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The Corrosion Inhibition Of Aluminium In 3.5% NaCl By Diisopropyl Thiourea

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Abstract: The Inhibition of Aluminum corrosion in 3.5% NaCl solution using diisopropyl thiourea (DISOTU) has been reported by weight loss, electrochemical polarization technique, impedance method and quantum mechanical measurement. It was found that the compound effectively reduces the aluminum corrosion in the sea water medium. It was also noticed that the mere adsorption of the compound on metal surface follows Langmuir adsorption isotherm. The inhibition efficiency (IE) increases as the inhibitor concentration is increased. Quantum mechanical studies confirm the adsorption of protective layer of inhibitor on aluminium surface.

Keywords : Corrosion inhibitor, Thiourea , Impedance measurements, Quantum studies.

Introduction

The ultra light metal of aluminium and its alloys are widely applied to the fields of aerospace, automobile, electronic products, etc. However, the surface of aluminium and its alloys needs to be protected when it is exposed to marine and hard water media. Organic compounds containing sulphur, nitrogen and oxygen atoms are capable of retarding metallic corrosion. As the thiourea molecule contains one sulphur and two nitrogen atoms, thiourea and its derivatives have been proved as potential corrosion inhibitors. While extensive investigations have been carried out on inhibitor properties of thiourea, due attention has not yet been paid to a systematic study of inhibitor action of thiourea derivatives. However, several substituted thiourea have been investigated as corrosion inhibitors[4]. Most of the effective organic inhibitors have heteroatoms such as O, N, S containing multiple bonds in their molecules through which they can absorb on the metal surface[5-8]. The corrosion inhibiting property of these compounds is attributed to their molecular structure. The lone pair determines the adsorption of these molecules on the metal surface. All the above studies reveal the one common observation that thiourea derivatives can be regarded as excellent corrosion inhibitors. The present paper describes a study of corrosion protection action of Diisopropyl thiourea on corrosion of aluminium in 3.5% NaCl using weight loss, gasometric measurements and various electrochemical techniques.

The present inhibitor is an organic compound with π-electrons and heteroatom's S, N & O. The molecule is large enough (Melting point :140) and sufficiently planar to block more surface area due to adsorption on mild steel. These factors favour the interaction of DISOTU with the aluminium. As far as we know no concrete report has been published so for DISOTU in sea water media. The optimized structure of the DISOTU is shown in figure 1. Different concentrations of inhibitor were prepared, and their inhibition efficiency in 3.5% salt water was investigated.

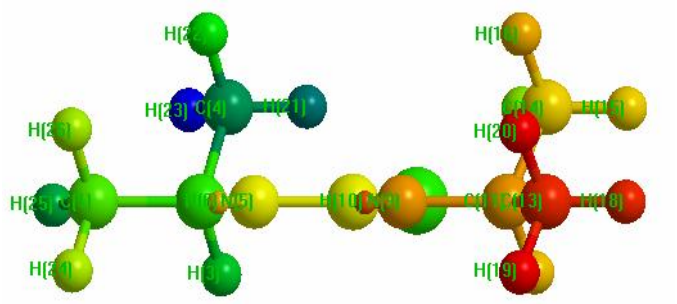

Figure 1.Optimized Structure of DISOTU

Experimental details

Aluminium specimens of compositions, Cu = 0.15%, Mg = 0.5%, Mn = 0.1%, Si = O.5%, Zn = 0.5%, and Aluminium remainder, and of size 4 x 1 x 0.020 cm were used for weight loss and gasometric studies. Aluminium cylindrical rod of the same composition as above and embedded in araldite resin with an exposed area of 0.7 cm^2 was used for potentiodynamic polarisation and AC impedance measurements.

The inhibitor was preliminarily screened by a weight loss method described earlier[9] Both cathodic and anodic polarisation curves were recorded in sea water media potentiodynamically (1 mv s-1) using corrosion measurement system BAS Model : 1OOA, computerised electrochemical analyser (made in West Lafayette, Indiana) and PL-10 digital plotter (DMP-40 series, Houston Instruments Division). A platinum foil(4 cm^2) and Hg/Hg2Cl /3.5%NaCl were used as auxiliary and reference electrodes, respectively. Double layer capacitance (Cdl) and charge transfer resistance values (R,) were obtained using AC impedance measurements as described in an earlier publication[10]. Quantum calculations were carried using Gaussian 03 software package. The energy of highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and dipole moment (μ) of the inhibitor were calculated with the above given computer code package.

