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Effects of Cyproconazole on Copper Corrosion as Environmentally Friendly Corrosion Inhibitor in Nitric Acid Solution

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The inhibiting influence of cyproconazole on the corrosion of copper in 0.5 M HNO_3 solution was investigated by means of potentiodynamic polarization and electrochemical impedance spectroscopy. The selective desorption of cyproconazole from copper metal surface was also studied by the differential polarization curves. Phenomenon of chemisorption accompanied by physisorption was proposed from the values of thermodynamics parameters (ΔG^0_{ads}) obtained. Results obtained from the experimental data show that cyproconazole acts as an effective eco-friendly corrosion inhibitor for copper in nitric acid. The adsorption of cyproconazole on copper surface from 0.5 M HNO_3 obeys the Langmuir adsorption isotherm.

Keywords: Corrosion inhibition, Nitric acid, Potentiodynamic polarization, Electrochemical impedance spectroscopy, Copper.

INTRODUCTION

Copper and its alloys are extensively used to industrial material due to its electrical, thermal, mechanical and relatively noble properties. However, the corrosion susceptibility is confirmed when the aggressive solution are present and copper corrosion resistance becomes less while the aggressive solution concentration increases[1,2]. One approach to preventing copper corrosion is the use of corrosion inhibitors. Unfortunately, most of these organic inhibitors are expensive and toxic to living beings at present. In view of environmental protection requirements, the use of these organic inhibitors is nowadays quite limited. So research on these new types of corrosion inhibitors of natural source and non-toxic type has been considered more important and desirable[3-6]. Cyproconazole as fungicides in agriculture is mass-produced, inexpensive and environment-friendly, which could be easily degraded to non-toxic compounds[7].

In present study, cyproconazole was investigated as an inhibitor for the corrosion of copper in 0.5 M HNO_3 solutions using potentiodynamic polarization, electrochemical impedance spectroscopy and differential polarization curves. The molecular structure is shown in Fig. 1.

EXPERIMENTAL

The aggressive solution of 0.5 M HNO_3 was prepared by dilution of Analytical grade 65 % HNO_3 with double distilled water. The concentration range of the inhibitors is from 10^{-5} to 10^{-3} in 0.5 M HNO_3 solution. The solution in the absence of inhibitors is taken as blank for comparison. The copper specimens (99.999 %) for electrochemical experiments and the specimens are embedded in epoxy resin with a geometrical surface area of 0.07 cm^2 exposed to the electrolyte.

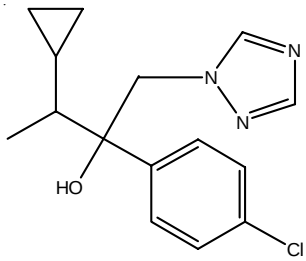

Fig. 1. Molecular structure of cyproconazole

The electrochemical measurements were performed through Autolab PGSTAT302N equipped with a conventional three-electrode glass cell with capacity of 500 mL and a saturated mercurous sulfate electrode (SSE) provided with a Luggin capillary as reference electrode were used. A freshly polished copper specimen and a platinum electrode of 10 cm^2 are used as working electrode and counter electrode, respectively. The cell was open to air and the measurement was carried out at 28 °C. The temperature was controlled by an aqueous thermostat. All the potentials reported are with reference to

SSE. Prior to all measurements, the samples are abraded with emery paper from 1000 to 2000 grit, respectively, degreased ultrasonically in ethanol and acetone and dried at room temperature. Prior to measurement, the open-circuit potential (OCP) was monitored in test solution at 28 °C until a steady-state was reached. The electrochemical impedance spectroscopy experiments were carried out at the open-circuit potential with a frequency range from 100 kHz to 0.01 Hz and a 10 mV peak-to-peak sine wave as the excitation signal. Tafel polarization curve was carried out from cathodic potential of -0.25 V *vs*. SSE to an anodic potential of +0.25 V *vs*. SSE with respect to the open circuit potential at a sweep rate 0.5 mV/s.

RESULTS AND DISCUSSION

Polarization curves: To understand the corrosion mechanism and effect of inhibitor concentration, the polarization curves of copper in 0.5 M HNO_3 solution without and with different concentrations of cyproconazole at 28 °C are shown in Fig. 1. The values of corrosion current density (J_{corr}), corrosion current (i_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (β_c), anodic Tafel slope (β_a) and inhibition efficiency (IE %) were presented in Table-1. IE (%) was calculated by the following expression[8]

$$IE(\%) = \frac{J^{o}_{corr} - J_{corr}}{J^{o}_{corr}} \times 100 \quad (1)$$

where J_{corr} and J^{o}_{crr} are the values of corrosion current density of uninhibited and inhibited specimens, respectively.

