2-AMINO-5-ETHYL-1,3,4-THIADIAZOLE AS INHIBITOR OF BRASS CORROSION IN 3% NaCl

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Abstract

The electrochemical behaviour of brass and anticorrosion effect of 2-amino-5-ethyl-1,3,4-thiadiazole (AETD) in chloride solution was investigated using electrochemical techniques. Results show that inhibition efficiency depended on inhibitor concentration and immersion time of brass electrode in inhibitor solution. Mechanism of brass corrosion inhibition by 2-amino-5-ethyl-1,3,4-thiadiazole includes adsorption of inhibitor on active sites on electrode surface. Adsorption of AETD in 3% NaCl solution obeys Langmuir adsorption isotherm.
Keywords: Brass, Corrosion, Inhibition, Chloride solution

Introduction

Copper and alloys are widely used in various industrial plants due to their mechanical characteristics, good thermal and electrical conductivity and relatively good corrosion resistance in different aggressive environments [1-3]. Hence, electrochemical behaviour of brass in sea water [1, 4], in solutions containing chloride and sulphate ions [5-7], as well as in nitrate and nitrite media [8, 9] is studied. Brass protection in aggressive media is related to the formation of a stabile protective film on metal surface composed of copper and zinc oxide. Composition and characteristics of protective film are affected by potential of formation as well as by zinc content in the alloy. However, under the influence of the industrial conditions brass undergoes dezincification. Numerous organic compounds are studied as potential inhibitors in order to reduce corrosion of copper and brass in various media as much as possible [3, 5, 10-14]. Most of the research is directed towards the use of azole compounds [15-17], amines [18-21], aminoacids [22-25] due to heteroatoms in their structure (S, O and N) known to have strong affinity towards copper favouring their adsorption on metal surface. In the past few years, thiadiazole compounds proved to be relatively good copper corrosion inhibitors. The inhibition effect is related to the possibility of adsorption of molecules of

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the studied compounds on metal surface and formation of protective complex with copper ions. This process disables formation of other corrosion products [26]. This paper brings the results of the study of the influence of 2-amino-5-ethyl-1,3,4-thiadiazole (AETD) on brass corrosion in 3% NaCl. Structure of 2-amino-5-ethyl-1,3,4-thiadiazole is presented in Figure 1.
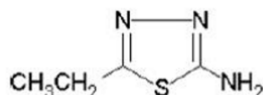

Fig.1. Molecular structure of 2-amino-5-ethyl-1,3,4-thiadiazole (AETD)

Experimental work

Working electrode (Cu37Zn) was prepared by method of casting upward, afterward it was sealed in a mixture based on methyl methacrylate. Prior to each measurement Cu37Zn electrode was polished with emery paper (SiC paper 800 and 2000) and alumina paste ($0.3\mu m$ Al_2O_3) then rinsed with distilled water and dried. Electrochemical measurements were performed in a three-electrode system using saturated calomel electrode (SCE) as the reference electrode and platinum as auxiliary electrode.

The following compounds were used in preparation of the solution: 3% sodium chloride solution (NaCl, VWR Prolabo Belgium), 2-amino-5-ethyl-1,3,4-thiadiazole (Sigma Aldrich Germany) all of p.a. purity. Starting solution of 2-amino-5-ethyl-1,3,4-thiadiazole was $1 \cdot 10^{-2}M$, while the set of working solutions ($1 \cdot 10^{-3}$ - $1 \cdot 10^{-6}M$) was obtained by diluting the starting solution. The effect of electrode immersion in inhibitor solution was also investigated and in that purpose $1 \cdot 10^{-2}M$ aqueous solution of AETD was used.

Electrochemical measurements were performed using a potentiostat (IVIUMSTAT XRe, IVIUM Technologies) with supporting software. Cyclic voltammetry was carried out from -0.8V vs SCE to 1.0V vs SCE. Linear potentiodynamic measurements were performed after open circuit potential (OCP) measurements during 30 min, from OCP to -0.5V vs SCE in cathodic and to 0.0V vs SCE in anodic direction. All the measurements were done in blank NaCl solution, solution of NaCl with inhibitor addition ($1 \cdot 10^{-6}$ - $1 \cdot 10^{-2}M$), as well as in NaCl solution after electrode pretreatment (5, 15, 30, 60 and 1080min) in aqueous $1 \cdot 10^{-2}M$ AETD. Scan rate during linear potentiodynamic measurements was 1mV/s and 10mV/s during cyclic voltammetry. All measurements were done in naturally aerated solutions at ambient temperature.

