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Corrosion Inhibition of Copper-Nickel Alloy by New Thiadiazole Derivatives in Natural Sea water – Electro-analytical and Surface Characterisation Study

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Abstract: The corrosion inhibition of copper-nickel alloy in natural sea water in the presence of two new thiadiazole derivativeas namely 2-amino-5-(4-ethoxy phenyl)-1,3,4-thiadiazole (AETD) and 2-amino-5-(4-pyridinyl)-1,3,4-thiadiazole (APTD) were   investigated using weight loss measurements and different electrochemical techniques such as potentiodynamic polarization and electrochemical impedance spectroscopy. Polarization measurements showed that the thiadiazole derivatives investigated are mixed type inhibitors, inhibiting the corrosion of copper-nickel alloy by blocking the active sites of the metal surface. Changes in the impedance parameters (charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl})) are related to adsorption of organic inhibitors on the metal surface, leading to the formation of a protective film, which grows with increasing exposure time. A combination of electrochemical methods and surface examination techniques are used to investigate the protective film and explain the mechanistic aspects of corrosion inhibition.
Keywords: copper- nickel alloy, thiadiazoles, polarisation, impedance spectroscopy, natural sea Water.

Introduction

Copper-nickel alloys are extensively used in marine applications because of their good electrical and thermal conductivities, corrosion resistance, and ease of fabrication of the equipment[1]. Copper-nickel alloys alloy is a material of selection for condensers and heat exchangers, where seawater is used as a coolant and in desalination plants[2]. Copper-nickel alloys are resistant to stress corrosion cracking by ammonia and sulphide ions and have good resistance to biofouling due to the release of copper ions[3].This alloy is also resistant to pitting and crevice corrosion in quiet seawater. The corrosion resistance of this alloy is related to the performance of the passive film, which is mainly composed of Cu_2O[4]. Azoles have been widely used as corrosion inhibitors in several environments[5-8].Among the azole compounds, the remarkable efficiency of thiadiazole as a corrosion inhibitor for copper alloys in aqueous environment has been well established for several decades.El-Azhar et al[9].,investigated the corrosion inhibition of mild steel by the new class of inhibitors [2,5-bis(n-pyridyl)-1,2,4-thiadiazoles] in acid media using weight loss and electrochemical impedance

spectroscopy. Results obtained reveal that these compounds are mixed type inhibitors and behave better in 1M HCl than 0.5M H_2SO_4. The influence of various thiadiazole compounds such as 2- amino-5-ethylthio-1,3,4-thiadiazole, 2-amino-5- ethyl-1,3,4-thiadiazole, 1,3,4-thiadiazole-2,5-dithiol (bismuthiol) and 2-amino-5-mercapto-1,3,4-thiadiazole and 2-methyl-5-mercapto-1,3,4-thiadiazole,on copper corrosion in chloride media was studied[10-13].

Materials and Methods

Materials

The material used for this study was copper-nickel alloy supplied in the form of sheet and the chemical composition (weight percent) of the alloy was 69.78% Cu, 29.43% Ni, 0.18% Fe, 0.06 %Sn and traces of Pb , Mn, Ni, Cr, As, Co, Al &Sr as analyzed by optical emission spectrophotometry. The inhibitors 2-amino-5-(4-ethoxy phenyl)-1,3,4-thiadiazoleand 2-amino-5-(4-pyridinyl)-1,3,4-thiadiazole (sigma Aldrich)and ethanol (Fischer) were used as received. The natural sea water was collected near National Thermal Power Corporation (NTPC), Ennore, Chennai, India. The structures of these inhibitors are shown in scheme 1.
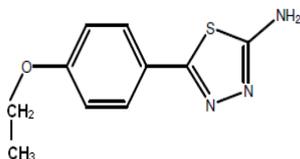
2-amino-5-(4-ethoxy phenyl)-1,3,4-thiadiazole(AETD)
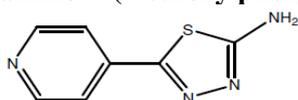
2-amino-5-(4-pyridinyl)-1,3,4-thiadiazole(APTD)

Scheme 1: Structures of thiadiazole derivatives

Methods

Weight-loss method

Weight-loss experiments were conducted with Cu-Ni alloy specimens of dimension 4 cm x 2.5 cm x 0.2 cm. The panels were polished mechanically with silicon carbide papers from 120 to 1200 grit followed by 5 μm diamond paste. The panels were degreased in acetone, thoroughly washed with double distilled water, dried and weighed. Then the panels were immersed in 300 ml of environment (natural sea water) with and without the addition of inhibitors. After immersion for a definite period (5 days) the panels were taken out, washed with distilled water, dried and the changes in weights were noted.