Results and Discussion

Weight loss and Gasometric measurements

Table 1 gives the values of inhibition efficiency for different concentrations of DISOTU for the corrosion of Al in 3.5% NaCl obtained from weight loss and gasometric measurements. It is found that the compound inhibits the corrosion of aluminium efficiently in salt water. The inhibition of corrosion of brought about by TDETU can be due to the following interactions:

1. The interaction between the lone pairs of electrons of the sulfur atom of the organic molecule and the positively charged metal surface[10].
2. The interactions between lone pairs of electrons of the nitrogen atoms and the positively charged metal surface[11].
3. The presence of two isopropyl groups in the molecule which shows inductive (+I) effect may enhance the electron density on the sulfur atom that escorts to better performance than the unsubstituted thiourea[12].

It is found that there is a good agreement between the values of inhibition efficiency obtained by weight loss and gasometric methods.

Potentiodynamic polarization studies

Table 2 gives values of corrosion kinetic parameters such as Tafel slopes (ba and bc),corrosion current (Icorr) and corrosion potential (Ecorr) and efficiency obtained from potentiodynamic polarization curves for aluminum in 3.5% NaCl having different concentrations of DISOTU.

It can be visualized from the table that values of Tafel slopes and I_{corr} are really much similar to those reported earlier[12,13]. Further it is established that enhancing the concentrations of DISOTU improves the values of both b_a and b_c, but the values of b_c are enhanced to a greater extent. So the inhibition of corrosion of aluminium in 3.5% NaCl is under cathodic control. E_{corr} values are shifted to less negative values in the presence of different

concentrations of compound. This can be attributed to the formation of strongly adsorbed film on the metal surface. The presence of increasing concentrations of DISOTU reduces I_{corr} values in 3.5% NaCl.

Impedance measurements

Corrosion inhibition of aluminium in 3.5% NaCl solution with and without inhibitor was investigated by electrochemical impedance spectroscopy measurements are presented **in table 3.** The values of the charge transfer resistance (R_t) is started to increase with the increase in concentration of compound in 3.5% NaCl solution whereas values of double layer capacitance (C_{dl}) are fetched down by increasing concentrations of inhibitor. This can be ascribed to increasing the adsorption of the compound on the aluminium surface with an increase in its concentration. Similar observation has been made earlier by Harikumar[15] for the corrosion inhibition of mild steel by Ampicilin drug.

Table 1. Values of inhibition efficiency for the corrosion of aluminium in 3. 5%NaCl in the presence of different concentrations of Diisopropyl thiourea (DISOTU) obtained from weight loss and gasometric measurements.

Concentration of Inhibitor (ppm)	Inhibition efficiency (%)	
	Weight loss Studies	Gasometric measurements
Blank	---	---
40	57	56.7
80	66	66.2
120	91	90.8

Table 2: Corrosion kinetic parameters of AL in 3.5%NaCl in the presence of different concentrations of DISOTU obtained from potentiodynamic polarization studies.

Con. DISOTU	E_{corr} (mV vs SCE)	I_{corr} (μA cm^{-2})	βa (mV dec^{-1})	βc (mV dec^{-1})	IE (%)	Ø
Blank	-875	350.57	184.0	175.3	-	
40 PPM	-867	120.37	170.2	152.0	57.10	0.57
80 PPM	-858	86.50	166.6	131.3	66.76	0.67
120 PPM	-776	32.45	110	105.2	90.74	0.91

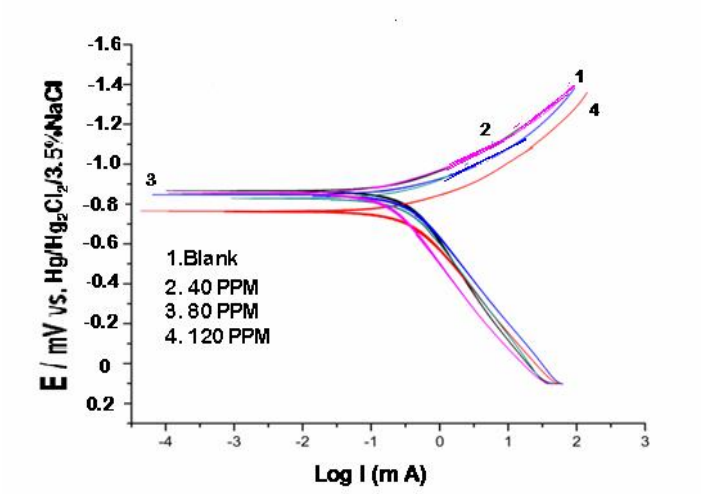

Figure 2 Tafel plots for the corrosion inhibition of AL in 3.5% NaCl in the presence of DISOTU

Table 3. Impedance parameters for the corrosion of AL in 3.5%NaCl in the presence of different concentrations of Diisopropyl thiourea .

