12,13]. It is reported that organic compounds containing polar groups including nitrogen, sulfur and oxygen[10,11,14-19] and heterocyclic compounds with polar functional groups and conjugated double bonds[20-24] can protect copper from corrosion.

The aim of this work is to investigate the effectiveness of a new derivate of thiadiazole named (5 - Methyl - [1, 3, 4] thiadiazol - 2 - ylsulfanyl)- acetic acid (4-dimethylamino-benzylidene)-hydrazid (MTYDBH) to suppress the corrosion of copper in 3.5% NaCl solutions. The inhibiting performance was evaluated by means of weight loss tests and various electrochemical techniques. Measurements were carried out under the influence of various experimental conditions, including MTYDBH concentration and solution pH. The adsorption free energy of MTYDBH on Cu was obtained by different methods and the type interaction between MTYDBH molecule and the copper surface was discussed.

2 EXPERIMENTAL

2.1. Sample preparation and electrochemical cell

The molecular structure of (5-Methyl-[1,3,4]thiadiazol-2-ylsulfanyl)-acetic acid 4-dimethylamino-benzylidene)-hydrazide is shown in Fig. 1 and the compound was prepared as microemulsion.

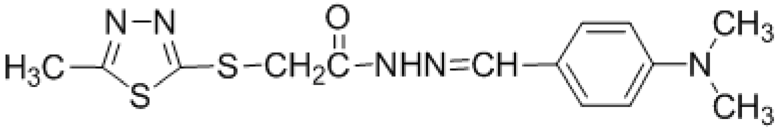

Figure 1. Molecular structures: (5-Methyl-[1,3,4]thiadiazol-2-ylsulfanyl)-acetic acid 4-dimethylamino-benzylidene)-hydrazide; (MTYDBH)

In the concentration studies, the concentration ranges of MTYDBH in 3.5% NaCl solution was 5–100mg/L (pH7.5,298 K). In pH studies, the pH of the solution ranged from 5.5 to 9.5 (298 K), and the concentrations of these compound was 50mg/L. In the studies of the immersion time, the concentration of these compound in 3.5% NaCl solution was 50mg/L (pH7.5, 298 K). The solution in the absence of the inhibitor was taken as blank for comparison. Three parallel experiments have been done under the same conditions for each test.

An electrochemical cell with a three-electrode configuration was used; a copper specimen, a platinum foil, and an Hg/HgCl electrode (SCE) (in saturated KCl) were used as working, counter, and reference electrodes, respectively. The copper specimens were 1.00 cm×1.00 cm×1.00 cm, and embedded in epoxy resin with a working area of 1 cm^2 exposed to the soultion. The copper electrode was first polished successively with emery paper emery paper from 1000 to 2000 grit. The electrode was then washed with doubly distilled water, degreased with acetone, washed using doubly distilled water again, and finally dried with tissue paper.

2.2. Weight loss experiment

The copper specimens (99.999%) for weight loss experiments were mechanically cut into 3.00 cm×1.50 cm×1.50 cm dimensions. The coupons were polished and dried as for the case of copper electrodes, weighed(W_0), and then suspended in a 500 cm^3 solution of 3.5% NaCl without and with different concentrations of MTYDBH for exposure 7days. The specimens were rinsed with distilled water, washed with acetone, dried between two tissue papers, and weighted again (W_1). The corrosion rate (v, gm^{-2} h^{-1}), and the inhibition efficiency (η_w) over the exposure time were calculated as follows (Eq.1, Eq.2):

$$v = \frac{W_0 - W_1}{s \times t} \qquad (1)$$

$$\eta_W = \frac{v_0 - v_1}{v_0} \times 100 \qquad (2)$$

Where v is the corrosion rate, $gm^{-2}h^{-1}$; W_0 and W_1 is the weight of copper before and after weight loss, respectively, g; s is the surface area of coupons, m^2; t is immersion time of coupons, h; v_0 and v_2 is the corrosion rate without and with MTYDBH, respectively.

2.3. Electrochemical experiment

The electrochemical measurements were conducted with PAR-STAT 2273 Potentiostat/Galvanostat. All potentials were measured versus SCE and tests were performed in aerated solution.

For potentiodynamic polarization experiments, the potential was scanned from -250 to +250 mV (versus open circuit potential (OCP)) at a scan rate of 1 mV s^{-1}, and the data were collected and analyzed. The inhibition efficiency was calculated as Eq.3:

$$\eta_i = \frac{I^0_{corr} - I_{corr}}{I^0_{corr}} \times 100 \qquad (3)$$

where I^0_{corr} and I_{corr} were the corrosion current density of copper without and with different concentration of MTYDBH in 3.5% NaCl solution, respectively.

