

Evaluation of Ethylenediaminetetra-acetic Acid Di-Sodium Salt as Corrosion Inhibitor for Mild Steel in 1M Hydrochloric Acid

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Abstract: The influence of ethylenediaminetetra-Acetic acid di-sodium salt (EDTA di-sodium) on the corrosion of mild steel in 1 M hydrochloric acid solution was investigated by means of weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The efficiency of EDTA di-sodium salt was compared with thiourea. Primary results obtained revealed that EDTA di-sodium salt performed as corrosion inhibitor for mild steel in 1M hydrochloric acid media. Polarization curves show that the behavior of EDTA di-sodium and thiourea are mixed-type inhibitors. EIS shows that the control step for corrosion process is a charge transfer mechanism.

Key words: corrosion inhibitor, ethylenediaminetetra-acetic acid di-sodium salt, thiourea, mild steel, electrochemical measurement

INTRODUCTION

Mild steel is widely used as a constitutional material in many industries due to its good mechanical properties and low cost. The corrosion of mild steel is of fundamental academic and industrial concern that has received a considerable amount of attention. Acid pickling baths are employed to remove undesirable scale from the surface of the metals. Once the scale is removed, the acid is then free for further attack on the metal surface. The use of inhibitor is one of the most practical methods for protection against corrosion, especially in acidic media.

A survey of literature reveals that the applicability of organic compounds as corrosion inhibitors for mild steel in acidic media has been recognized for a long time. Compounds studied as inhibitors include triazole derivatives [Bentiss, *et al.* 1999a; Bentiss, *et al.* 1999b; Mernari, *et al.* 2002; Ramesh and Rajeswari, 2004], bipyrazolic derivatives [Touhami, *et al.* 2000], surfactants [Algaber, *et al.* 2004; Branzoi, *et al.* 2000] aromatic hydrazides [Quraishi, *et al.* 2001], organic dyes [Oguzie, *et al.* 2004; Oguzie, *et al.* 2005.], Poly (4-vinylpyridine) [Larabi, *et al.* 2004] and thiosemicarbazide-type organic compounds [Ita, and Offiong, 1999; Benali, *et al.* 2006]. These compounds can adsorb on the mild steel surface and block the active sites decreasing the corrosion rate.

The aim of this work is to study the effect of ethylenediaminetetra-Acetic acid di-sodium salt (EDTA di-sodium salt), $C_{10}H_{16}N_2O_8Na_2$, Fig. 1, on corrosion inhibition of mild steel in 1 M hydrochloric acid solutions comparing with thiourea.

Experimental:

Commercially mild steel metal was used. Sample was mechanically polished using SiC paper in successive grades from 200 to 1500 and was rinsed with methanol. The acid solutions were made from AR grade HCl. Appropriate concentration of acid was prepared by using distilled water. For weight loss experiments, mild steel specimens for each inhibitor were immersed in test acid solution for one hour at 30 °C. After one hour the mild steel specimen were taken out, rinsed in water and methanol and finally dried. Then the loss in weight was determined by analytic balance.

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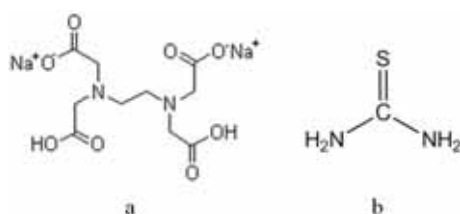


Fig. 1: Molecular structures for EDTA di Sodium salt (a) and thiourea (b)

For electrochemical experiments, the measurements were carried out in a three electrodes water jacket cell with a graphite counter electrode and saturated calomel electrode (SCE) as reference. potentiodynamic polarization curves were obtained starting from E_{corr} with the potential scan rate of $125 \mu\text{V/s}$. EIS measurement was carried out on steady state open circuit potential (OCP) disturbed with amplitude of 10 mV A.C. sine wave at frequencies between 0.01 Hz and 100 KHz. Measurements were performed at 30°C using Gamry instrument Potentiostat/Galvanostat/ZRA (Ref600 model).

RESULTS AND DISCUSSION

Weight loss experiments:

Values of inhibition efficiency IE% and corrosion rate (mpy) obtained from weight loss method for various concentrations of EDTA di-sodium and thiourea are summarized in Table 1 and 2. The inhibition efficiency IE % was obtained by:

$$IE\% = \frac{W^{\circ} - W}{W^{\circ}} \times 100$$

where W° and W are the corrosion rates of mild steel in the absence and presence of the inhibitor, respectively. It can be found that the rise in the inhibitor concentration lead to an increase inhibition efficiency.