Potentiodynamic polarization studies

The polarization studies were carried out with Cu-Ni alloy strips having an exposed area of1 cm^2. The cell assembly consisted of Cu-Ni alloy as working electrode, a platinum foil as counter electrode and a saturated calomel electrode (SCE) as a reference electrode with a Luggin capillary bridge. Polarization studies were carried out using the Electrochemical work station (Model: CHI 760C, CH Instruments, USA) at a scan rate of 1mV/s. The degreased working electrode is then inserted into the test solution and immediately cathodically polarized at -1.0 V (SCE) for 15 minutes to reduce any oxides on the alloy surface [14]. The cathodic and anodic polarization curves for brass in the test solution with and without various concentrations of the inhibitors were recorded at a scan rate of 1 mV/s. The inhibition efficiencies of the compounds were determined from corrosion current densities using the Tafel extrapolation method. Each experiment was repeated atleast three times to check the reproducibility.

Electrochemical impedance studies

A.C. impedance measurements were conducted at room temperature using an AUTOLAB with Frequency Response Analyzer (FRA), which included a potentiostat model PGSTAT 12. An ac sinusoid of ± 10 mV is employed. The alloy specimen with an exposing surface area of 1cm^2 is used as the working

electrode. A conventional three electrode electrochemical cell of volume 500 ml is used. A saturated calomel electrode (SCE) is used as the reference and platinum plate electrode is used as the counter. All potentials are reported vs SCE.

Scanning electron microscopy

The scanning electron microscopy has unique capabilities for analyzing the surfaces and it is one of the most versatile techniques available for the examination and analysis of the micro structural surface characteristics of the solid surface. The alloy specimens were immersed for the period of 1 hr in sea water with and without optimum concentration of inhibitors, after which they were taken out, washed with distilled water and dried. The morphological changes on the copper-nickel alloy surfaces due to the adsorption of inhibitors were investigated using the micrographs obtained by Scanning electron microscope (JSM-840A SEM JOEL-Japan, Link ISIS, and Oxford instrument UK**).**

Results and Discussion

Weight-loss measurements

The weight loss measurements are the best known and simplest of all corrosion monitoring techniques. The corrosion rates and inhibition efficiencies of copper-nickel alloy with different concentrations of AETD and APTD in natural sea water at room temperature (30^oC) are given in Tables 1. The corrosion rate (CR) and percentage inhibition efficiency (IE %) were calculated using the following equation [15].

$$CR(mmpy) \; = \; \frac{87.6 \, xW}{DxAxT}$$

$$IE\% \; = \; \frac{CR_{(bl)} - CR_{(inh)}}{CR_{(bl)}}x \, 100$$

where W is the weight-loss, D is the density, T is the immersion time, A is the area of the specimen and $CR_{(inh)}$ and $CR_{(bl)}$ are the corrosion rate of copper-nickel alloyin the presence and absence of inhibitors respectively. The corrosion rate decreases with increase in the concentration of the inhibitor. The inhibition efficiency increases with the increase in the concentration of the inhibitor upto the optimum level, thereafter it was found to decrease slightly, which is due to the interaction between adsorbed molecules at the sites. The extent of inhibition depends on the nature and concentration of the inhibitor. The optimum concentration was evaluated on the basis of inhibition efficiency and it was found to be 300ppm for AETD and APTD in natural sea water. The inhibitors have shown the maximum inhibition efficiency of 94.58 and 96.81 respectively for AETD and APTD in natural sea water. The inhibition of corrosion by these compounds can be attributed to their adsorption on the metal surface because of the following interactions.

- The interaction between the π-electrons of the thiadiazole ringand the positivelycharged metal surface, and

- The interaction between the lone pair of electrons of the atoms of nitrogen and the positively charged metal surface

An increase in the size of the molecule of these compounds can lead to more surface coverage and thereby more corrosion inhibition.

Inhibition of corrosion of coper-nickel alloy in natural sea water can be explained in the following way. The adsorption of thiadiazole derivatives on the surface of Cu-Ni alloy leads to the formation of a protective layer of Cu(I)-chloridecomplex on the surface of alloy. Actually the formation of a thiadiazole film starts with the chemisorption of the inhibitor molecule on to the slightly oxidized areas of the copper surface. The adsorption of thiadiazolemolecules on the oxidized parts of the copper surface was found to occur much faster than on bare metal zones. The film formed in this way has a limited hydrophobic action, which succeeds in protecting Cu-Ni alloy in the corroding medium by blocking main reaction centers on the metal surface.