Results and discussion

Behaviour of the open circuit potential of brass in 3% NaCl without and with the addition of various concentrations of inhibitor during 30 min is presented in Figure 2A, whereas Figure 2B shows values of open circuit potential of brass electrode after immersion for 5, 15, 30, 60 and 1080 min in tested inhibitor solution. Open circuit potential values become more negative with the increase of AETD concentration as well as with longer immersion time, which can be ascribed to inhibitor molecule adsorption

on active sites on electrode surface [11, 27] or to a formation of a film on brass surface that will be discussed further on [28]. The open circuit potential value shift under the influence of inhibitor is not significant so it can be assumed that AETD behaves as mixed-type inhibitor in tested solution.
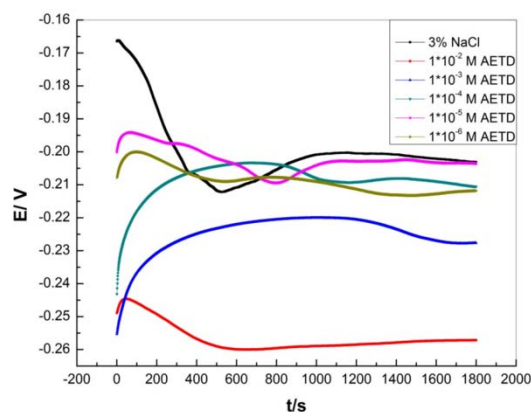

A)
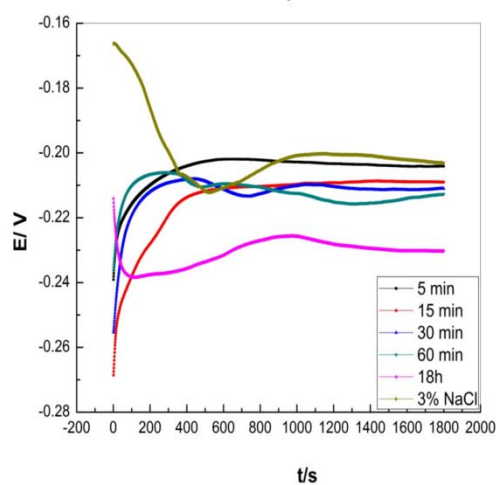
B)

Fig. 2. Open circuit potential of brass in 3% NaCl A) without and with the addition of various concentrations of AETD, B) after immersion for 5, 15, 30, 60 and 1080 min in tested inhibitor solution

It can be observed that OCP values remain almost unchanged regardless the exposure time, when it is 5 or up to 60 min. This shows that the stability of the formed layer does not vary much in that time period. After the pretreatment for 18h film that is formed shows increased stability and compactness in comparison to the one formed during shorter pretreatment.

Since zinc standard electrode potential is more negative in reference to copper, anodic zinc dissolution is expected to occur in tested solutions and can be presented as following [14]:

$$ZnO_{(s)} + H_2O = Zn^{2+} + 2OH^- \tag{1}$$

$$Zn + 4Cl^- = ZnCl_4^{2-} + 2e^- \tag{2}$$
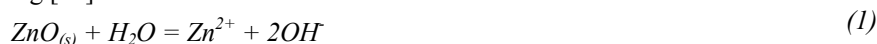
In chloride solutions copper dissolution takes place according to the following equations [29]:

$$Cu = Cu^+ + e^- \tag{3}$$

$$Cu^+ = Cu^{2+} + e^- \tag{4}$$

Process of copper dissolution in chloride media can be initiated by Cu_2O formation [30]

$$2Cu + H_2O = Cu_2O + 2H^+ + 2e^- \tag{5}$$

Cathode process in studied conditions corresponds to oxygen reduction reaction [14]:

$$O_2 + 2H_2O + 4e^- = 4OH^- \tag{6}$$

In cyclic voltammograms of brass presented in Figure 3A, oxidation peak can be observed in 3% NaCl without inhibitor addition as well as with the addition of AETD concentration between $1 \cdot 10^{-6}$ and $1 \cdot 10^{-4}$M. In the presence of $1 \cdot 10^{-3}$M AETD, oxidation current peak is shifted towards positive values indicating a delay of oxidation proceses under studied conditions. The intensity of current peak is also diminished that shows the inhibitory action of AETD. The increase of inhibitor concentration ($1 \cdot 10^{-2}$M) leads to the significant current density decrease and the disappearance of oxidation peak indicating pronounced inhibitory effect of AETD in chloride environment. Current peak occurence is assumed to be a result of CuCl formation according to the reaction [29, 30]:

$$Cu^+ + Cl^- = CuCl \tag{7}$$

Beside this one, two more oxidation peaks, although of significantly lower intensities, can be observed in CV curves. The second peak indicates the process of $CuCl_2^-$ complex formation according to the reaction [28]:

$$CuCl + Cl^- = CuCl_2^- \tag{8}$$

Whereas the third peak is attributed to the process of $CuCl_2^-$ dissolution into bulk solution or process of complex oxidation to Cu^{2+} specie as described by the following reactions [28, 29]:

$$CuCl_2^-{}_{(ads)} = CuCl_2^-{}_{(sol)} \tag{9}$$

$$CuCl_2^-{}_{(ads)} = Cu^{2+} + 2Cl^- + 2e^- \tag{10}$$

Current peak indicating reduction of CuCl to Cu is also visible in CV curves [31]. Significant decrease of current density in the presence of inhibitor in tested NaCl solution can be explained by the formation of protective layer on electrode surface [32]. Mechanism of inhibition of copper corrosion processes by means of azole and azole derivatives application can be described as following:

$$Cu + inh = Cu(inh)_{ads} = Cu^{n+} + ne^- + inh \qquad\qquad (11)$$
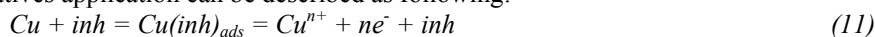
Curves recorded during brass polarization in 3% NaCl solution after electrode pretreatment in $1 \cdot 10^{-2}$M AETD solution for 5, 15, 30, 60 and 1080min are shown in Figure 3B. From figure 3B it is obvious that electrode pretreatment in inhibitor solution does not lead to significant change of the electrode behaviour in 3% NaCl. Comparison of CV curves recorded with electrode modified by pretreatment and the bare electrode in NaCl solution containing inhibitor leads to the same conclusion. Result of the analysis of CV curves recorded after pretreatment in AETD is that no matter how long the pretreatment is**,** brass dissolution takes place in accordance with previously presented reactions. The same result is achieved by Zhang and coworkers [33].
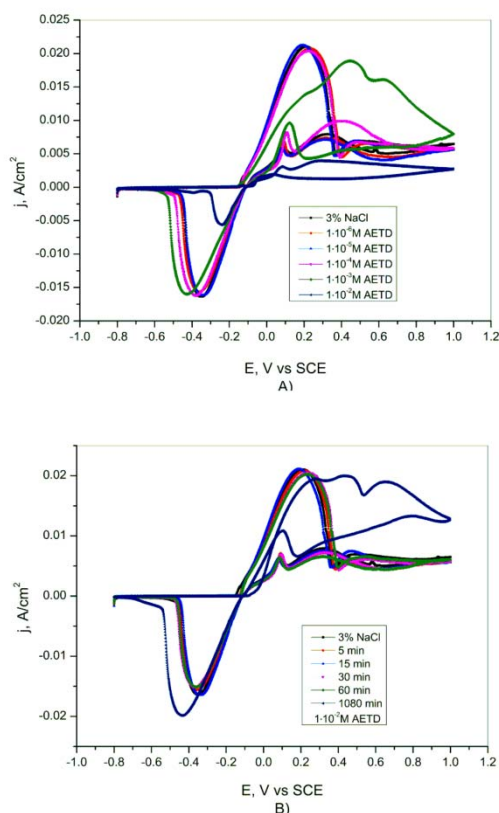

Fig. 3. Cyclic voltammogram of brass in 3% NaCl A) in the presence of various concentrations of AETD, B) after electrode pretreatment in $1 \cdot 10^{-2}$M AETD for 5, 15, 30, 60 and 1080min. Scan rate 10mV/s.