Electrochemical impedance spectroscopy (EIS) measurements were carried out on steady OCP disturbed with amplitude of 10 Mv a.c. sine wave at frequencies from 100 kHz to 10 mHz. The inhibition efficiency obtained from EIS measurements was calculated as follows (Eq.4):

$$\mathrm{IE\%} = \frac{R_{ct} - R^0_{ct}}{R_{ct}} \times 100 \qquad (4)$$

where R_{ct} and R^0_{ct} were the resistance of charge transfer with and without different concentration of MTYDBH, respectively.

3. RESULTS AND DISCUSSION

3.1. Influence of inhibitor concentration

3.1.1. Potentiodynamic polarization measurements

The potentiodynamic polarization curves of the copper electrode in 3.5% NaCl solution without and with 5, 10, 20, 50, 100 mg/L MTYDBH present are shown in Fig.2. It is obvious from Fig.2 that with the increasing of concentration, the polarization curves move to lower current densities and the corrosion potential values slightiy shifted in a positive direction. The effect is more significant in 100mg/L MTYDBH.

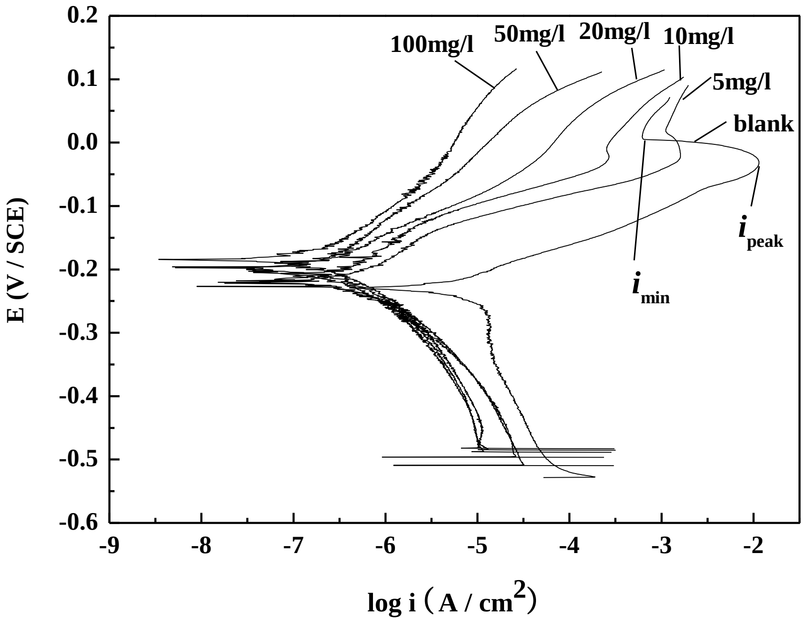

Figure 2. Polarization curves for copper in 3.5% NaCl solution with different concentrations of MTYDBH.

In Fig.2, we can see that the anodic branch of Cu in 3.5% NaCl solution in absence of MTYDBH shows a three distinct region:

Firstly, due to the dissolution of Cu^0 into Cu^+, the current at low-potentials extend to the peak current density (i_{peak}) [3] (Eq.5) :

$$Cu \longrightarrow Cu^{+} + e^{-} \qquad (5)$$

Secondly, the current dentisy decrease to a minimum value (i_{min}) owing to formation of CuCl[20] (Eq.6):

$$Cu^{+} + Cl^{-} \longrightarrow CuCl \qquad (6)$$

And finally, the formed CuCl transforms to $CuCl_2^{-}$ and the current density increase again, through which the dissolution of copper occurs[25,26] (Eq.7):

$$CuCl + Cl^{-} \longrightarrow CuCl_2^{-} \qquad (7)$$

The i_{corr} and E_{corr} parameters were obtained from the extrapolation of anodic and cathodic Tafeal lines located next to the linearized current regions. The values of i_{corr}, β_c, β_a, Ecorr andη_i obtained from Fig.2 is listed in Table 1. Here, compare to the blank solution, the value of $i_{corr,}$ β_c and β_a decrease with slight positive shifts in E_{corr} in the present of MTYDBH. The decrease in i_{corr} value is due to the decrease in the chloride ions attack on the copper surface due to the adsorption of the inhibitor molecules[27]. The value ofη_i increase in the present of MTYDBH and with the increaseing of concentration. The maximum values of inhibition efficiencies is 98.48% at 100mg/L. Fig.3 shows the relationship between the i_{corr} of Cu andη_i under different concentrations. There is a peak in the curve ofη_i with a minimum value in the curve of i_{corr}, which is attributed to the dissolution of the adsorbed film. It indicates that the electrode surface becomes saturated with inhibitor molecules at a certain concentration.

