Effect of Avogadro natural oil on the corrosion inhibition of mild steel in hydrochloric acid solution

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Abstract The inhibition action of Avogadro natural oil on corrosion of mild steel in one molar hydrochloric acid solution was investigated by gravimetric and potentiodynamic polarization techniques. The surface morphology of as-corroded samples was assessed with high resolution scanning transmission electron microscopy equipped with energy dispersive spectroscopy (HR-STEM/EDS). From the results, the presence of Avogadro natural oil in the metal–acidic interface decreased the corrosion rate with all the exposure times. The inhibition efficiency (%IE) increases with the concentration of the inhibitor considered. Results obtained from gravimetric measurements indicate that the natural oil exhibited higher efficiencies of 93.26 % after 384 h of exposure time and 98.26 % recorded in the potentiodynamic polarization method, both at 4.5 g/v inhibitor addition. Equally, results from the linear polarization indicated higher potential value with an increase in the polarization resistance (R_p) and lower current density for the inhibited samples than the uninhibited mild steel sample. The inhibitive effect of this oil was explained in view of adsorption on the metal surface. The adsorption process follows the Langmuir adsorption isotherm.

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Introduction

The wide usage of mild steel for numerous applications has been attracted by its properties, including low cost and availability [1, 2]. However, the ability of mild steel to resist corrosion attack in some environments remains insufficient, and a search for method(s) for improving this limitation has become necessary. In the literature, various techniques have been reported as addressing the degradation characteristics of mild steel in some environments. Among these methods, the use of inhibitors has gained recognition as an effective and promising means of improving the corrosion resistance of mild steel [1–14].

Recently, chemical and synthetic compounds used as inhibitors for corrosion prevention have been regarded as non-ecologically friendly inhibitors [1, 6, 15] and also expensive [2]. In that direction, plant oils have become important inhibitors that are considered cheap, safe and non-toxic for a wide range of corrosion prevention and control [1, 3]. In this work, the potential of Avogadro natural oil as a corrosion inhibitor on mild steel in one molar hydrochloric acid (1 M HCl) has been investigated using gravimetric and potentiodynamic polarization techniques.

Experimental procedures

Materials and sample preparation

A mild steel coupon of $20 \times 10 \times 3$ mm with chemical composition shown in Table 1 was used for the corrosion study. The samples were degreased in ethanol, dried, weighed and stored in a desiccator. The initial weight of each sample was taken and recorded. A concentration of 1 M HCl was prepared fresh as required for the experiment. Avogadro natural oil was used as an inhibitor in mild steel/HCl acid solution. The natural oil used was obtained from Technology Innovation Agency, Chemical Station, Ga-Rankuwa, Tshwane University of Technology, Pretoria. The corrosion measurements were conducted at 298 K in a static solution.

Gravimetric and electrochemical corrosion measurement

The gravimetric corrosion test was carried out on the previously weighed samples with and without inhibitor at 298 K. The volume of the solution was 100 mL with

Table 1 Chemical composition of the mild steel used

Element	C	Mn	Si	P	S	Al	Ni	Fe
Composition (wt%)	0.15	0.45	0.18	0.01	0.031	0.005	0.008	Balance

and without the addition of the Avogadro natural oil inhibitor. The Avogadro natural oil inhibitor's concentration was varied from 1.5, 3.0, and 4.5 g/v in 100 ml of 1 M HCl acidic solution. For each sample in the Avogadro natural oil–HCl solution after the corrosion test, they were washed, dried and weight taken at intervals of 96, 192, 288 and 384 h of exposure time. The corrosion rate (mm/year), degree of surface coverage (θ) and inhibitor efficiency (%IE) were determined.

An electrochemical corrosion test was conducted using the potentiodynamic polarization technique according to ASTM G3-89 and ASTM 5-94 standards. The conventional three-electrode electrochemical cell system was used. The electrochemical cell was made of a 500-ml Pyrex glass conical flask suitable for the conventional three-electrode system. The mild steel samples were used as the working electrode, graphite rods as the counter electrodes, and Ag/Ag; 3 M KCl as the reference electrode (SCE). Electrochemical measurements were carried out with the General Purpose Electrochemical Software with the NOVA 3.0 package. All the measurements were made at room temperature in mild steel–Avogadro natural oil–1 M HCl solution. From the Tafel corrosion analysis, the corrosion rate, potential and linear polarization resistance were obtained.

