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CORROSION INHIBITION OF ALUMINIUM BY CYCLOHEXYLAMINE DITHIOCARBAMATE IN ACIDIC SOLUTION

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ABSTRACT. The role of cyclohexylamine dithiocarbamate (CHDTC) in the corrosion inhibition of aluminium in 1 M HCl solution is investigated by weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy, and scanning electron microscopy techniques. The results suggest that CHDTC is a good inhibitor with mixed-type character for aluminium in acidic solution. Both anodic and cathodic processes on the metal surface are hindered and there is a direct relationship between the concentration of CHDTC and the inhibition efficiency. The inhibition mechanism involves the adsorption of CHDTC on the metal surface as seen from the equivalent circuit analysis of the EIS results. Weight loss experiments are carried out with aluminium samples in 1 M HCl solution at room temperature and the same trend of inhibition is produced. Scanning electron microscopy (SEM) is used to image the surface at the different stages of the corrosion inhibition processes. Adsorption of CHDTC molecules onto the aluminium surface can be concluded as a function of concentration.

Keywords: *Aluminium, corrosion inhibition, cyclohexylamine dithiocarbamate, acidic solution, weight loss, polarization, EIS, SEM*

INTRODUCTION

Among non-ferrous metals, aluminium is the most widely used metal with the largest total production. It enters a large number of applications as a pure metal or alloyed [1]. Aluminium has valuable electrical industrial applications due to its negative value of standard electrode potential [2].

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The literature is abundant with research studies on the corrosion behavior of aluminium and its alloys in aqueous acidic solutions [3-11]. The corrosion inhibition of aluminium involves the strong adsorption of inhibitor molecules on the metal surface and ultimately suppressing the cathodic and anodic processes.

Dithiocarbamate derivatives have been extensively studied due to their antimicrobial activity and the various applications in industrial and chemical processes, such as vulcanization accelerators, flotation agents, fungicides, pesticides, and corrosion inhibitors. One of the most interesting properties of dithiocarbamates is their strong metal-binding ability and the ease to form self-assembled monolayers (SAMs) on metallic surfaces making them useful to many applications including corrosion inhibitors [12].

There has been a good number of research articles employing green or biocompatible corrosion inhibitors as a safe alternative [13,14]. Dithiocarbamates are considered as safe biocompatible compounds.

In this paper, the synthesized compound cyclohexylamine dithiocarbamate (CHDTC) is tested as a corrosion inhibitor for aluminium in 1 M HCl aqueous solution using weight loss, polarization, electrochemical impedance spectroscopy (EIS), and scanning electron microscopy (SEM) techniques. The obtained results showed that dithiocarbamate could serve as an effective corrosion inhibitor. For organic compounds, it is well established that corrosion inhibition occurs via adsorption of their molecules on the metal surface. The efficiency of inhibition depends on multiple factors including the chemical characteristics of the adsorbed layers.

RESULTS AND DISCUSSION

Weight loss measurements

Table 1 shows the results of the weight loss experiments. It is evident that CHDTC inhibits the corrosion rate of aluminum in 1 M HCl and the inhibition efficiency increases with increasing the inhibitor concentration. We can see that the optimum inhibition efficiency was achieved around $2x10^{-3}$ M and a further increase in the inhibitor concentration did not improve the inhibition efficiency. This may be attributed to adsorption saturation of the inhibitor on the metal surface. The effect of varying the immersion time in the inhibitor and temperature of solution on the inhibition efficiency was studied for selected concentrations but no apparent effect was noticed. However, all experiments were carried out at 25 ^{o}C using a water bath.

Table 1. Percent inhibition of CHDTC from weight loss experiments of Al in 1 M HCl. Time of immersion is 24 h. for all samples. The surface area was approximately 9.6 cm^2

Sample no.	CHDTC concentration M	Mass before g	Mass after g	Mass change g	Corrosion Rate ($mg/h.cm^2$)	Inhibition Efficiency %
0	0	2.1063	1.9906	0.1157	0.50217	
1	2.0×10^{-6}	2.1245	2.0584	0.0661	0.28689	42.9
2	8.0×10^{-6}	2.1220	2.0620	0.0600	0.26042	48.1
3	3.0×10^{-5}	2.1038	2.0532	0.0506	0.21962	56.3
4	1.0×10^{-4}	2.1271	2.0779	0.0492	0.21354	57.5
5	2.0×10^{-3}	2.1130	2.0720	0.0410	0.17795	64.6
6	8.0×10^{-3}	2.1183	2.0755	0.0428	0.18576	63.0

Polarization measurements

Potentiodynamic polarization curves of aluminium in 1 M HCl solution without and with different concentrations of the inhibitor CHDTC are shown in Figure 1. It is observed that both the cathodic and anodic processes are hindered upon the addition of CHDTC. The polarization curves were recorded for inhibitor concentrations ranging between 2×10^{-6} and 8×10^{-3} M at around 25 ^{o}C. The electrochemical parameters such as corrosion current density (Icorr), corrosion potential (Ecorr), Tafel constants, ba and bc, and % inhibition efficiency were calculated from Tafel plots (Table 2). It is observed that the presence of the inhibitor lowers the corrosion current density and reaches a minimum value at the highest inhibitor concentration. It is also observed that Ecorr values and the Tafel constants ba and bc do not change significantly as a function of the inhibitor concentration indicating that CHDTC behaves as a mixed type inhibitor.