Table 1. Polarization parameters of copper in 3.5% NaCl solution with different concentrations of MTYDBH at 298 K.

	C (mg/L)	**i_{corr} (μA cm^{-2})**	**E_{corr} (mV)**	**βc (mV s^{-1})**	**βa (mV s^{-1})**	**η_i(%)**
BLANK	0	4.05	-218	177.204	47.599	—
MTYDBH	5	0.2121	-219.71	37.44	36.006	94.76
	10	0.1237	-217.956	23.115	32.054	96.95
	20	0.08709	-197.934	26.073	25.786	97.85
	50	0.07296	-199.019	30.517	25.7	98.2
	100	0.0617	-186.209	28.21	27.984	98.48

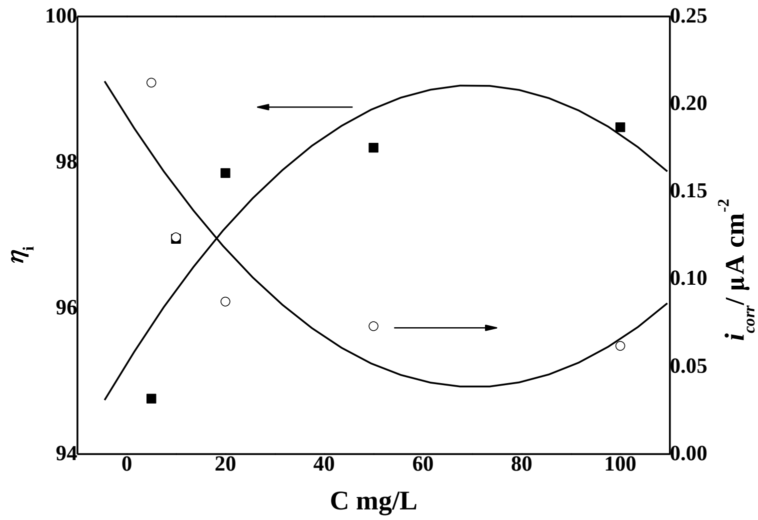

Figure 3. Variations of i_{corr} and η with different concentrations of MTYDBH for Cu in 3.5% NaCl solution at 298 K.

3.1.1. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance is a powerful tool in the investigation of the corrosion and adsorption phenomena[28]. Typical Nyquist impedance plots obtained for Cu electrade at open-circuit potential without and with different concentrations of MTYDBH in 3.5%NaCl solution are shown in Fig.4. It is observed that there is a increase in the diameter of capacitive loop with the increasing of concentration of MTYDBH, which indicate that the corrosion resistance of copper increases gradually, either. And it also indicate that MTYDBH can protect copper electrode from being corroded well.

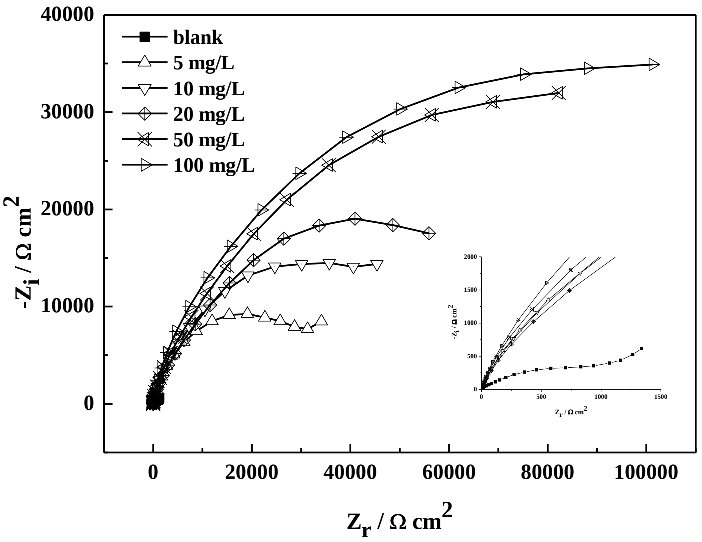

Figure 4. Nyquist and Bode plots for copper in 3.5% NaCl solution with different concentrations of MTYDBH

The parameters obtained by fitting the equivalent circuit are listed in Table.2. And the equivalent circuit is showed in Fig.5, where R_s reprensents the solution resistance, R_f is the film resistance, R_{ct} the charge transfer resistance, CPE1 is composed of the membrane capacitance C_f and the deviation parameter n_1, CPE2 is composed of the double-layer capacitance C_{dl} and the deviation parameter n_2.