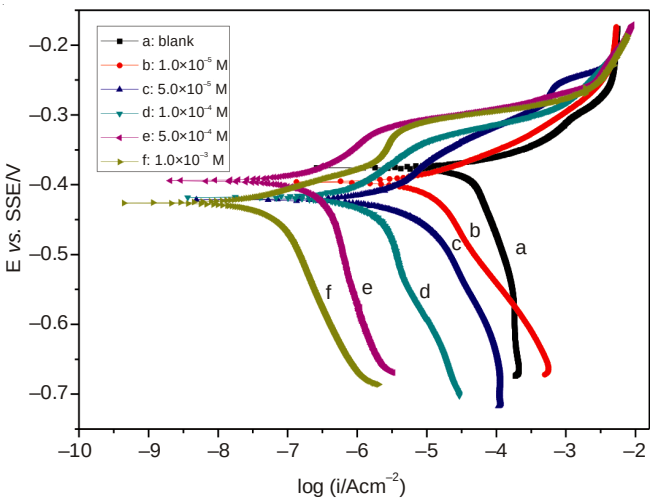

Fig. 1. Polarization curves for copper in 0.5 M HNO_3 solution containing various concentrations of cyproconazole at 28 °C

The corrosion rate of copper in 0.5 M HNO_3 solution decreased from 14.86 mm/year of the blank to 0.01 mm/year of 10^{-3} M concentration of cyproconazole (Table-1). The decreased in the corrosion rate suggests that the inhibition efficiency increases with the increase in the inhibitor concentration. From the Table-1 it was clear that the J_{corr} value decreases from 636.8 to 0.62 μAcm^{-2} with the addition of 10^{-3} M concentration of cyproconazole. The addition of cyproconazole didn't alter the value of E_{corr} significantly indicating the mixed type of inhibiting behaviour of the inhibitor[9]. The polarization curves exhibit no steep slope in the anodic range (as shown in Fig. 1), meaning that no passive films are formed on the copper surface.

The differential treatment of the potentiodynamic anodic polarization curve can acquire the desorbing-peak figure of cyproconazole inhibitor, as shown in Fig. 2

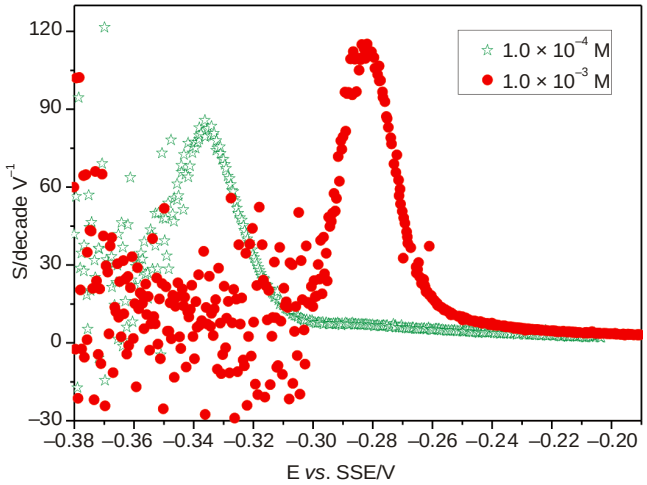

Fig. 2. Differential polarization curves of copper electrode in 0.5 M HNO_3 solution containing various concentrations of cyproconazole

The Y-axis of Fig. 2 is indicated as a semi-logarithmic slope of the anodic polarization curve, which is defined as follows[10]:

$$D = \frac{d \log J_{corr}}{dE} \quad (2)$$

where E is the potential of the electrode. Fig. 2 shows that the desorption onset potential, the desorption peak potential and the desorption completion potential are -0.3, -0.28 and -0.26V with a concentration of 10^{-3} M cyproconazole, respectively. Comparison of different differential polarization curves with 10^{-4} M cyproconazole, it is found that the desorption peak potential was shifted to more positive direction with increasing