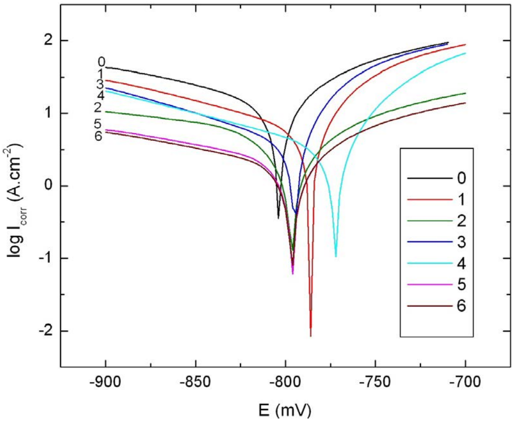

Figure 1. Polarization curves for the corrosion of aluminium in 1 M HCl in the absence and presence of different concentrations of CHDTC in M as listed in Table 1 (first two columns). Scan rate: 10 mV/s.

Table 2. Electrochemical corrosion parameters of Al in 1M HCl without and with different concentrations of CHDTC

Curve no. (Figure 1)	CHDTC Concentration M	Icorr μA cm^{-2}	Corrosion Rate mm/Year	Inhibition Efficiency % (using Icorr)	Inhibition Efficiency % (using Corrosion Rate)
0	0	14.3	167.0		
1	2.0×10^{-6}	6.2	72.7	56.6	56.5
2	8.0×10^{-6}	5.4	63.7	62.0	61.9
3	3.0×10^{-5}	4.1	48.4	71.4	71.0
4	1.0×10^{-4}	3.3	39.0	76.9	76.7
5	2.0×10^{-3}	2.1	25.1	85.0	84.9
6	8.0×10^{-3}	1.9	21.8	86.9	86.9

Electrochemical impedance spectroscopy

The Electrochemical impedance measurements (Nyquist plots) were obtained for the different aluminium samples at the open-circuit potential after immersion in various concentrations of the inhibitor for 30 minutes. The impedance diagrams were then recorded for aluminium in 1 M HCl and are shown in Figure 2. The experimental data were fitted using the equivalent circuit shown in Figure 3 from which the circuit parameters were evaluated.

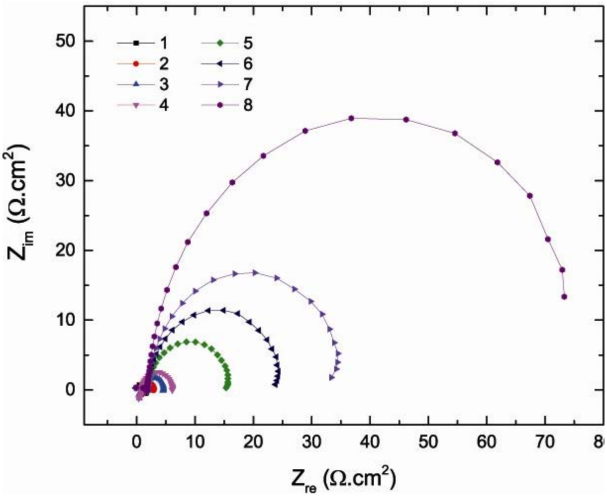

Figure 2. Nyquist plots of the EIS measurements for pure aluminium in 1.0 M HCl solution after immersion of the aluminium samples in different molar concentrations of the inhibitor 1) 0, 2) 2.0×10^{-6}, 3) 8.0×10^{-6}, 4) 3.0×10^{-5}, 5) 1.0×10^{-4}, 6) 5.0×10^{-4}, 7) 2.0×10^{-3} and 8) 8.0×10^{-3}.

The values of the electrochemical parameters: R_s, C_{DL}, R_{CT} and the calculated percent inhibition efficiency (%IE) are listed in Table 3. We noticed that the values of R_{CT} and the IE% increase with increasing the inhibitor concentration. However, the values of C_{DL} decreased upon increasing the inhibitor concentration. The decreasing trend in C_{DL} is due to the adsorption of the inhibitor on the surface of aluminium. The impedance curves consist of one single capacitive loop indicating that the corrosion of aluminium is primarily dominated by charge transfer. The shapes of the impedance curves are similar indicating that the corrosion mechanism is similar in all the samples. The diameter of the capacitive loop in the presence of inhibitor are always larger than that in blank solution, and extends as a function of the inhibitor concentration. This indicates that the impedance of inhibited metal is directly proportional to the inhibitor concentration.