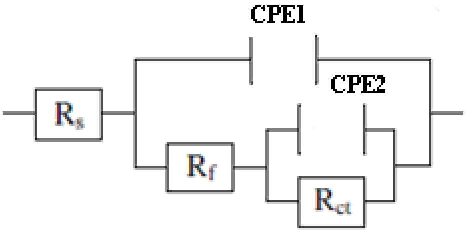

Figure 5. The equivalent circuit model used to fit the EIS experiment data.

Table 2. Impedance parameters of copper in 3.5% NaCl solution with different concentrations of MTYDBH

	C (mg/L)	Rs (Ω cm2)	CPE1 (μF cm-2)	Rf (Ω cm2)	CPE2 (μF cm-2)	Rct/Rp (Ω cm2)	IE (%)
BLANK	0	1.301	247	43.31	455	1109	—
MTYDBH	5	4.272	5.09	301	2.62	45610	97.57
	10	1.499	3.83	151.1	2.86	64530	98.28
	20	5.154	5.04	2097	2.95	90230	98.77
	50	4.079	22.4	402	2.64	166300	99.33
	100	2.417	2.38	454	14.87	175400	99.37

Table 2 shows that the value of R_{ct} increase in the present of MTYDBH and with the increaseing of its concentration compare with the blank. It reveals that the addition of MTYDBH depress the charge transfer process, and desrease the corrosion rate of copper. The recorded impedance values increase with increasing the inhibitor concentration indicating that the electrode surface gets more protection. The inhibition efficiencies (IE%) calculated from R_{ct} also increase with the increaseing of concentration. At 100mg/L, the maximum values are 99.37%. Compared with the blank, the values of R_f with inhibitor increase, and the CPE1 values tend to decrease significantly, which indicated that the charge transfer process of the corrosion reaction in 3.5% NaCl solution is inhibited effectively by forming the adsorption film on the surface of copper. Fig. 6 shows that R_{ct} increases with the increase in the inhibitor concentration before it starts to decrease slightly in neutral solution. And the trend of inhibition efficiencies (IE%) is consistent withη_i in potentiodynamic polarization measurement.

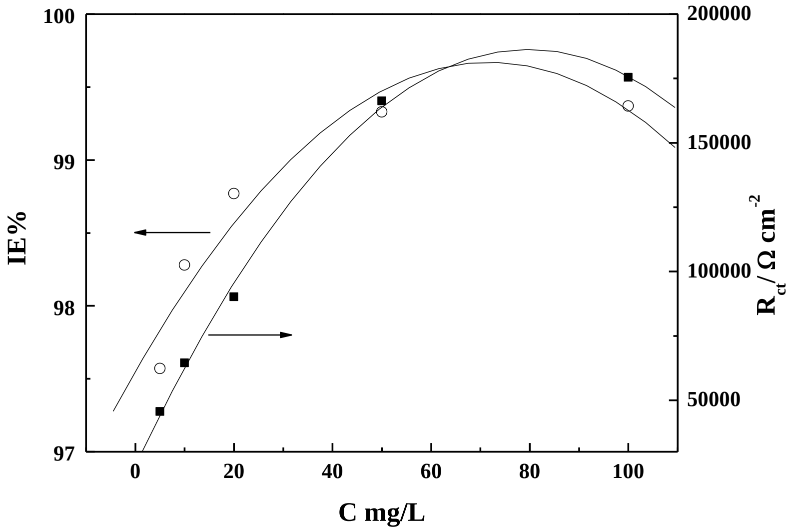

Figure 6. Variations of R_{ct} and IE% with different concentrations of MTYDBH for Cu in 3.5% NaCl solution at 298 K.

3.1.3. Weight loss measurements

Table 3. Weight loss results of copper immersed in 3.5% NaCl solution with different concentrations of MTYDBH at 298 K for 7 days.

C(mg/L)	0	5	10	20	50	100
v	13.47	1.2745	0.6548	0.4554	0.2695	0.1253
η_w	_	90.54	95.14	96.62	98.00	99.07

