Corrosion Inhibition of Copper in Sea Water Using Derivatives of Thiosemicarbazides

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Abstract

Three corrosion inhibitors namely: 4-allyl-3-thiosemicarbazide $C_4H_9N_3$ S, 4-(1-methyl)-3-thiosemicarbazide,4-tolyl-3-thiosemicarbazide were tested as corrosion inhibitors for copper in sea water environmnt.Copper samples were tested using potentiodynamic polarization technique in the absence and in the presence of corrosion inhibitors.   High inhibition efficiencies (≥95%) were shown by the tested inhibitors. The best performance was shown by 4-tolyl-3-TSC.

Introduction

Semicarbazide, known as carbohydrazide, is the chemical compound with the formula $OC(NH_2)(N_2H_3)$. It is a water-soluble white solid. It is a derivative of urea prepared by treating urea with hydrazine.   A thiosemicarbazide is the analog with sulfur atom in place of oxygen atom. Semicarbazones are derived by the condensation reaction between a ketone (or aldehyde) and a semicarbazide [1].

Thiosemicarbazide and its derivatives are used as corrosion inhibitors for different metallic substrates [2-7]. *Thiosemicarbazide* and thiocarbohydrazide functionalized chitosan were evaluated as ecofriendly *corrosion* inhibitors for carbon steel in hydrochloric acid solution [2]. Al-Bonayan [3] used thiosemicarbazide and 4-phenyl thiosemicarbazide as corrosion inhibitors of carbon steel in 2 N H_3PO_4 solutions. The inhibition efficiency increases with increase in inhibitors concentrations and decreases with raising temperature. The influence of thiosemicarbazide, phenylthiosemicarbazide on the corrosion rate of steel in 2 MHCl was investigated [4]. Results showed that all the compounds investigated acted as cathodic-type inhibitors. The corrosion inhibition efficiency of synthesized 2-(1-methyl-4-((E)-(2-methylbenzylidene)amino)-2-phenyl-1H-pyrazol-3(2H)-ylidene)-hydrazineecarbothioamide (HCB) on mild steel in 1.0 M HCl was investigated [5]. The results showed that HCB inhibited mild steel corrosion in acidic solution and inhibition efficiency increased with an increase in the concentration of the inhibitor. The inhibition efficiency of 1,4-bis (2-nitrobenzylidene) thiosemicarbazide (BBTS) on the corrosion of mild steel in 1 mol/L HCl was investigated [6]. The results showed that this compound had good inhibiting properties for mild steel corrosion in hydrochloric acid and BBTS was a mixed-type inhibitor. In the study of Wazzan [7], thiosemicarbazide, arylisothiocynates, and 1-aryl-2,5-dithiohydrazodicarbonamides were investigated as corrosion inhibitors of copper in an aqueous chloride solution.

The present paper compares the corrosion inhibition efficiency of some thiosmicarbazide derivatives in sea water environment.

2. Experimental

Disc specimens were prepared from electrolytic copper (99.9 %) having a diameter of 1.5 cm^2. Disc specimens were fixed in the corrosion cell so that an area of 0.785 cm^2 was exposed to the testing solution. Specimens were polished using SiC papers successively up to 2400 grits to acquire a mirror-like finish. After polishing, specimens were thoroughly washed with distilled water and dried in air.

Potentiodynamic polarization curves were measured on the Cu electrodes using a conventional three-electrode cell with a Ag/AgCl reference electrode and a Pt sheet counter electrode. The potential was controlled using a computerized potentiostat (AutoLab PG STAT 30). The potential was scanned from -0.3 V below the E_{corr} towards 1 V above the E_{corr} at a scan rate of 1 mVs^{-1}.Experiments were carried out in 0.6 mol L^{-1}NaCl solution simulating sea water environment. Corrosion parameters: corrosion current (I_{corr}), corrosion potential (E_{corr}) and corrosion rate (CR) were deduced from the analysis of polarization curves using the AutoLab software.

Three corrosion inhibitors namely: (1)4-allyl-3-thiosemicarbazide (ATSC) whose molecular formula is$C_4H_9N_3S$, (2)4-(1-methyl)-3-thiosemicarbazide (MTSC) whose molecular formula is $C_{11}H_{11}N_3S$, (3)4-tolyl-3-thiosemicarbazide(TTSC)$C_8H_{11}N_3S$were dissolved in the least amount of dimethylformamide (DMF) or sodium hydroxide and added in the desired amount to the testing media (3.5% NaCl) so as to give 500, 100 , and 2000 ppm. Measurements were performed at 20 ± 1^oC while the testing solution was open to air.