Table 3. Electrochemical impedance parameters evaluated for the aluminium electrode in 1 M HCl after immersion in various inhibitor concentrations using the equivalent circuit in Figure 3

Concentration of inhibitor (M)	R_S Ohm.cm^2	C_{DL} mF/cm^2	R_{CT} Ohm.cm^2	IE%
0	1.31	131	0.97	
2.0 x10^{-6}	1.11	89	1.91	49.2
8.0 x10^{-6}	1.17	92	2.19	55.7
3.0 x10^{-5}	0.871	48	5.26	81.6
1.0 x10^{-4}	1.87	56	14.2	93.2
5.0 x10^{-4}	1.92	44	22.9	95.8
2.0 x10^{-3}	1.94	48	33.5	97.1
8.0 x10^{-3}	2.16	34	75.0	98.7

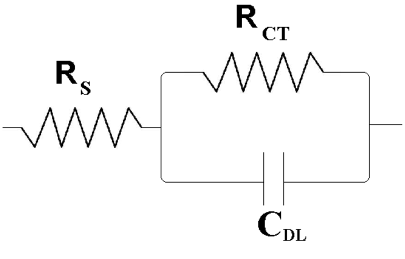

Figure 3. The equivalent circuit for the metal-solution interface used to model the EIS data for Al in 1 HCl solution.

Scanning Electron Microscopy (SEM) surface analysis

To provide a closer look at the surface modifications and hence establish a link between the surface morphology and the corrosion mechanism, scanning electron micrographs were taken for aluminium samples immersed in 0.1 M HCl for 60 minutes. Prior to that the samples were immersed in different concentrations of the inhibitor CHDTC for 30 minutes. The longer immersion times were needed to cause noticeable difference in the SEM images. The image in Figure 4a is for aluminium in the corrosive medium without the inhibitor (HCl only). Figure 4(b-d) are for aluminium in the corrosive medium pretreated with an inhibitor concentration of 2.0 x10^{-6}, 1.0 x10^{-4}, and 8.0 x10^{-3}, respectively. It is clear that the absence of the inhibitor increases the roughness of the surface of aluminium upon immersion in HCl solution (Figure 4a). The molecules of CHDTC adsorb to the surface as a function of concentration making a protective layer that decreases the rate of corrosion of aluminium (Figure 4b-4d).