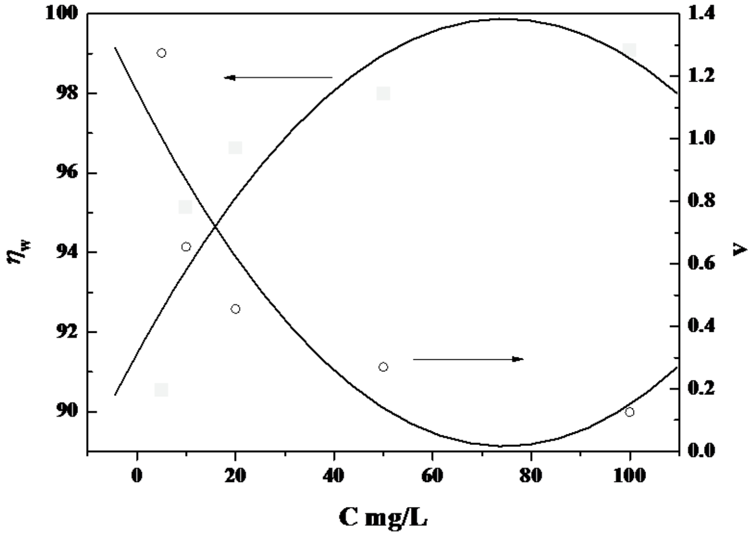

Figure 7. Variations of v andη_w with different concentrations of MTYDBH for Cu in 3.5% NaCl solution at 298 K.

The inhibition efficiency (η_w) and corrosion rate (v, g m^{-2} h^{-1}) obtained from weight loss measurements at different concentrations of MTYDBH in 3.5% NaCl solution is shows in Table 3. The inhibition efficiencies increase and the corrosion rate decreases obviously with increasing the concentration of MTYDBH, which indicates that MTYDBH has a good performance on inhibition of corrosion for copper in 3.5% NaCl solution. The maximum efficiencies reach 99.5% at the highest concentration. And the results show good agreement with the results obtained from both polarization carves and EIS. The relationship betweenη_w and v is shown in Fig. 7. There is a peak in the curve of η_w at a certain concentration and the results show good agreement between measurements obtained from both polarization carves and EIS.

3.2 Adsorption isotherm

As we known, whether the adsorption mechanism of the inhibitors is physical or chemical adsorption can be investigated by the adsorption isotherm. In this study, results obtained from electrochemical techniques and weigh loss measurements are involved to study the adsorption mechanism of the inhibitors.

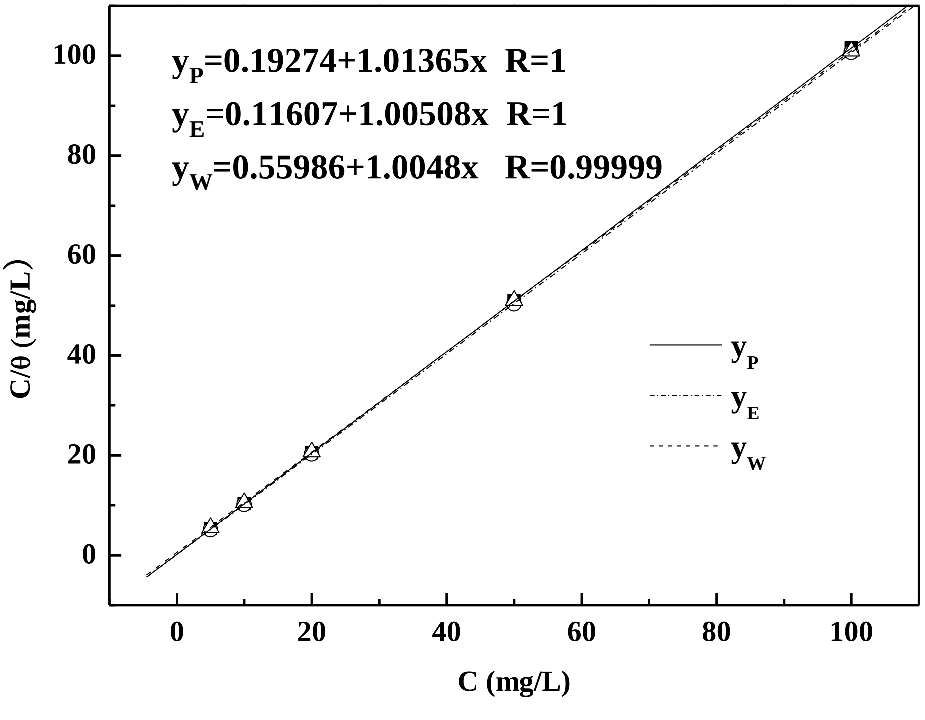

Figure 8. Langmuir adsorption isotherm of MTYDBH on the surface of copper in 3.5% NaCl solution at 298 K.

The surface coverage is defined as the value of the inhibition efficiency (Tables 1–3). To suppose that the adsorption behavior obey the Langmuir isotherm (Eq.8):

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (8)$$

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G^{0}{}_{ads}}{RT} \right) \qquad (9)$$

Where, K_{ads} is the equilibrium constant of the adsorption process, C is the oncentration of the inhibitor.

