

INFLUENCE OF INORGANIC INHIBITOR ON COPPER CORROSION IN ACIDIC MEDIUM

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Summary: In this paper behavior of inorganic compound (2-amino-5-ethyl-1,3,4-thiadiazole) as inhibitor of copper corrosion in acidic medium (HCl solution) was examined. In addition to examination the effects of different concentrations of the inhibitor on the corrosion processes, research also included investigation of influence of immersion time of copper electrode in 2-amino-5-ethyl-1,3,4-thiadiazole (AETDA) solution on protective film formation on electrode surface (copper electrode). During this study next experimental methods are used: open circuit potential measurements (OCP), linear voltammetry measurements (LV) and cyclic voltammetry measurements (CV). Shift of open circuit potential toward negative values indicate that on copper surface comes to formation of corrosion product and adsorption of molecule inhibitor. Copper oxidation is consequence of existing defect in structure layer and layer dissolution on electrode surface. Results show that inhibition efficiency depend on inorganic inhibitor concentration and immersion time of copper electrode in inhibitor solution (azole derivatives solution). Inhibition mechanism of AETDA is explained by forming compact protective film on copper surface. Adsorption of 2-amino-5-ethyl-1,3,4-thiadiazole on copper surface in 0.05M HCl solution obeys the Langmuir adsorption isotherm. The value of adsorption energy amount: $\Delta G = -39,52$ kJ/mol.

Key words: copper, HCl, oxidation, corrosion inhibition, inorganic inhibitor, acidic medium, AETDA

Introduction

Copper has been one of more important materials in industry owing to its high electrical and thermal conductivities, mechanical workability, and its relatively noble properties [1, 2]. Thus, corrosion of copper and its inhibition in a wide variety of media, particularly when they contain chloride ions, have attracted attention of a number of investigators [1, 3]. Azole derivatives like benzotriazole, mercaptobenzothiazole, benzimidazole, and

imidazole are well-known corrosion inhibitors for copper [1, 4]. The present paper reports on the behavior of 2-amino-5-ethyl-1,3,4-thiadiazole (AETDA) as an inhibitor for copper corrosion in HCl solutions. Based on structure (Figure1), can be expected that in acid medium, this compound show high inhibition efficiency for copper corrosion. In addition, it is nontoxic and inexpensive compound [1].

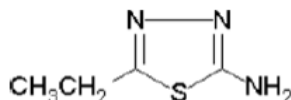


Figure1. Molecular structure of 2-Amino-5-ethyl-1,3,4-thiadiazole (AETDA)[1]

Experimental

Electrode preparation

Copper electrode was used as working electrode.

Reagents

HCl solution (0.05 M) was used during experiment. 2-Amino-5-ethyl-1,3,4-thiadiazole (AETDA) was used as inhibitor in the wide range of concentrations $1.0 \cdot 10^{-6}$ M - $1.0 \cdot 10^{-2}$ M. Also, immersion time of copper electrode in inhibitor solution ($1.0 \cdot 10^{-2}$ M) was studied.

Electrochemical measurements

The electrochemical characteristics of copper in HCl solution, in the presence of inhibitor was investigated in the following way:

- Linear potentiodynamic measurements; Cyclic potentiodynamic measurements;
- Electrode was immersed for a certain time (5, 15, 30 and 60 min) in $1 \cdot 10^{-2}$ M AETDA;
- The electrode was immersed for a certain time 5, 15, 30 and 60 min, in $1 \cdot 10^{-2}$ M AETDA solution.

Results and discussion

Open circuit potential

Change of open circuit potential values was followed in 0.05 M HCl with and without addition of various concentration of inhibitor during 10 min and results are showed in table 1

Table 1. Open circuit potential of copper in 0.05 M HCl with and without addition of various concentration of AETDA

C_{inh} [M]	E_{pok} [V _{ZKE}]
/	-0.181
$1.0 \cdot 10^{-6}$	-0.119
$1.0 \cdot 10^{-5}$	-0.086
$1.0 \cdot 10^{-4}$	-0.096
$1.0 \cdot 10^{-3}$	-0.087
$1.0 \cdot 10^{-2}$	-0.115

Change of OCP indicate direction of the corrosion processes in the examined solutions[1, 5]. Based on the OCP values shown in the table it can be assumed that comes to adsorption of inhibitor molecule on copper surface [6].

Polarization measurements

Cyclic voltammetry

Cyclic voltammogram of copper obtained in a hydrochloric acid solutions without and with the addition of 2-amino-5-ethyl-1,3,4-thiadiazole is shown in Figure 2.