Surface morphology

The surface morphology of as-received and as-corroded mild steel were examined with high resolution scanning transmission electron microscope equipped with energy dispersive spectroscopy to analyze the elements on the surface (Joel JSM-7600F).

Results and discussion

Results

Table 1 shows the chemical composition of as-received mild steel sample used. The results obtained from the gravimetric corrosion measurement for mild steel in 1 M HCl solution along with the variation in inhibitor concentration can be found in Table 2 and Fig. 1. Table 3 shows the electrochemical corrosion data obtained for mild steel–HCl–Avogadro natural oil interface, while Fig. 2 indicates the polarization curves for the mild steel. The SEM micrographs of the surface morphology of as-corroded uninhibited/inhibited mild steel–HCl samples are presented in Fig. 3a, b. Percentage inhibition efficiency (%IE) for Avogadro natural oil using different methods for corrosion assessment can be found in Fig. 4, while in Fig. 5, the Langmuir adsorption isotherms have been demonstrated for the interfaces.
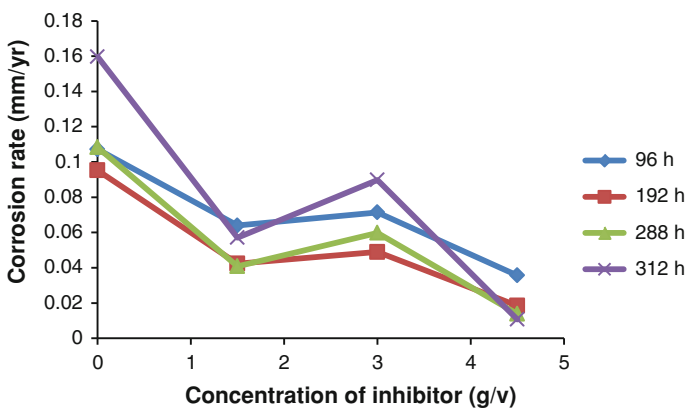
Discussion

Gravimetric measurement

Avogadro natural oil was used for the study of mild steel–HCl corrosion behavior with different inhibitor concentrations at 298 K. At each concentration, the

Table 2 Corrosion rate (CR), degree of surface coverage (θ) and inhibition efficiency for mild steel in 1 M HCl solution with and without Avogadro natural oil addition obtained from gravimetric technique at 298 K

| Exposure time (h)	Concentration of inhibitor (g/v)	CR (mm/year)	Degree of surface coverage (θ) in HCl	Inhibition efficiency (%) in HCl
96	0	0.1072	–	–
	1.5	0.0640	0.4013	40.13
	3.0	0.7140	0.3333	33.33
	4.5	0.0357	0.6666	66.66
192	0	0.0953	–	–
	1.5	0.0424	0.6118	61.18
	3.0	0.0490	0.4856	48.56
	4.5	0.0185	0.8049	80.49
288	0	0.1084	–	–
	1.5	0.0409	0.6226	62.26
	3.0	0.0598	0.4483	44.83
	4.5	0.0139	0.8710	87.10
384	0	0.1597	–	–
	1.5	0.0571	0.6421	64.21
	3.0	0.0898	0.4372	43.72
	4.5	0.0107	0.9326	93.26