3. Results and Discussion

Figures 1-3 show the cyclic anodic polarization curves of the tested corrosion inhibitors. The best behavior is shown by inhibitor MTSC where a clear passive region exhibited by the inhibitor at all concentrations (500-2000 ppm). On the other hand, areas under the cyclic polarization loop is small indicating the low susceptibility of copper towards pitting corrosion in the presence of the inhibitor. Alternatively, corrosion inhibitor TTSC shows a comparable behavior to inhibitor MTSC showing the same passive region as inhibitor MTSC. However, the areas under the cyclic polarization loop is relatively higher than the one shown by inhibitorMTSC indicating more susceptibility towards pitting corrosion. The worst behavior is shown by corrosion inhibitor ATSC where no noticeable passive regions are obtained.

Table (1) shows the corrosion parameters derived from the polarization curves. Very low corrosion currents and corrosion rates are shown by the tested inhibitors. Corrosion inhibition efficiencies as high as 98% are shown. According to Table (1), the highest inhibition efficiency is shown by Inhibitor (3) followed by Inhibitor (2) and finally Inhibitor (1).

Table 1. Corrosion parameters including corrosion current (I_{corr}), corrosion potential (E_{corr}) and corrosion rate (CR) derived from potentiodynamic curves of copper in 0.6 M NaCl in the absence (blank) and in the presence of corrosion inhibitors
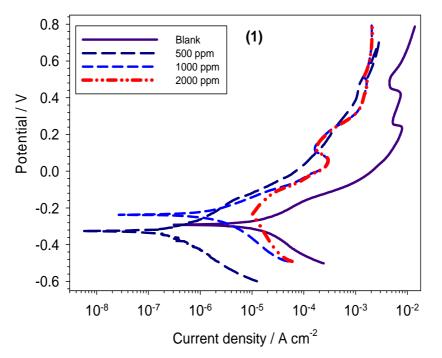
	E_{corr} / V	I_{corr}/ Acm^{-2}	Corrosion Rate/ mm/y	% Inhibition
Blank				
	-0.236	1.479x 10^{-5}	0.1716	
ATSC C$_4$H$_9$N$_3$S				
500 ppm	-0.237	6.432 x 10^{-6}	0.0482	71.911
1000 ppm	-0.411	1.048 x 10^{-6}	0.0078	95.454
2000 ppm	-0.390	1.863 x 10^{-6}	0.0082	95.221
MTSC C$_{11}$H$_{11}$N$_3$S				
500 ppm	-0.240	6.54 1x10^{-7}	0.0049	94.463
1000 ppm	-0.275	1.018 x 10^{-6}	0.0076	95.571
2000 ppm	-0.320	1.795 x 10^{-6}	0.0079	95.954
TTSC C$_8$H$_{11}$N$_3$S				
500 ppm	-0.329	3.783 x 10^{-7}	0.0028	98.369
1000 ppm	-0.360	6.297 x 10^{-7}	0.0047	97.261
2000 ppm	-0.365	1.249 x 10^{-6}	0.0055	96.795

Figure 1: Potentiodynamic polarization curves of copper in 0.6 mol L^{-1}NaCl
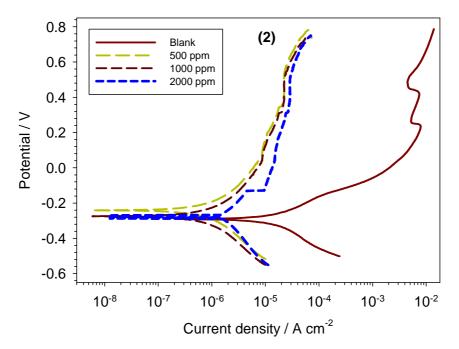in the presence of ATSC at 20ºC

Figure 2: Potentiodynamic polarization curves of copper in 0.6 mol L^{-1}NaCl
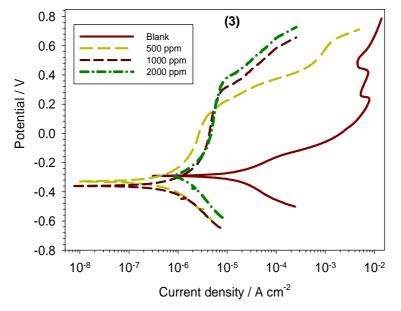in the presence of MTSC at 20ºC

Figure 3: Potentiodynamic polarization curves of copper in 0.6 mol L^{-1}NaCl

in the presence of TTSC at 20ºC

During the anodic polarization of copper in the salt solution containing inhibitors, anodic current density is considerably reduced compared to the current density obtained in the solution without the inhibitor. The extent of reduction of the current density is increased with the increase of the inhibitor concentration for inhibitor TTSC, slightly decreased in the presence of ATSC and remains unaffected in the presence of MTSC. The enhancement in corrosion resistance of copper in the presence of the thiosemicarbazide inhibitor can be attributed to the formation of a protective layer on copper surface. For example; the inhibitor 4-(1-methyl)-3-thiosemicarbazide has the form MTSC-H in weakly acidic, neutral, and weakly alkaline media where the H enotes hydrogen attached to the N atom of the molecule. The inhibitor form a protective film of Cu(I)MTSC complex on the copper surface, i.e. [8-10]:

$$Cu + MTSC\text{-}H = Cu(1)MTSC + e^- \qquad [3]$$

The degree of surface coverage at different concentrations of inhibitor can be obtained from the following expression:

$$\theta = \frac{I_{corr(b)} - I_{corr(inh)}}{I_{corr(b)}} \times 100 \qquad [4]$$

where $I_{corr(b)}$, $I_{corr(inh)}$ represent corrosion current densities in the absence and in the presence of the inhibitor, respectively. Polarization curves were used to deduce the surface coverage values (Table2) for different inhibitor concentrations. The interaction of inhibitor with the copper surface is best described using the Langmuir isotherm. This isotherm is [11-12]:

$$\theta/1\text{-}\Theta = AC\ exp\ [-E^{\#}/RT] = KC \qquad [5]$$

where θ is the surface coverage, $E^{\#}$ is the activation energy, C is the concentration in mol L^{-1} and K is the constant of the adsorption process. The above equation can be simplified as:

$$C/\Theta = 1/K + C \qquad [6]$$

Table 2: The degree of surface coverage versus concentration of the inhibitor

Concentration, ppm	500	1000	2000
θ of ATSC	71.911	95.454	95.221
θ of MTSC	95.57	95.571	95.954
θ of TTSC	98.369	97.261	96.795

A plot of C/θ versus C yields a straight line with intercept 1/K. Figure4-6 show the relationship between C/θ and C for the three tested inhibitors. Linear regression of the obtained straight line was used to obtain 1/K and consequently K.The relationship between the adsorption constant (K) and the standard free energy of adsorption (ΔG^o) is given by [13]:

$$K = 1/55.55 \ exp[-\Delta G^o/RT] \qquad\qquad [7]$$

where R is the universal gas constant and T is the absolute temperature. Standard free energy of adsorption (ΔG^o) of -35.242, -37.659 and-38.605 kJ mol^{-1}are obtained for ATSC, MTSC and TTSC, respectively. The negative value of ΔG^o indicates the spontaneity of the adsorption reaction of the inhibitors on the copper surface. It also points to chemisorption occurring in the interaction of inhibitors and the surface of copper where charge sharing or transfer from the inhibitor molecules to the copper surface forms a co-ordinate type of bond.

Thiosemicarbazide derivatives inhibit the corrosion of copper by adsorption at the metal/solution interface. Corrosion inhibition results from the presence of free electron pairs in the sulphur atoms, p-electrons on the aromatic rings, molecular size and the formation of metallic complexes. The unshared and p-electrons interact with d-orbital of Cu to provide a protective film. The inhibitive properties of such compounds depend on the electron densities around the active center, the higher the electron density at the active center, the   more influence is   the inhibitor [14-15].
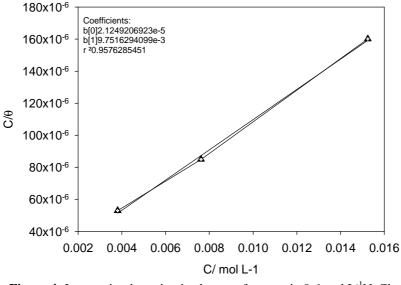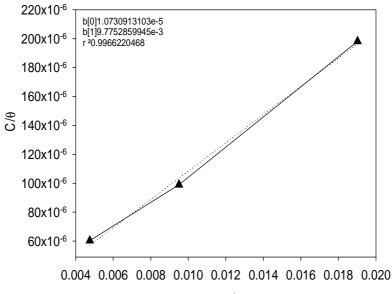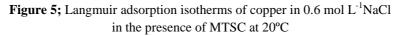

Figure 4; Langmuir adsorption isotherms of copper in 0.6 mol L^{-1}NaCl
in the presence of ATSC at 20ºC

Figure 5; Langmuir adsorption isotherms of copper in 0.6 mol L^{-1}NaCl
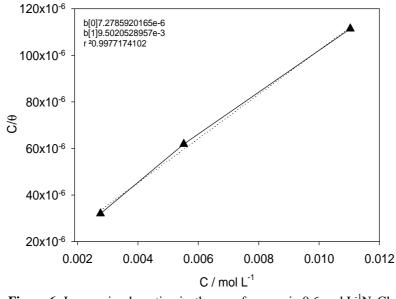in the presence of MTSC at 20ºC

Figure 6: Langmuir adsorption isotherms of copper in 0.6 mol L^{-1}NaCl
in the presence of TTSC at 20ºC

4. Conclusions

Thiosemicarbazide derivatives show quite high corrosion inhibition efficiency (>95). The high inhibition efficiency of thiosemicarbazides can be attributed to the formation of a protective film of Cu(I) Inhbitor complex on the copper surface. The inhibition efficiency of tested thiosemicarbazides obeys Langmuir adsorption isotherms while the calculated free energy of adsorption indicates chemisorptions of the inhibitor on copper surface.

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