Potentiodynamic polarization curves of brass in 3% NaCl without and with the addition of various AETD concentrations ($1 \cdot 10^{-6}$ - $1 \cdot 10^{-2}$M) are presented in Figure 4A and it is obvious that there is only a minor change of corrosion potential values in AETD concentration interval $1 \cdot 10^{-6}$- $1 \cdot 10^{-3}$M. The addition of $1 \cdot 10^{-2}$M AETD shifts corrosion potential to more negative values. Inhibitor concentration increase leads to a decrease of both cathodic and anodic current density indicating that AETD behaves as mixed-type inhibitor with more pronounced effect on cathodic processes in tested solution [34]. The increase of anodic current density and its approaching the value recorded in blank chloride solution can be ascribed to the defects in the film structure as well as to the film dissolution [35], both allowing agresive ions contact with brass surface resulting in metal corrosion.
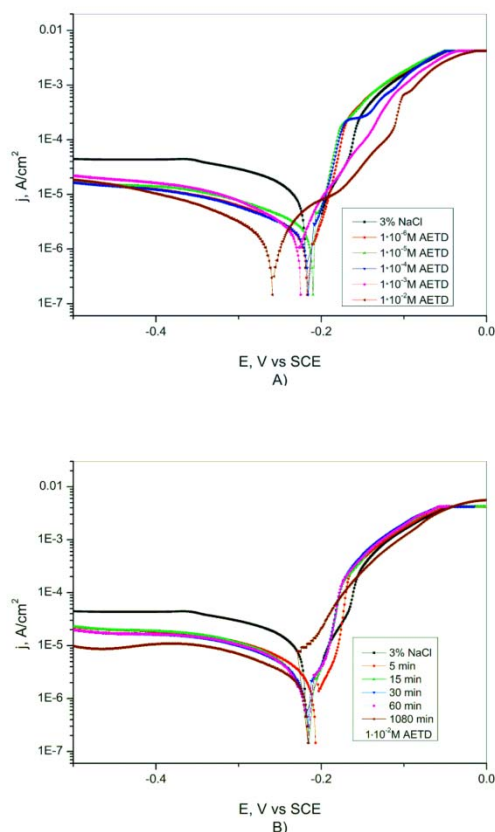

Fig. 4. Brass polarization curves in 3% NaCl A) without and with various concentrations of AETD, B) after pretreatment for 5, 15, 30, 60 and 1080min in AETD. Scan rate 1mV/s.

Brass polarization curves recorded in 3% NaCl after pretreatment in aqueous AETD solution for 5, 15, 30, 60 and 1080min are presented in Figure 4B. It can be noticed that values of corrosion potential change insignificantly in regard to the

measurements conducted without pretreatment. Polarization curves recorded after pretreatment show more pronounced decrease of cathodic current density in comparison to the anodic current. This behaviour is indicative for AETD molecule adsorption on the cathodic active sites and formation of protective film, able to inhibit cathode processes in chloride solution, during electrode pretreatment. More pronounced effect with the prolonged pretreatment leads to an assumption that more stabile and compact layer forms on electrode surface. Corrosion parameters for brass and inhibition efficiency values are presented in Table 1. Inhibition efficiency is determined using following equation:

$$IE\% = [(j_{corr} - j_{corr(inh)}) / j_{corr}] \cdot 10 \qquad (12)$$

where: j_{corr}– corrosion current density in uninhibited solution; $j_{corr(inh)}$ – corrosion current density in inhibited solution.

Table 1.Electrochemical parameters of brass in 3%NaClwithout and with the addition of AETD and after thepretreatment in AETD for different time periods