Fig. 1 Variation of corrosion rate with concentration of inhibitor for mild steel in 1 M HCl with and without Avogadro natural oil addition at 298 K

corrosion rate (mm/year) was calculated and the inhibitor efficiency IE(%) was determined using Eqs. 1 and 2 below;

$$CR = \frac{W_o - W_a}{A_t} \tag{1}$$

Table 3 Electrochemical corrosion data obtained for mild steel in 1 M HCl solution with and without Avogadro natural oil addition obtained from polarization technique at 298 K

| S/N	C (g/v)	I_{corr} (A/cm^2)	b_a (v/dec)	LPR R_p (Ω cm^2)	$-E_{corr}$ (V)	CR (mm/year)
1	0	1.10E−3	0.60101	45.202	0.44027	1.4650
2	1.5	1.33E−04	0.08060	94.249	0.36773	0.1769
3	3.0	8.53E−05	0.07729	141.06	0.36707	0.1136
4	4.5	1.91E−05	0.16304	573.05	0.36329	0.0255
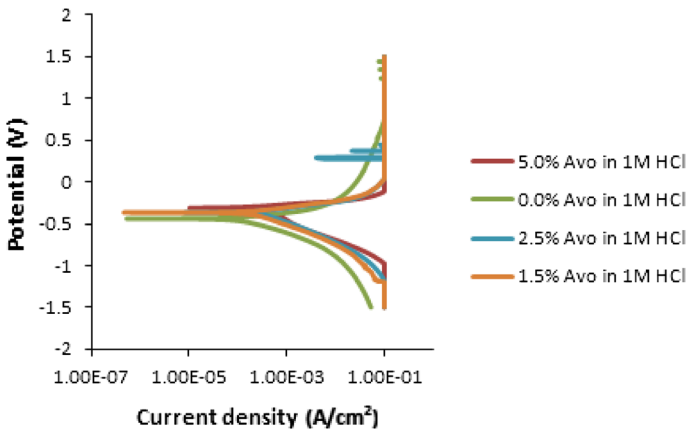
Fig. 2 Linear polarization of mild steel in 1 M HCl solution with and without Avogadro natural oil addition at 298 K