TABLE-1
POLARIZATION PARAMETERS AND CORRESPONDING INHIBITION EFFICIENCIES FOR THE CORROSION OF COPPER AT DIFFERENT CONCENTRATIONS OF CYPROCONAZOLE AT 28 °C

Concentration (M)	β_a (mV dec^{-1})	β_c (mV dec^{-1})	E_{corr} Obs (V)	J_{corr} (μA cm^{-2})	i_{corr} (μA)	Corrosion rate (mmpy)	IE (%)
Blank	280.2	33.0	-0.376	636.80	44.99	14.86	-
1.0×10^{-5}	184.5	51.8	-0.396	176.56	12.47	4.12	72.3
5.0×10^{-5}	150.0	69.0	-0.422	58.31	4.12	1.36	90.8
1.0×10^{-4}	237.3	66.7	-0.418	18.05	1.28	0.42	97.2
5.0×10^{-4}	328.8	72.0	-0.395	3.99	0.28	0.09	99.4
1.0×10^{-3}	165.7	35.2	-0.427	0.62	0.04	0.01	99.9

TABLE-2
IMPEDANCE PARAMETERS AND INHIBITION EFFICIENCY FOR THE CORROSION OF COPPER IN 0.5 M HNO_3 SOLUTION WITHOUT AND WITH ADDITION OF VARIOUS CONCENTRATIONS OF CPNA AT 28 °C

Concentration (M)	R_{ct} (Ω cm^2)	f_{max} (Hz)	C_{dl} (μF cm^{-2})	IE (%)
Blank	437.7	3.162	115.1	-
1.0×10^{-5}	1082.0	1.995	73.8	59.5
5.0×10^{-5}	1380.0	1.995	57.8	68.3
1.0×10^{-4}	3117.0	1.585	32.2	86.0
5.0×10^{-4}	12140.0	0.7943	16.5	96.4
1.0×10^{-3}	20550.0	0.5012	15.51	97.9

of inhibitor concentration. The more positive value of desorption peak potential means that the enhancement of IE % with increasing of cyproconazole concentration is more likely to reach a steady-state for the adsorption process[11].

Electrochemical impedance spectroscopy: The Nyquist representations of the impedance behaviour of copper in 0.5 M HNO_3 solution with and without addition of various concentrations of cyproconazole were given in Fig. 3. The charge-transfer resistance (R_{ct}) values were calculated from the difference in impedance at lower and higher frequencies as suggested by Barouni *et al.*[12].

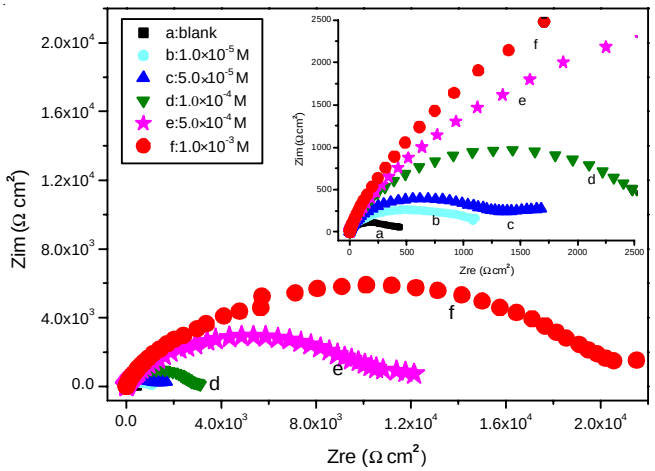

Fig. 3. Nyquist plots of copper in 0.5 M HNO_3 for different concentrations of cyproconazole at 28 °C

The double layer capacitance (C_{dl}) and the frequency at which the imaginary component of the impedance is maximal (-Zmax) are found as represented in eqn. 3[13]:

$$C_{dl} = \frac{1}{2\pi f_{max}} \times \frac{1}{R_{ct}} \quad (3)$$

The inhibition efficiency got from the R_{ct} was calculated by the following relation[14]:

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

where R^0_{ct} and R_{ct} are charge-transfer resistance values in the absence and presence of the inhibitor, respectively. It is seen in Table-2 that addition of inhibitor increases the values of R_{ct} and reduces the C_{dl}. The R_{ct} values tend to increased could be attributed to the formation of the barrier film which prevented the nitric acid from attacking the copper metal surface[15]. The value of C_{dl} is always smaller in the presence of the organic molecules of cyproconazole than in its absence might be attributed to the gradual replacement of water molecules by the adsorption of the inhibitors at copper/solution interface[16,17].