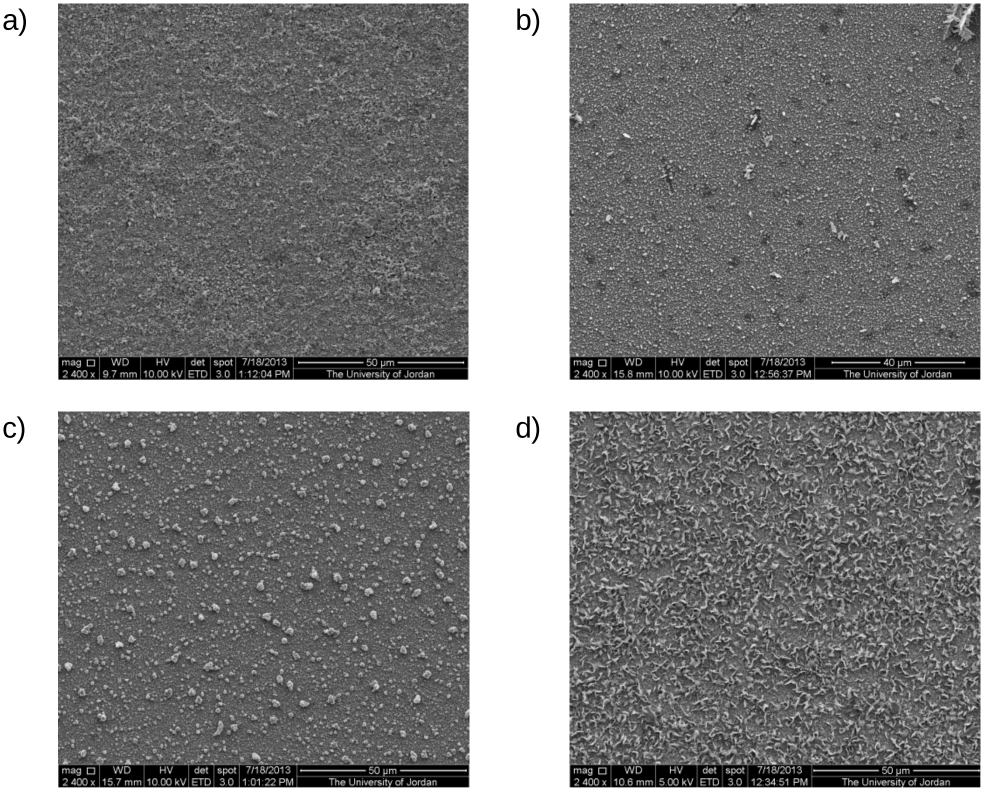

Figure 4. SEM images (x2400) of aluminium surface after immersion in 0.1 M HCl for 60 minutes pretreated (for 30 minutes) with CHDTC of concentrations (M): a) 0, b) 2.0 x10^{-6}, c) 1.0 x10^{-4} and d) 8.0 x10^{-3}.

CONCLUSIONS

Cyclohexylamine dithiocarbamte, CHDTC, showed reasonable corrosion inhibiting behavior for aluminium in 1 M HCl. In weight loss studies, the %IE of the CHDTC increases with increasing the inhibitor concentration. Polarization measurements suggest that CHDTC behave as a mixed-type inhibitor for aluminium in 1 M HCl. The electrochemical impedance study shows that the application of CHDTC as an inhibitor increases R_{CT} values and decreases C_{DL} values in 1 M HCl, suggesting that corrosion inhibition is governed by surface adsorption. This finding is also supported by SEM images. The different techniques used to in this study showed the same trend in corrosion inhibition with differences in %IE absolute values due to the individual technique parameters and sensitivity.

EXPERIMENTAL SECTION

Cyclohexylamine was purchased from Aldrich (99%), sodium hydroxide, NaOH (Aldrich), carbon disulfide, CS_2 (97%) and ethanol, absolute (99%), sulfuric acid, H_2SO_4 (98%), potassium ferrocyanide, $K_3Fe(CN)_6$ (99.0%), potassium chloride, KCl (99.9%), Hydrochloric acid, HCl (98%) and ammonium peroxydisulfate, $(NH_4)_2S_2O_8$ (99%) were all of analytical grade and used as received. The sodium salt of cyclohexyl dithiocarbamate (CHDTC) was synthesized as reported in the literature with modification [3].

Aluminium samples of size 2 cm x 2 cm x 0.2 cm were cut to be used for weight loss measurements. For potentiodynamic polarization studies, the exposed area of the aluminium surface was adjusted to be 1 cm^2. Electrodes were polished with emery papers of fine grade and degreased with acetone and rinsed with distilled water. Distilled water was used to prepare all solutions of 1 M HCl.

For the weight loss measurements, aluminium samples were polished, cleaned and dried in a stream of nitrogen then weighed accurately. Each of the samples was then fully immersed in a 50 mL beaker containing 1 M HCl and a different concentration of the inhibitor, CHDTC. The solutions were kept in a water bath set at room temperature. The aluminium samples were removed after 6 hours of immersion, washed with distilled water, dried, and weighed. At least three aluminium samples were used to produce an average value for the weight loss.

Electrochemical experiments were carried out with a VoltaLab PGZ 100 potentiostat in a double-wall three-electrode glass cell. Prior to measurements, the surface of the working electrode (Al) was carefully polished with alumina slurry, rinsed several times with distilled water, and then sonicated for about 1 minute. All reported potential values are versus the saturated calomel electrode (SCE) as a reference electrode and all measurements were carried out at room temperature. A platinum wire was used as the auxiliary electrode. Solutions' pH values were measured with a Hanna calibrated digital pH meter (Switzerland). All glassware for electrochemical experiments were carefully cleaned by immersion in a solution of concentrated sulfuric acid containing ammonium peroxydisulfate $(NH_4)_2S_2O_8$ for overnight followed by copious rinsing with distilled water.

Aluminium samples were immersed in the test solution for a few minutes until a steady open-circuit potential (OCP) was attained. The polarization curves were measured from a cathodic potential of -100 mV to an anodic potential of +100 mV with respect to the open circuit potential (OCP) at a scan rate of 10 mV/s. The generated Tafel plots were analyzed by extrapolation to evaluate the corrosion potential (Ecorr) and the corrosion current densities (Icorr). Several measurements were carried out for each experiment to ensure the reproducibility of data. EIS measurements were carried out in the 10 Hz - 100 kHz frequency range at OCP for the aluminium electrode at different CHDTC concentrations in a thermostated cell set at room temperature. There was 10 points per decade in all measurements and the AC sine wave amplitude was 10 mV. The surface of the aluminium samples immersed in 0.1 M HCl solution with and without the adsorption of CHDTC were analyzed using Inspect F50/FEG scanning electron microscope (FEI, The Netherlands) at an accelerating voltage of 5–10 kV.

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