Table 1Weight loss measurements of copper-nickel alloy at different concentrations of AETD and APTD in natural sea water

Inhibitor Concentration (ppm)	Corrosion Rate x 10^{-2} (mmpy)	Inhibition Efficiency (%)
Blank	13.46	-
AETD		
100	4.84	64.04
200	2.38	82.38
300	0.73	94.58
400	0.74	94.50
APTD		
100	4.37	67.53
200	2.09	84.47
300	0.43	96.81
400	0.43	96.81

Potentiodynamic polarization studies

The cathodic and anodic polarization curves of Cu-Ni alloy in natural sea water containing optimum concentrations of AETD and APTD are shown in Figure 1.It is evident that in the presence of inhibitor, the cathodic and anodic curves were shifted towards noble direction and the shift was found to be dependent on inhibitor concentration. Tables 2 illustrate the corresponding electrochemical parameters. The E_{corr} values were shifted in the presence AETD and APTD, which clearly indicated that the inhibitors control the anodic and cathodic reactions and thus act as mixed-type inhibitors. The current density also decreased with increasing concentrations of the inhibitors. The corrosion rates inhibition efficiencies were calculated from polarization curves using the following equation[16].

$$CR = \frac{3.27 \times 10^{-3} \times I_{corr} \times EW}{D}$$

$$IE\% = \frac{I_{corr} - I_{corr\,(inh)}}{I_{corr}} \times 100$$

Where CR is the corrosion rate (mmpy), D is the density (g cm^{-3}), EW is the equivalent weight of the specimen, IE is the inhibition efficiency and $I_{corr\,(inh)}$ and I_{corr} are corrosion current density in the presence and absence of inhibitors respectively.

The inhibition efficiency of AETD and APTD in natural sea water attained a maximum value of 93.70 and 95.25% at 300 ppm concentration respectively. The values of inhibition efficiency increase with increasing concentration of inhibitor, indicating that a higher surface coverage was obtained in the solution with the optimum concentration of inhibitor. The corrosion rate of Cu-Ni alloy in natural sea water was found to be 12.20 x 10^{-2} mmpy and it was minimized by adding the inhibitors to a lower value of 0.77 x 10^{-2}mmpy and 0.58mmpydue to the adsorption of AETD and APTD on the metal surface respectively.
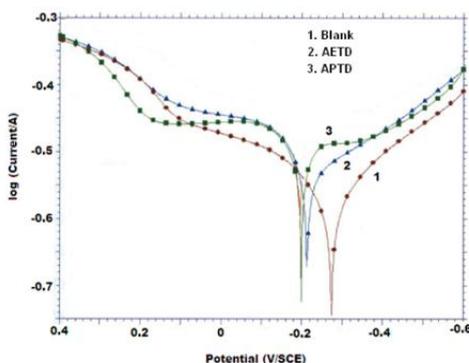

Fig. 1Polarization curves of copper-nickel alloy in natural sea watercontainingoptimum concentrationsof AETD and APTD

Table 2Tafel polarization parameters for the corrosion of copper-nickel alloy in natural sea water at different concentrations of AETD and APTD

Inhibitor concentration (ppm)	I_{corr} ($\mu A\ cm^{-2}$)	E_{corr} (mV vs. SCE)	Corrosion rate x 10^{-2} (mmpy)	Inhibition efficiency (%)
Blank	9.67	-275	12.20	-
AETD				
100	3.88	-256	4.90	59.84
200	2.51	-239	3.17	74.02
300	0.61	-224	0.77	93.70
400	0.62	-228	0.78	93.61
APTD				
100	3.59	-245	4.53	62.87
200	2.32	-226	2.93	75.98
300	0.46	-203	0.58	95.25
400	0.47	-206	0.59	95.16

Electrochemical Impedance studies

The corrosion behaviour of cupro-nickel alloy in natural sea water in the presence of thiadiazole derivatives was investigated by EIS method at room temperature. Nyquist plots of cupro-nickel alloy in inhibited and uninhibited sea water containing different concentrations of AETD and APTD after immersion of 24 hrs is shown in Figure 2. The percent inhibition efficiency (IE %) of corrosion of cupro-nickel alloy was calculated as follows[17]:

$$I.E\ \% = \frac{(R_{ct})^{-1} - R_{ct(inh)})^{-1}}{(R_{ct})^{-1}}\ x\ 100$$

where, $R_{ct(inh)}$ and $R_{ct}$are the charge-transfer resistance values with and without inhibitors respectively. IE% attained 96.12 after 24 hrs immersions with optimum concentration of APTD,which was comparatively higher than that of AETD in natural sea water.
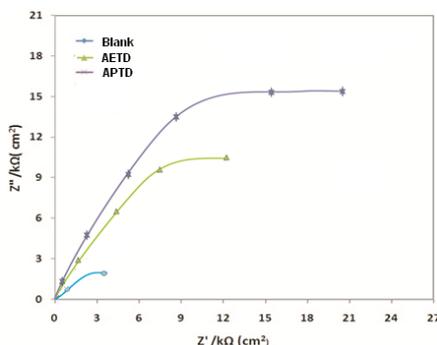