$$IE(\%) = \frac{(CR_a - CR_p)\,100}{CR_a} \qquad (2)$$

where W_0 and W_a are the specimen weights before and after immersion in the tested solution, A is the area of the mild steel specimen, and t is the exposure time (h). CR_a and CR_p are the corrosion rate in the absence and present of inhibitor, respectively. From the results, the corrosion rate (CR) of the mild steel–HCl decreased with addition of inhibitors and exposure times considered (Table 2; Fig. 1). Specifically, at 96 h of exposure time for 4.5 g/v Avogadro natural oil addition, LPRcorrosion rate decreased from 0.1072 to 0.0357 mm/year indicating inhibition efficiency (IE) of 66.66 %, while at 192, 288 and 384 h of exposure time for 4.5 g/v Avogadro natural oil addition, the corrosion rate decreased from 0.0953 to 0.0185, 0.1084 to 0.0139 and 0.1597 to 0.0107 mm/year with IE of 80.49, 87.10 and 93.26 %, respectively. The corrosion behavior in the natural oil was attributed to the increase in the element that forms stable oxides as evidenced in the EDS (Fig. 3b). The thin layer of the oxides adheres to the metal surface resulting in a decrease in the corrosion rate. This is similar to the results reported elsewhere [16, 17].
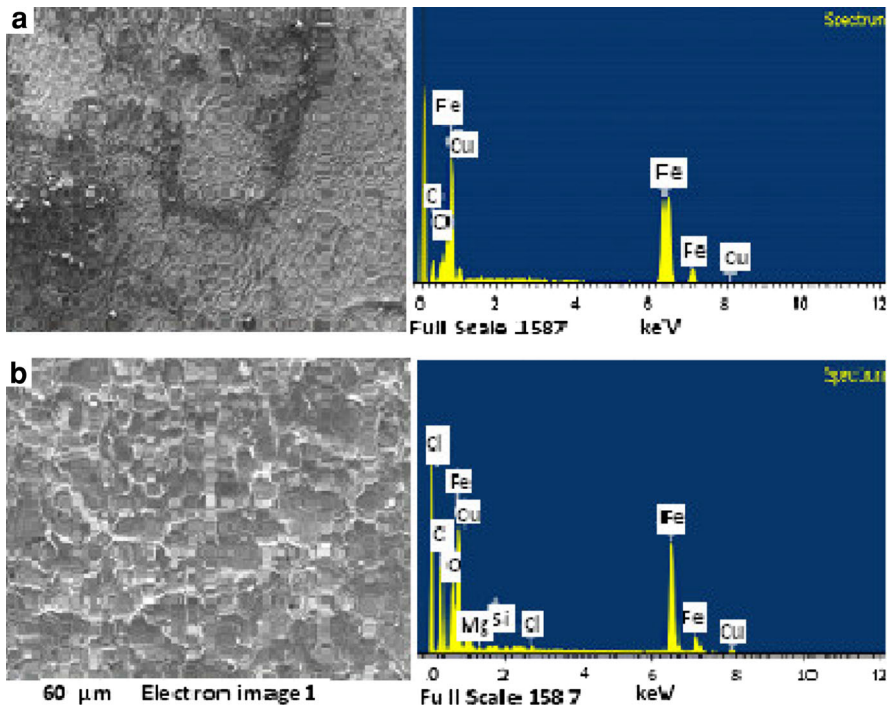
Fig. 3 SEM micrograph of as-corroded **a** inhibited mild steel in HCl solution–4.5 g/v Avogadro natural oil addition and **b** uninhibited condition in HCl solution after 288 h of exposure time
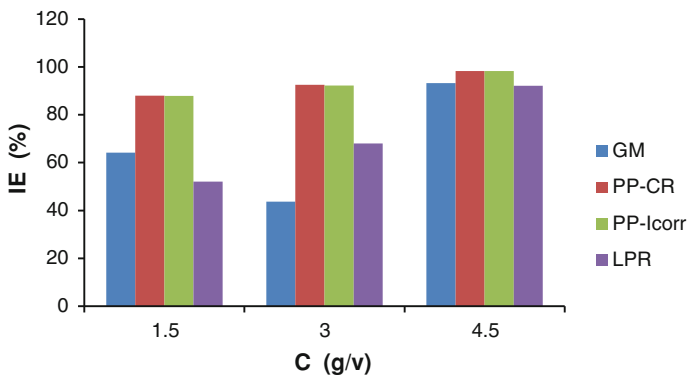
Fig. 4 Comparison of inhibitor efficiency (%IE) values for mild steel–1 M HCl solution–Avogadro natural oil concentration obtained by gravimetric at 384 h (*GM*), potentiodynamic polarization–corrosion rate (*PP–CR*), potentiodynamic polarization–corrosion current (*PP–I$_{corr}$*), and linear polarization resistance (*LPR*)
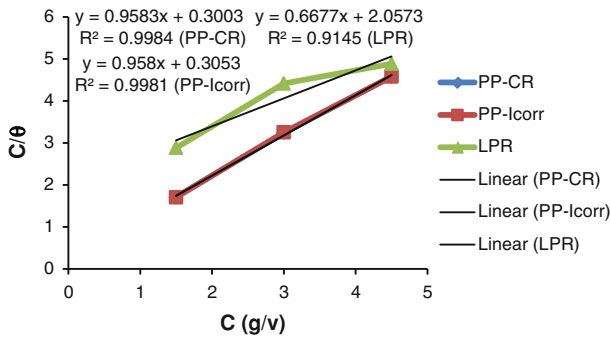
Fig. 5 Langmuir's isotherm adsorption of Avogadro natural oil on the mild steel surface in 1 M HCl

Linear polarization–corrosion studies

In the electrochemical corrosion study, LPRpotentiodynamic measurement was used to assess the corrosion of mild steel–HCl with varying concentrations of Avogadro natural oil. Potentiodynamic polarization–corrosion rate (PP–CR), potentiodynamic polarization–current density (PP–I_{corr}) and linear polarization resistance (LPR) were used as criteria for evaluation of corrosion resistance of mild steel in the environment. Figure 2 indicates the polarization curves for mild steel at 298 K. In general, there was a decrease in LPRcorrosion rate and anodic current density with LPRaddition of LPRinhibitor at all concentrations. Thus, the inhibited system is believed to have shifted towards the passive region (cathodic region), while the corrosion potential (E_{corr}) and polarization resistance (R_p) increases with inhibitor concentrations. This is in agreement with reports elsewhere [11, 16]. The inhibited mild steel showed that LPRcorrosion rate decreased from 1.4650 mm/year to 0.1769, 0.1136 and 0.0255 mm/year at 1.5, 3.0 and 4.5 g/v Avogadro natural oil additions, respectively. However, based on the changes in anodic and cathodic branches for both environments, the inhibitor is believed to be mixed-type.