Table 1: Polarization parameters and EIS parameters for mild steel in 1 M HCl with different concentrations of EDTA di-sodium.

Technique	Parameters	Blank	Inhibitor concentration (mg/l)				
			10	20	40	80	160
Weight loss	Weight loss(mpy)	281.20	269.39	260.67	242.96	237.90	232.83
	IE%	0	4.20	7.30	13.60	15.40	17.20
Polarization parameters	Ecorr (mV)	493	488	475	469	459	446
	Icorr ($\mu\text{A}/\text{cm}^2$)	615	591	572	544	523	510
	β_a (mV/decade)	0.12	0.11	0.12	0.10	0.12	0.11
	β_c (mV/decade)	0.14	0.13	0.12	0.12	0.14	0.12
	IE%	0	3.90	6.99	11.54	14.95	17.07
EIS parameters	Rp (ohm. cm ²)	36.5	37.68	40.45	42.49	43.51	44.51
	Cdl ($\mu\text{F}/\text{cm}^2$)	173.9	152.9	121.3	118.3	103.8	97.2
	IE%	0	3.13	9.76	14.09	16.11	17.99

Table 2: Polarization parameters and EIS parameters for mild steel in 1 M HCl with different concentrations of thiourea.

Technique	Parameters	Blank	Inhibitor concentration (mg/l)				
			10	20	40	80	160
Weight loss	Weight loss(mpy)	281.20	233.96	187.00	164.39	125.98	101.94
	IE%	0	16.80	33.50	41.54	55.20	63.75
Polarization parameters	Ecorr (mV)	493	510	512	507	514	513
	Icorr ($\mu\text{A}/\text{cm}^2$)	615	504	431	371	298	234
	β_a (mV/decade)	0.12	0.11	0.10	0.11	0.10	0.12
	β_c (mV/decade)	0.14	0.13	0.13	0.13	0.12	0.13
	IE%	0	18.05	29.92	39.67	51.54	61.95
EIS parameters	Rp (ohm. cm ²)	36.5	68.27	73.64	84.64	86.59	95.55
	Cdl ($\mu\text{F}/\text{cm}^2$)	173.9	147.4	135.2	127.2	114.5	85.4
	IE%	0	46.53	50.43	56.87	57.84	61.8

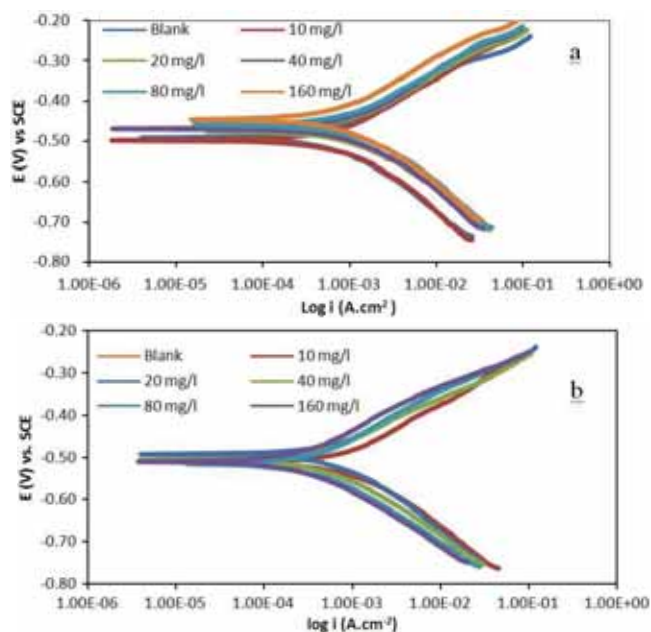


Fig. 2: Polarization curves for mild steel in 1 M HCl with different concentrations of EDTA di-sodium (a) and thiourea (b)

Polarization measurements:

The effect of the concentration of EDTA di-sodium and thiourea are shown in Fig.2 which presents the anodic and cathodic Tafel curves of mild steel in 1 M HCl. Values of anodic β_a and cathodic β_c Tafel constant and corrosion current density are listed in Table 1 and 2. These values were calculated from the intersection of the anodic and cathodic Tafel lines of the polarization curve at E_{corr} . The inhibition efficiencies are calculated by the following expression:

$$IE\% = \frac{i_{uninhibit} - i_{inhibit}}{i_{uninhibit}} \times 100$$

where $i_{uninhibit}$ and $i_{inhibit}$ are respectively, the corrosion current density without and with EDTA di-sodium or thiourea in 1 M HCl solution.