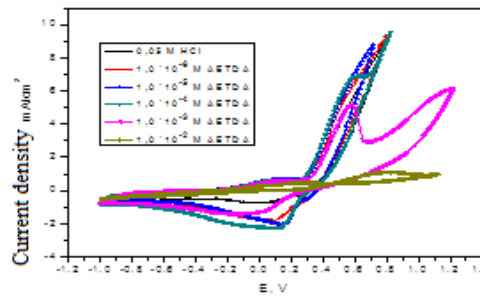
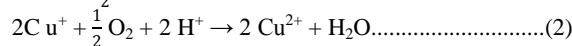
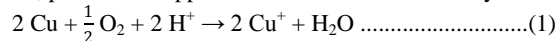
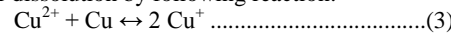


Figure 2. Cyclic voltammogram of copper recorded in 0.05M HCl in the presence of various concentrations of 2-amino-5-ethyl-1,3,4-thiadiazole. Scan rate 10mV/s

CV curves shown in figure 2 indicate that on 0,2 V vs. SCE comes to rapid increase of current density pointing on more intensive copper oxidation. In acid chloride nature aerated solution, process of copper dissolution can be shown by following reactions [1, 9]:



Increase of concentration Cu^{2+} ions causes further copper dissolution by following reaction:



Also, in HCl solutions come to reaction between copper and Cl^- ions by following reactions [8]:

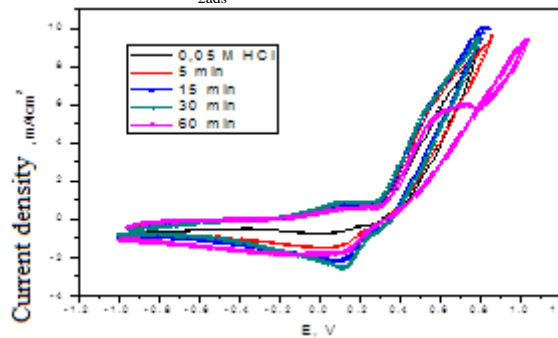
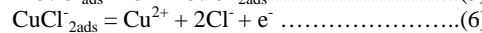
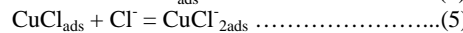
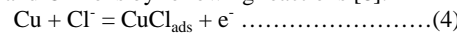
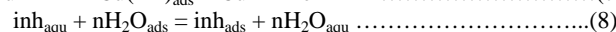
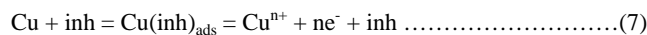


Figure 3. Cyclic voltammogram of copper in a 0.05M HCl solution after immersion in $1 \cdot 10^{-2}$ M AETDA solution for various periods of time (5, 15, 30 and 60 min). Scan rate 10mV/s

From figure 3 was noticed that on potential 0.1 V exist anode current peak which indicate that after electrode immersion in inhibitor solution and during potentiodynamic measurements in 0.05 M HCl come to dissolution of copper. Inhibition mechanism of azole compounds can be explains by following reactions [10]:



Linear voltammetry

Besides the cyclic potentiodynamic measurements, for a complete understanding of corrosion processes and mechanisms of action of AETDA linear potentiodynamic measurements were performed.

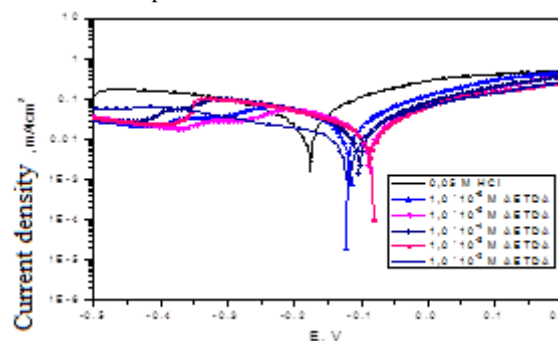


Figure 4. Potentiodynamic polarization curves for copper in 0.05 M HCl with and without addition of various concentrations of AETDA. Scan rate 1 mV/s.