At the concentration of 5×10^{-4} M or more, cyproconazole acts as an excellent corrosion inhibitor with inhibition efficiencies about 96.4 %. The IE % values obtained from the electrochemical impedance spectroscopy measurements are in good agreement with that obtained from potentiodynamic polarization.

Adsorption isotherm: In order to determine the best fit for surface coverage (θ) to various isotherms, several adsorption isotherms are considered, such as Langmuir, Bockris-Swinkels, Temkin and Frumkin isotherms[18]. Results reveal that the Langmuir isotherm (eqn. 5) provides the better description of the adsorption behaviour of cyproconazole on the metal surface[19].

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (5)$$

where K is the equilibrium constant of the inhibitor adsorption process and C is the inhibitor concentration. Plot C/θ *versus* C yield a straight line (Fig. 4) with regression coefficient, R^2 and the slopes (Table-3) almost equal to 1. This suggests that cyproconazole in present study obeyed the Langmuir isotherm and there is negligible interaction between the adsorbed molecules.

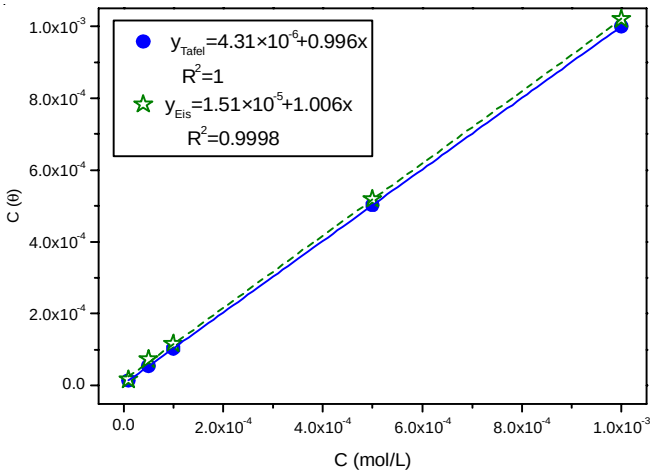

Fig. 4. Langmuir adsorption isotherm of cyproconazole on the surface of copper in 0.5 M HNO_3 solution at 28 °C

According to Langmuir adsorption isotherm, eqn. 6 is applicable[14]:

$$K = \frac{1}{55.5} \exp(-\Delta G^0_{ads} / RT) \quad (6)$$

where ΔG^0_{ads} is the free energy of adsorption, the value 55.5 in the above equation is the molar concentration of water in solution in mol/L[20]. The negative values of ΔG^0_{ads} indicated that the adsorption of cyproconazole molecule is a spontaneous process. Generally, values of ΔG^0_{ads} up to -20 kJ mol^{-1} are consistent with physisorption while those around -40 kJ mol^{-1} or higher are associated[21]. Though there is a little difference between the ΔG^0_{ads} values obtained from different methods (shown in Table-3), the absolute values of ΔG^0_{ads} are all around 40 kJ/mol, it was suggested that the adsorption of cyproconazole molecule on metal surface was a spontaneous process and chemisorption was dominant.

TABLE-3
CALCULATED K AND ΔG^0_{ads} OF THE ADSORPTION REACTION FOR COPPER IN PRESENCE OF DIFFERENT INHIBITORS IN 0.5 M HNO_3 SOLUTION, AT 28 °C

	Slope	R^2	$K(M^{-1})$	ΔG^0_{ads} (kJ mol^{-1})
Polarization	0.996	1.0000	231928.2	-40.9
EIS	1.006	0.9998	66299.4	-37.8

Conclusion

The compound cyproconazole showed an excellent inhibitive performance for copper in 0.5 M HNO_3 solution. Inhibition efficiency increases with increase in the concentration of the cyproconazole and its efficiency attains more than 96.4 % at 5×10^{-4} M at 28 °C. Polarization curves indicated that the inhibitor behave mainly as mixed-type inhibitor. The adsorption of cyproconazole on copper surface from 0.5 M HNO_3 obeys the Langmuir adsorption isotherm. Phenomenon of chemisorption accompanied by physisorption was proposed from the values of thermodynamics parameters (ΔG^0_{ads}) obtained. The inhibitor efficiency determined by electrochemical polarization and electrochemical impedance spectroscopy were in good agreement.

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