Surface degradation of samples

From the surface morphology of LPRuninhibited mild steel–HCl interface in Fig. 3a, severe pits, cracks and selective dissolution of intermetallic occurred at the surface, whereas there was an improvement in the surface morphology of mild steel that was treated with the inhibitor. From the SEM–EDS evaluation, it is clear that the increased value of O is due to the formation of the ferrous hydroxide, whereas, for C, it is due to the presence of LPRactive constituent in the inhibitor that acts as the active inhibitor and complexes with the mild steel surface as compared with mild steel in Avogadro natural oil–HCl medium (Fig. 3b) which equally corresponds to the higher corrosion resistance obtained from the linear polarization study.

Inhibitor efficiency and adsorption mechanism

The inhibitor efficiency (%IE) of the Avogadro natural oil inhibitor for mild steel in HCl solution was computed using the equation reported [17, 18]. The computed data for the IE using gravimetric (GM), potentiodynamic polarization–corrosion rate (PP–CR), potentiodynamic polarization-corrosion density (PP–I_{corr}), and linear polarization resistance (LPR) are presented in Fig. 4 for 1 M HCl–Avogadro natural oil environment. From Fig. 4, it can be seen that %IE of the HCl/Avogadro natural oil increases with an increase in the inhibitor concentrations. The reasons are that, as the inhibitor concentration increases, the surface area covered by these inhibitors increased hence higher %IE were obtained. Inhibitor efficiencies of 66.66, 80.49 and 93.26 % were obtained at 4.5 g/v inhibitor addition using LPRgravimetric method, whereas they were 98.26, 98.26 and 92.11 %IE for PP–CR, PP–I_{corr}, and LPR, respectively, at 4.5 g/v Avogadro natural oil. It can be said that both the natural oils exhibited a mixed-type corrosion inhibition because of the simultaneous change in the anodic and cathodic regions during the electrochemical measurement. These results were found to be in agreement with a previous study [16]. The inhibitor efficiencies expressed as the relative reduction in corrosion rate can be linked to the amount of adsorbed inhibitors on the metal surface interface. An adsorption isotherm gives knowledge about the interaction between the adsorbed molecules and the metal surface. Equally, it is believed that the corrosion reaction are retarded from occurring over the active sites of the metal surface covered by adsorbed inhibitors species, whereas the corrosion reaction occurs normally on the inhibitor's free area. The inhibitor's efficiency can be said to correlate with the fraction of the surface area covered with LPRadsorbed inhibitor, which eventually lowered the corrosion rate of the mild steel. The mechanism of adsorption for the oil on to the surface of the mild steel has shown that the relationship between C/θ against C is linear at 298 K (Fig. 5). Since the correction factor (R^2) for mild steel–HCl–inhibitor are approximately unity, Avogadro natural oil, PP–CR (0.9994)/PP–I_{corr} (0.9983)/LPR (0.9947), the adsorption mechanism is believed to have followed LPRLangmuir adsorption isotherm.

Conclusions

1. The eco-friendly Avogadro natural oil has been demonstrated to be a good corrosion inhibitor for a mild steel–HCl environment at 298 K.
2. Addition of Avogadro natural oil reduces the corrosion rate of mild steel in 1 M HCl solution.
3. The inhibitive action of Avogadro natural oil increases with concentration.
4. Inhibitor efficiency of 81 % was obtained at 4.5 g/v Avogadro natural oil addition and the Langmuir adsorption isotherm was proposed for the aluminium alloy.
5. These occurrences have been attributed to the formation of thin oxides which adhered to the metal surface and interfered with the reaction sites, thus serving as a barrier to the formation of pits and their growth.

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