According to polarization curves present in figure 4 it can be seen that corrosion potential moves toward positive values with increase inhibitor concentrations. Besides that current density decreases with increasing AETDA concentration indicating that AETDA acts as anode inhibitor in examined conditions. The values of inhibition efficiency (IE%) were calculated from polarization data according to the equation [1, 2]:

$$IE\% = [(j_{kor} - j_{kor(inh)}) / j_{kor}] \cdot 100 \dots\dots\dots(10)$$

where j_{Corr} and $j_{Corr(inh)}$ - are the corrosion currents in absence and presence of AETDA, respectively

Solution	Immersion time [min]	E_{Corr} [V vs. SCE]	j_{Corr} [$\mu A/cm^2$]	bc	ba	θ	IE [%]
0.05 M HCl	/	-0.183	48 200	-0.318	0.164	/	/
$1.0 \cdot 10^{-6}$ M AETDA	/	-0.118	11 200	-0.088	0.073	0.7676	76.76
$1.0 \cdot 10^{-5}$ M AETDA	/	-0.088	10 600	-0.106	0.085	0.7801	78.01
$1.0 \cdot 10^{-4}$ M AETDA	/	-0.104	10 500	-0.070	0.061	0.7822	78.22
$1.0 \cdot 10^{-3}$ M AETDA	/	-0.085	7 900	-0.083	0.061	0.8361	83.61
$1.0 \cdot 10^{-2}$ M AETDA	/	0.119	7 500	-0.188	0.142	0.8444	84.44

Table 3. Electrochemical parameters of copper in 0.05 M HCl in absence and presence of inhibitor

It is clear from table 3 that increase of concentrations of AETDA increasing inhibition efficiency. Also increase of AETDA concentration leads to decrease of corrosion current density. Nevertheless, according to results presents in table 3 it can be said that with longer immersion time, values of IE increase and j_{corr} decrease.

Adsorption isotherm

Primary information about interaction between inhibitor and metal surface can be obtained from adsorption isotherm. Langmuir adsorption isotherm obtains from equation [4]:

$$\frac{\theta}{1-\theta} = AC \exp\left(\frac{-\Delta G}{RT}\right) = KC \dots \dots \dots (11)$$

$$-\Delta G = \left(\ln K - \ln \frac{1}{55,55}\right) RT \dots \dots \dots (14)$$

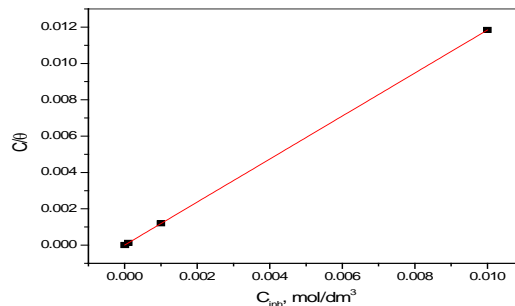


Figure 6. Langmuir adsorption isotherm of AETDA in 0.05 mol/dm³ HCl

The value of adsorption energy amount:

$$\Delta G = -39,52 \text{ kJ/mol}$$

The negative value of the free energies of adsorption indicates strong adsorption of AETDA molecules on copper surface [4].

Conclusions

Shift of open circuit potential toward negative values indicate that on copper surface comes to formation of corrosion product and adsorption of molecule inhibitor. Cyclic and linear potentiodynamic measurements indicate that in presence of inhibitor come to copper dissolution lower intensity compared to copper dissolution in bare HCl solution. In the presence of AETDA comes to formation protective layer on copper surface which prevents further intensive dissolution of metal. Adsorption of 2-amino-5-ethyl-1,3,4-thiadiazole on copper surface in hydrochloric acid solution obeys the Langmuir adsorption isotherm.

References

[1] E. M. Sherif, Corrosion Science 48 (2006) 4065-4079
 [2] E. M. Sherif, Applied Surface Science 252 (2006) 8615-8623

[3] E. M. Sherif, Su-Moon Park, Electrochimica Acta 51 (2006) 6556-6562
 [4] M. M. Antonijević, M. Petrović, M. Radovanović, M. Radičević, Zaštita materijala 48 (2007) 29-37
 [5] E. Sidot, N. Sonissi, L. Bousselmi, E. Triki, L. Robbiola, Corrosion Science 48 (2006) 2241-2257
 [6] El-Sayed M. Sherif, R. M. Erasmus, J. D. Comins, Electrochimica Acta 55 (2010) 3657-3665
 [7] S. M. Milić, M.M. Antonijević, Corrosion Science 51 (2009) 28-34
 [8] N. A. Al-Mobarak, K. F. Khaled, M. N. H. Hamed, K. M. Abdel-Azim, Arabian Journal of Chemistry 4 (2011) 185-193
 [9] M. Scendo, Corrosion Science 49 (2007) 3953-3968
 [10] Sudheer, M. A. Quraishi, Corrosion Science 70 (2013) 161-169