The linear-relationship of C/θ vs C is shown in Fig.8. The K_{ads} values can be obtained from the intercepts of the straight lines. According to Langmuir adsorption isotherm, the relation between K_{ads} and the free energy of adsorption ΔG^0_{ads} just like the Eq.9 and the values of ΔG^0_{ads} can be calculated[29,30]. Thermodynamic parameters for MTYDBH obtained from Langmuir adsorption isotherm in different methods are given in Table 4.

Table 4. Thermodynamic parameters for the adsorption in 3.5% NaCl solution at 298 K.

	Method	**K_{ads} (10^5 L/mol)**	**ΔG^0_{ads} (kJ/mol)**
MTYDBH	Polarization	17.4327	-45.556
	EIS	28.9481	-46.813
	Weight loss	6.0551	-41.640

Generally speaking, if the value of ΔG^0_{ads} is less than 20 kJ/mol or lower, the type of adsorption is regarded as physical adsorption, and the corrosion inhibition takes action due to the electrostatic interactions between the charged molecules and the charged metal. And if the absolute value of ΔG^0_{ads} is more than 40 kJ/mol, it is considered as chemical adsorption owing to the covalent bond formed by the charge sharing or a charge transfer[31,32].

As shown in Table 4, the values of ΔG^0_{ads} are all negetive, which reveal that the adsorption behavior of MTYDBH for copper in 3.5% NaCl solution is spontaneous. And values of ΔG^0_{ads} are all between -41 kJ/mol and -47 kJ/mol, which indicate that the type of absorption is chemical adsorption. However, the covalent bonds between the inhibitor molecules and the copper surface are weak due to the values of ΔG^0_{ads} get close to 40 kJ/mol.

3.3. Influence of the pH

3.3.1. Polarization measurements

Polarization curves of copper in 3.5% NaCl solution under different pH conditions with the concentration 50mg/L of MTYDBH are shown in Fig.9. Here, the polarization curves move to lower current densities and the corrosion potential values shifted in a positive direction with the increasing of PH.

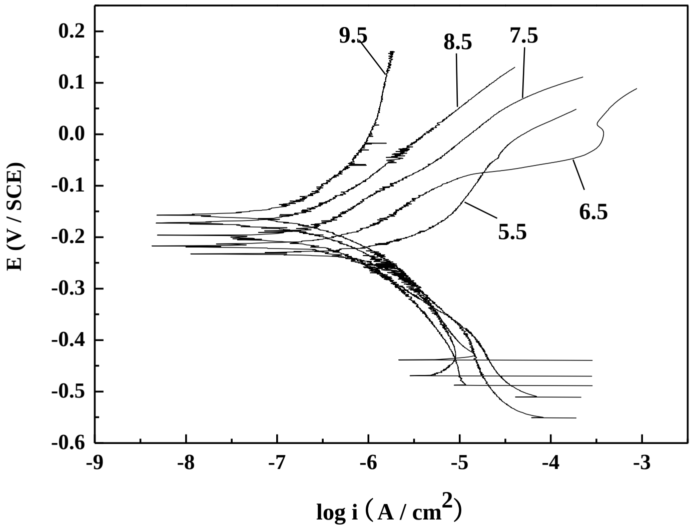

Figure 9. Polarization curves of copper in 3.5% NaCl solution with MTYDBH under different pH conditions at 298 K

Table 5. Polarization parameters of copper in 3.5% NaCl solution with MTYDBH under different pH conditions at 298 K.

	C (mg/L)	pH	i_{corr} (μA cm^{-2})	E_{corr} (mV)	βc (mV s^{-1})	βa (mV s^{-1})	η_i(%)
BLANK	0	7.5	4.05	-218	177.204	47.599	—
MTYDBH	50	5.5	0.4477	-231.569	38.548	28.803	88.95
		6.5	0.117	-215.432	25.017	21.578	97.11
		7.5	0.07296	-199.019	30.517	25.7	98.2
		8.5	0.05853	-172.415	26.763	30.759	98.55
		9.5	0.04475	-156.059	29.652	31.293	99.00

The values of i_{corr}, β_c, β_a, E_{corr} andη_i obtained from Fig.9 are listed in Table 5. Here, compare with the neutral condition, the value of i_{corr} decrease in acicid condition but increased in alkaline condition. The corrosion potentials (E_{corr}) shift slightly to the more positive values compared with the blank, and the variation of β_a and β_c values also confirms that both the electrochemical dissolution of copper and oxygen reduction are obviously restrained by the presence of the inhibitors.