Fig.2 Nyquist diagram of cupro-nickel alloy in natural sea water containing optimum

concentration of AETD and APTD after immersion of 24 hours.

This behaviour was attributed to more surface coverage of APTD on the cupro-nickel alloy surface from sea water. The inhibition efficiency values determined using the polarization curves were lower than those determined by EIS experiments, this difference was probably due the shorter immersion time in the case of the polarization measurements. Impedance parameters derived from these investigations are given in Table 3. In the presence of optimum concentration of inhibitors, R_{ct} values increased, whereas C_{dl} values tended to decrease. The term (C_{dl}) is voltage dependant and in aqueous media this capacitance is typically a few tens of microfarads per square centimeter, and the measured value can be used to estimate the effective area of a

corroding electrode. The decrease in C_{dl} values was caused by adsorption of thiadiazole derivatives on the metal surface. The tendency to decrease in C_{dl}, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the thiadiazole derivatives function by adsorption at the metal-solution interface. The change in R_{ct} and C_{dl}values was caused by the gradual replacement of water molecules by the chloride ions of the sea water and adsorption of the substituted thiadiazole molecules on the metal surface, reducing the extent of dissolution[18].

Table3   Electrochemical Impedance data of copper-nickel alloy in natural seawater containing different concentrations of AETD and APTD.

Inhibitor concentration (ppm)	$R_{ct}x\ 10^4$ $(\Omega\ cm^2)$	C_{dl} $(\mu F\ cm^{-2})$	IE (%)
Blank	0.242	6.427	-
AETD			
100	0.619	1.512	60.89
200	1.004	0.314	75.89
300	4.662	0.042	94.81
APTD			
100	0.683	0.772	64.57
200	1.125	0.192	78.49
300	6.234	0.027	96.12

Scanning Electron Microscopy

SEM investigations were carried out to verify whether the studied inhibitors, AETD and APTD are adsorbed on the alloy surface. The SEM micrograph for cupro-nickel alloy surface in the absence and presence of optimum concentration of thiadiazole derivatives are shown in Figure 3(a,b and c). The micrographs of the surface after polarization experiment are analyzed. The alloy surface in the absence of inhibitors was found to be severely affected in seawater (Fig. 3a). The metallic surface seems to be not affected by corrosion in the presence of AETD and APTD inhibitor molecules (Fig. 3 b and c). At the optimum concentration of the inhibitors, the surface is covered by a thin film of inhibitor which effectively controls the dissolution of the alloy. A comparison of SEM micrographs obtained in the absence and in the presence of the AETD and APTD molecules reveals a significant inhibiting effect of these compounds.
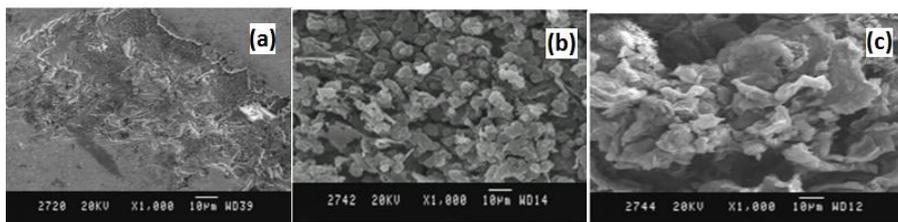

Fig. 3   SEM micrographs of copper-nickel alloy immersed in natural sea water containing optimum concentration of (a)blank (b)AETD and (c)APTD

Conclusions

1. Both AETD and APTD show good inhibition efficiency in natural sea water. The %IE of APTD was higher than that of AETD.
2. The polarization studies indicated that the inhibitors considerably shifts the corrosion potential to less negative values and greatly decreases the corrosion current density. These studies give valuable information regarding Cu-Ni alloy in the absence and presence of thiadiazole derivatives, which is proved to be a mixed inhibitor, predominantly anodic in nature.
3. Electrochemical impedance spectroscopy shows that R_{ct}values increase, while C_{dl} values decrease in the presence of AETD and APTD.
4. SEM studies confirm the presence of protective film on the alloy surface.

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