Concentration of Inhibitor (ppm)	3.5%NaCl	
	Charge Transfer resistance (R_t) Ohm.cm^2	Double layer capacitance (C_{dl}) µF.cm^{-2}
Blank	26	188
40	126	163
80	134	101
120	150	65

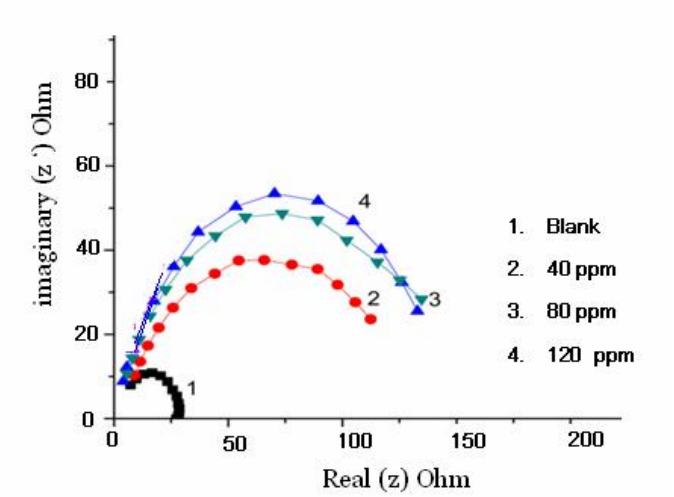

Figure 3. Impedance plots for the corrosion inhibition of Al in the presence and absence of inhibitor.

Table 4: Quantum mechanical parameters for DISOTU on the corrosion of steel in salt water.

Inhibitor	LUMO (eV)	HOMO (eV)	aE (Cal.Mol^{-1})	Dipole moment (Debye)
DIISOPROPYL THIOUREA	0.65961	-7.73488	8.399	4.0

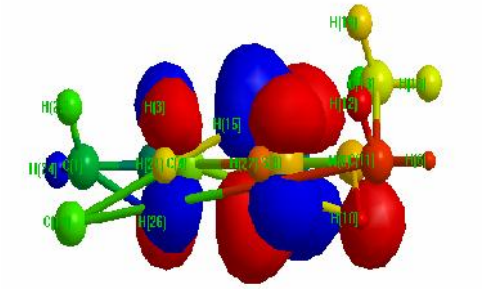

Figure 4. HOMO of DISOTU

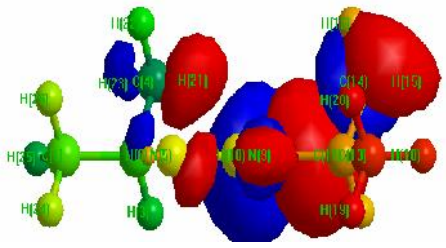

Figure.5.LUMO of DISOTU

Quantum mechanical studies

The computed quantum chemical parameters like energy of highest occupied molecular orbital (EHOMO), energy of lowest unoccupied molecular orbital (ELUMO), LUMO- HOMO, energy gap (DE), dipole moment (µ), are summarized in Table 4. From figure 4 and 5, it can be observed that HOMO and LUMO energy orbitals were strongly localized on one isopropyl moiety and nitrogen, sulphur atoms of thiourea moiety and almost nil, on another isopropyl moiety .This could be due to larger size of the compound .Also consolidating the opinion of several researchers that p electrons and hetero atoms are responsible for inhibition activity[16-20].

According to Tang et al[21], when a molecule possess similar frontier orbitals, its inhibition efficiency can be correlated to the energy levels of HOMO and LUMO and the difference between them. It has been enormously claimed that, higher the value of E_{HOMO}, greater is the ease for an inhibitor to donate electrons to unoccupied d orbital of metal atom.In addition, the lower the LUMO energy, the easier the acceptance of electrons from metal surface, as the LUMO−HOMO energy gap decreased and the efficiency of inhibitor improved and higher is the inhibition efficiency. The gap between HOMO–LUMO energy levels of molecules was another prominent parameter that needs to be considered. Smaller the value of ΔE of an inhibitor, higher is the inhibition efficiency of that inhibitor. It has been reported that, large values of the dipole moment will enhance corrosion inhibition[22-24].

Conclusions

1. Diisopropyl thiourea inhibits the corrosion of aluminium effectively in 3.5%NaCl .
2. The inhibition of corrosion reaction follows cathodic control.
3. Rt and Cdl values obtained from impedance measurements confirm the better performance of the compound.
4. The quantum chemical parameters substantiate the inhibition efficiency of DISOTU determined by electro chemical methods.

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