Generally speaking, the cathodic process of copper could be described as following reactions:

$$2H_3O^+ + 2e^- \longrightarrow H_2 + 2H_2O \qquad (10)$$

$$O_2 + 4H^+ \longrightarrow 2H_2O \qquad (11)$$

$$O_2 + 2H_2O \longrightarrow 4OH^- \qquad (12)$$

where reactions (10) and (11) are the cathodic reactions in acid media, and reaction (12) is that under neutral or alkaline conditions. It can been seen from Eq.12 that the presence of OH^- can restrain the process of oxygen reduction to some extent.

The maximum values of inhibition efficiencies is 99% at pH9.5. It indicates that MTYDBH has a better performance on inhibition of corrosion for copper and the efficiency order of MTYDBH under different pH conditions is 9.5 > 8.5 > 7.5 > 6.5> 5.5.

3.3.2. Electrochemical impedance spectroscopy (EIS)

Nyquist plot of copper in 3.5% NaCl solution under different pH conditions with MTYDBH in the concentration of 50mg/L is shown in Fig.10. The impedance data obtained by fitting the equivalent circuit are given in Table 6.

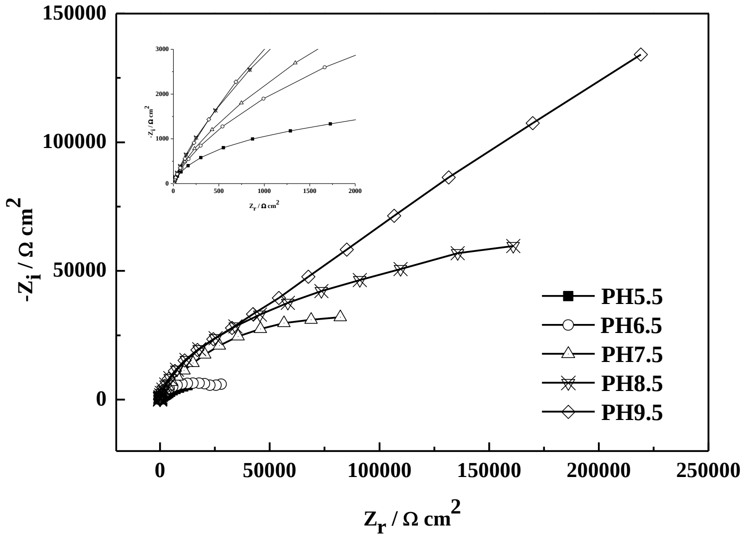

Figure 10. Nyquist diagrams of copper in 3.5% NaCl solution with MTYDBH under different pH conditions at 298 K

Table 6. Impedance data of copper in 3.5% NaCl solutio n with MTYDBH under different pH conditions at 298 K.

	C (mg/L)	PH	Rs (Ω cm2)	CPE1 (μF cm-2)	Rf (Ω cm2)	CPE2 (μF cm-2)	Rct/Rp (Ω cm2)	IE (%)
BLANK	0	7.5	1.301	247	43.31	455	1109	—
A	50	5.5	3.193	12.4	1410	187	31340	96.46
		6.5	0.6042	6.46	1885	39.67	37190	97.02
		7.5	4.079	22.4	4.02	2.64	166300	99.33
		8.5	0.0875	10.7	51.07	1.67	363300	99.69
		9.5	0.09993	2.17	30260	13.3	948900	99.88

As shown in Table 6, the values of R_f with MTYDBH also increase remarkably compared with the blank and with the increasing of PH. The inhibition efficiencies at each condition are extremely high, and the maximum values is 99.88% at the PH9.5. And the result is the same as the polarization result, the efficiency order is 9.5 > 8.5 > 7.5 > 6.5> 5.5. In alkaline condition, the charge transfer process of the corrosion reaction is inhibited better than in neutral and acicid condition, and the forming adsorption film on the surface of copper is thicker.

3.4. Quantum chemistry calculations

The Quantum chemistry calculation was analyzed with HyperChem 7.5 Professional software. Geometric structures and electronic properties of MTYDBH were calculated by PM3 semiempirical method. The optimized molecular structures and the frontier molecule orbital density distribution of MTYDBH are shown in Fig.11.