C_{inh}	t [min]	E_{corr} [Vvs SCE]	b_c	b_a	j_{corr}[A/cm^2]	IE [%]
0	/	-0.225	-0.306	0.106	$1.31 \cdot 10^{-5}$	/
$1 \cdot 10^{-6}$ M	/	-0.218	-0.309	0.026	$3.5 \cdot 10^{-6}$	73.3
$1 \cdot 10^{-5}$ M	/	-0.217	-0.175	0.027	$2.53 \cdot 10^{-6}$	77.9
$1 \cdot 10^{-4}$ M	/	-0.216	-0.206	0.026	$2.35 \cdot 10^{-6}$	82.1
$1 \cdot 10^{-3}$ M	/	-0.228	-0.179	0.053	$2.27 \cdot 10^{-6}$	82.7
$1 \cdot 10^{-2}$ M	/	-0.258	-0.070	0.049	$8.97 \cdot 10^{-7}$	93.1
	5	-0.207	-0.077	0.047	$2.84 \cdot 10^{-6}$	78.3
	15	-0.218	-0.059	0.030	$2.75 \cdot 10^{-6}$	79.0
	30	-0.22	-0.043	0.026	$2.56 \cdot 10^{-6}$	80.5
	60	-0.219	-0.054	0.024	$2.17 \cdot 10^{-6}$	83.4
	1080	-0.226	-0.053	0.015	$1.91 \cdot 10^{-6}$	85.4

Based on the results presented in Table 1 it can be noticed that with AETD concentration increase current density decreases in the whole investigated concentration range while at the same time IE increases. Anodic and cathodicTafel slopes (bc and ba) changes point to the formation of protective film on electrode surface [5, 36, 37]. The results also show that the exposure of brass electrode to AETD solution for certain time period leads to current density decrease and IE increase. Values of IE accentuate the importance of proper selection of inhibitor concentration as well as optimal pretreatment time.

Adsorption isotherm

Inhibitor adsorption on metal surface is assumed to be one of the crucial steps in corrosion inhibition mechanism. Elemental informations on interaction between inhibitor and surface of metals can be obtained based on the adsorption isotherm. Mechanism of AETD adsorption on brass surface is tested using Langmuir adsorption isotherm. Figure 5 shows correlation between C/θ and AETD concentration, obtained from surface coverage degree and corresponding AETD concentration.
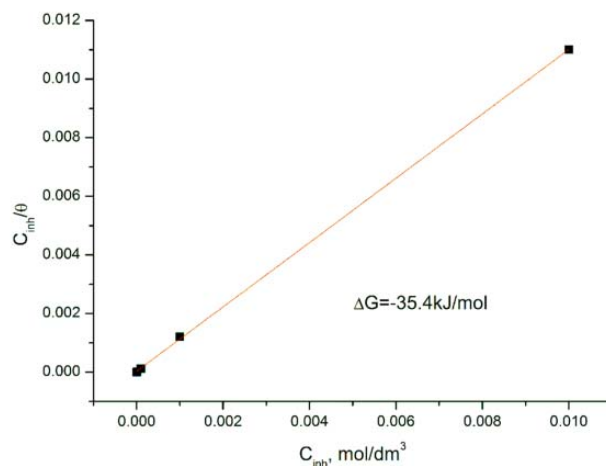
Fig. 5. Langmuir adsorption isotherm of AETD on brass surface in 3% NaCl

Based on the slope of the Langmuir adsorption isotherm, which is 1.1, it can be concluded that one inhibitor molecule gets adsorbed on one active site on the surface of brass. The adsorption of AETD in chloride media can be presented by supstitution reaction between inhibitor molecule and molecule of water on metal surface:

$$AETD_{(sol)} + H_2O_{(ads)} = AETD_{(ads)} + H_2O_{(sol)} \tag{13}$$
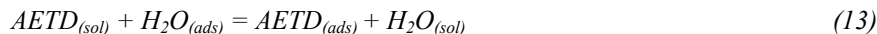
Gibbs free energy of adsorption value is -35.4kJ/mol. This ΔG value suggests strong adsorption of AETD molecule on electrode surface [10, 38].

Conclusion

Results of the experimental studies**,** i.e. OCP shift towards negative values in the presence of inhibitor as well as in the case when electrode is previously immersed in aqueous AETD solution, indicate that AETD molecule adsorbs on brass surface.

Cyclic voltammetry and linear potentiodynamic measurements indicate that protective film containing inhibitor molecules forms on brass surface. Inhibitor concentration and pretreatment time have a decisive influence on the stability of that film. As the stability of film increases IE increases as well. OCP measurements and potentiodynamic measurements show that AETD behaves as mixed-type inhibitor with more pronounced effect on cathodic processes under the studied conditions.

Adsorption of AETD on brass in 3% NaCl occurs according to the Langmuir adsorption isotherm.

Acknowledgements

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