The anodic and cathodic Tafel lines for mild steel in presence of EDTA di-sodium or thiourea were almost parallel upon increasing inhibitor concentrations. This suggests that the inhibitor act by simple blocking the mild steel surface [Manahan, 1996]. In the other words, the inhibitor decreasing the exposed surface area for corrosion as well as it doesn't affect the mechanism of mild steel dissolution or hydrogen evolution reaction. Only when the change in E_{corr} value is no less than 85 mV, a compound can be recognized as an anodic or a cathodic type inhibitor [Ashassi-Sorkhabi, et al. 2004]. The largest displacement of the corrosion potentials (E_{corr}) were about 53 mV and 11 mV in presence of EDTA di-sodium and thiourea, respectively. Therefore, EDTA di-sodium and thiourea are acts as corrosion mixed-type inhibitors.

EIS measurements:

The results of EIS were figured by Nyquist plots, Fig 3. Double layer capacitance values (Cdl) and polarization resistance values (R_p) were obtained from impedance as described elsewhere (Ashassi-Sorkhabi, et al. 2004). The fitted values of R_p and Cdl are listed in Table 1 and 2. The inhibition efficiencies $IE\%$ is calculated by polarization resistance (R_p) as follows:

$$IE\% = \frac{R_{p_{uninhibit}} - R_{p_{inhibit}}}{R_{p_{uninhibit}}} \times 100$$

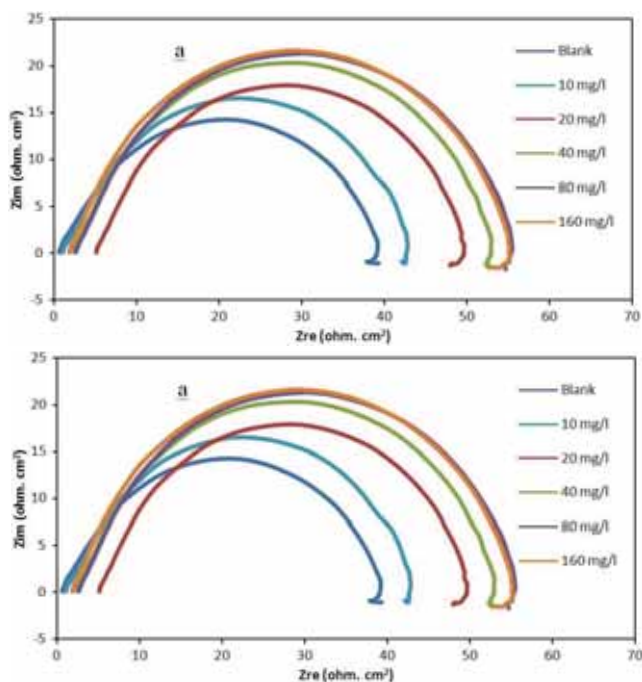


Fig. 3: Nyquist plots for mild steel in 1 M HCl with different concentrations of EDTA di-sodium(a) and thiourea(b)

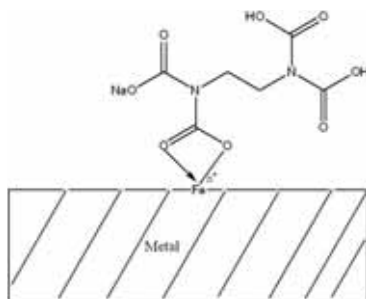


Fig. 4: Interaction between carboxylate groups in EDTA with the metal

The R_p values increase with the increase in concentration of either EDTA di-sodium or thiourea, indicating an insulated adsorption layer's formation; the decrease in C_{dl} values suggested a decrease in local dielectric constant between the metal and electrolyte induced by the adsorption of EDTA di-sodium or thiourea [Khaled and Hackerman, 2004].

Fig.4 shows that the carboxylate groups in EDTA adsorbed on the steel surface through the lone pairs of electrons of the oxygen atoms forming a covering film. This arrangement of the oxygen atoms may lead to the conclusion that the carboxylate compound is forced to be adsorbed horizontally onto the steel surface. This adsorption gives rise to a large covered surface area with a small number of adsorbed molecules. Therefore, good inhibition efficiency could be obtained by relatively low concentrations of the inhibitor.

CONCLUSION

- EDTA di-sodium compounds can adsorb on the mild steel surface and block the active sites decreasing the corrosion rate.
- Polarization curves indicated that the EDTA di-sodium and thiourea behave mainly as mixed-type inhibitors.
- EIS showed that the charge transfer controls the corrosion process in the uninhibited and inhibited solutions either for EDTA di-sodium or thiourea.
- Inhibition efficiencies increase with increasing inhibitors concentration.

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