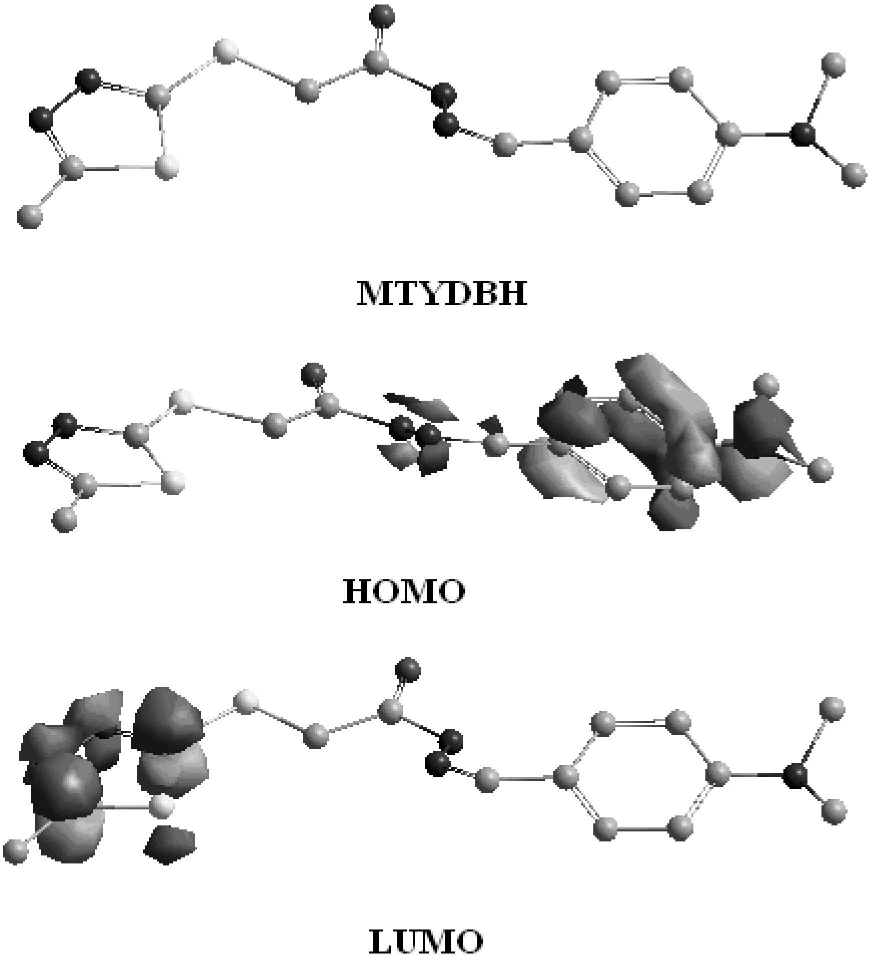

Figure 11. Molecular structure and HOMO–LUMO of MTYDBH

E_{HOMO} represent the electron donating ability of the molecule. The higher the value of E_{HOMO}, the eassier it donate electrons. E_{LUMO} is often associated with the electron accepting ability of the molecule. Low values of $\mathrm{E}_{\mathrm{LUMO}}$ reveal a tendency of the molecule to accept electrons[33]. For HOMO (see Fig. 11) of MTYDBH, it can be observed that the benzene ring, -C=N-, -N-N-,and -$N(CH_3)_2$ has larger electric density, which indicated that this functional group can adsorb on the surface of copper by donate electrons to vacant d-orbitals of copper atoms. For the LUMO, thiazole ring has larger electron density, which indicated that the thiazole ring accept the electrons from s- orbitals of copper atoms. Therefore, MTYDBH molecule adsorb on a parallel with the surface when there is an adsorption between MTYDBH molecule and copper atoms, which result in the high inhibiton efficiency.

4. CONCLUSIONS

Inhibitive actions of the synthesized (5-Methyl-[1,3,4]thiadiazol-2-ylsulfanyl)-acetic acid (4-dimethylamino-benzylidene)-hydrazid (MTYDBH) on the corrosion of copper in 3.5% NaCl solutions have been studied and the results are summarized as follows:

1.Potentiodynamic polarzation measurements showed that the present of MTYDBH in 3.5%NaCl solutions decrease corrosion currents and slightly shifts the corrosion potional in a positive direction; this effect is increased by increasing the MTYDBH concentration. Weight loss measurement gave an inhibition efficiency of about 99.07% with 100mg/L MTYDBH present.

2.Results from EIS revealed the mechanism of corrosion inhibition is by forming a protective adsorption film on copper surface. Adsorption behavior obeys the Langmuir adsorption isotherm and the calculated free energy of adsorption of MTYDBH on Cu reveals a weak chemical adsorption of the inhibitor on the metal surface.

3.The corrosion resistance of copper with inhibitors under alkaline conditions is better than that under near neutral or conditions acidic and the order is alkaline **>** neutral **>** acidic.

4.Results obtained from weight loss, potentiodynamic polarization and impedance measurements are in good agreement. It reveals that MTYDBH is a good inhibitor for copper corrosion in 3.5% NaCl solution.

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