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Inhibitive, Adsorptive and Thermodynamic Study of Hypoxanthine against the Corrosion of Aluminium and Mild Steel in Sulphuric Acid

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Abstract

The corrosion inhibition potentials of hypoxanthine (HYP) on aluminium and mild steel in 0.1 M H_2SO_4 were investigated at 303 and 333 K using gravimetric, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation techniques. The results obtained, indicated that HYP exhibited efficient inhibition properties for aluminium and mild steel corrosion in the acidic media. Results obtained from potentiodynamic polarisation studies showed that HYP acted as a mixed corrosion inhibitor by retarding anodic and cathodic half reactions while those obtained from impedance spectroscopy studies revealed that the inhibition of aluminium and mild steel corrosion occurred via the mechanism of adsorption. Synergistic effects in the presence of iodide ions increased the efficiency of HYP only for the corrosion of mild steel in H_2SO_4. Adsorption of HYP on the metal surfaces was spontaneous and supported Langmuir and Temkin adsorption isotherms.

Keywords: Acid corrosion, adsorption, EIS, inhibition efficiency, HYP.

Introduction

Corrosion of metals is an electrochemical process that occurs whenever a metal is in contact with an aggressive medium such as acids, bases and salts. The susceptibility of a metal to corrosion depends on the nature of the metal and the environment.

Despite the invention and over-usage of plastics in most industrial applications, metals still rule manufacturing industries. Metals like steel (iron) and aluminium are commonly used in most industries. Mild steel is one of the best preferred materials for industries due to its easy availability and excellent structural properties. Aluminium on the other hand, is the most widely used metal after steel due to its versatility.

Most often, during industrial processes such as pickling, etching, these metals are made to come in contact with aggressive media such as acids, bases and salts thereby exposing them to corrosion attack. Several researches have been carried out on the protection of metals against corrosion [1-4] however, due to strict environmental regulations, the continued usage of non environmentally friendly chemical compounds as corrosion inhibitors have faced relentless condemnation. Consequently, large numbers of organic compounds, principally those containing hetero atoms like oxygen, nitrogen or sulphur groups in conjugated systems are been investigated as corrosion inhibitors for different metals in various aggressive media.

Although some plants extracts have been found to be useful as eco-friendly inhibitors [5,6], the actual constituents of the extracts that are responsible for inhibition have been difficult to determine making it difficult to elucidate the specific mechanism for corrosion inhibition. Hence, the challenge for search of corrosion inhibitors, whose actual chemical structures and eco-friendliness have been established are on the increase. Purines are organic compounds with hetero atoms like O and N in their aromatic rings. They are non toxic and biodegradable hence, can be used as eco-friendly inhibitors against the corrosion of metals in various aggressive media [7,8]. In view of this, the present study sets to investigate the potential of hypoxanthine (HYP), as an inhibitor, for the corrosion of aluminium and mild steel in 0.1 M H_2SO_4 solutions using gravimetric, electrochemical impedance spectroscopy and potentiodynamic techniques.

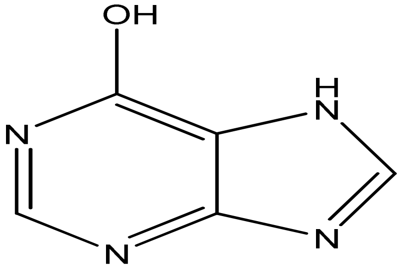

Figure 1: Chemical structure of hypoxanthine (HYP)

2. Materials and methods

2.1 Materials

Aluminium sheet (AA 1060 type) of 98.5% purity and mild steel sheet of composition (wt.%: Mn (0.6), P (0.36), C (0.15), Si (0.03) and the rest Fe) were used in this study. Acid solutions of 0.1 M H_2SO_4 were prepared by diluting analytical grades with distilled water. Solutions of hypoxanthine (HYP) were prepared at the concentration range 2.0 x 10^{-3} – 10.0 x 10^{-3} M in the acid media. The effect of iodide ions on inhibition efficiency was studied at 303 K by combining 5.0 x 10^{-3} M KI. All reagents were obtained from Zayo-Sigma Chemicals. Figure 1 shows the molecular structure of hypoxanthine (HYP).

2.2 Methods

2.2.1 Gravimetric analysis

Weight loss measurements were carried out in accordance with an earlier report [9-11]. Tests were conducted under total immersion conditions in 150 mL of the aerated and unstirred test solutions. Immersion time varied from 1 to 5 days (120 h) in 0.1 M H_2SO_4. The coupons were retrieved from test solutions after every 24 h, appropriately cleaned, dried and re-weighed. The weight loss was taken to be the difference between the weight of the coupons at a given time and its initial weight. The effect of temperature on corrosion inhibition of Al and mild steel by HYP was investigated by performing experiments at 303 and 333 K. All tests were run in duplicates.

2.2.2 Electrochemical measurements

Metal samples for electrochemical experiments were machined into test electrodes of dimension 1 × 1 cm^2 and sealed with epoxy resin in such a way that only one square surface area (1 cm^2) was left uncovered. Electrochemical tests were conducted in a Model K0047 corrosion cell using a VERSASTAT 400 complete DC voltammetry and corrosion system, with V3 Studio software. A graphite rod was used as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. The latter was connected via a Luggin capillary. Measurements were performed in aerated and unstirred solutions at the end of 1 h of immersion at 303 K. Impedance measurements were made at corrosion potentials (E_{corr}) over a frequency range of 100 kHz– 10 mHz, with a signal amplitude perturbation of 5 mV. Potentiodynamic polarization studies were carried out in the potential range 1000 to 2000 mV for aluminium and ± 250 mV for mild steel respectively, versus corrosion potential at a scan rate of 0.33 mV/s. Each test was run in triplicate [10,12].

3. Results and discussion

3.1 Gravimetric analysis

3.1.1Effect of concentration of hypoxanthine on the corrosion of aluminium (Al) and mild steel (MS) in 0.1 M H_2SO_4

Figure 2 shows the variation of weight loss (g) with time (hr) for the dissolution of aluminium and mild steel in 0.1 M H_2SO_4 in the absence and presence of 0.002 – 0.01 M HYP. Inspection of the plots on Figure 2 clearly reveals that weight losses of aluminium and mild steel in the acidic environment decreased in the presence of HYP compared with the blank solutions. Calculated values of corrosion rate (gh^{-1} cm^2) and inhibition efficiency (IE%) from the weight loss measurement are presented in Table1.

Results presented in the table show that corrosion rate decreases in the presence of HYP compared to the blanks alone signifying that HYP in H_2SO_4 solution inhibits the corrosion of aluminium and mild steel respectively and that the extent of corrosion inhibition is a function of the concentration of the inhibitor and type of metal.

3.2 Electrochemical measurements at 303 K

Impedance and potentiodynamic polarization tests were undertaken at 303 K to study the inhibiting effect of HYP on the electrochemical corrosion behavior of aluminium and mild steel in 0.1 M H_2SO_4. The optimum concentration of 0.01 M HYP was used for the electrochemical measurements.

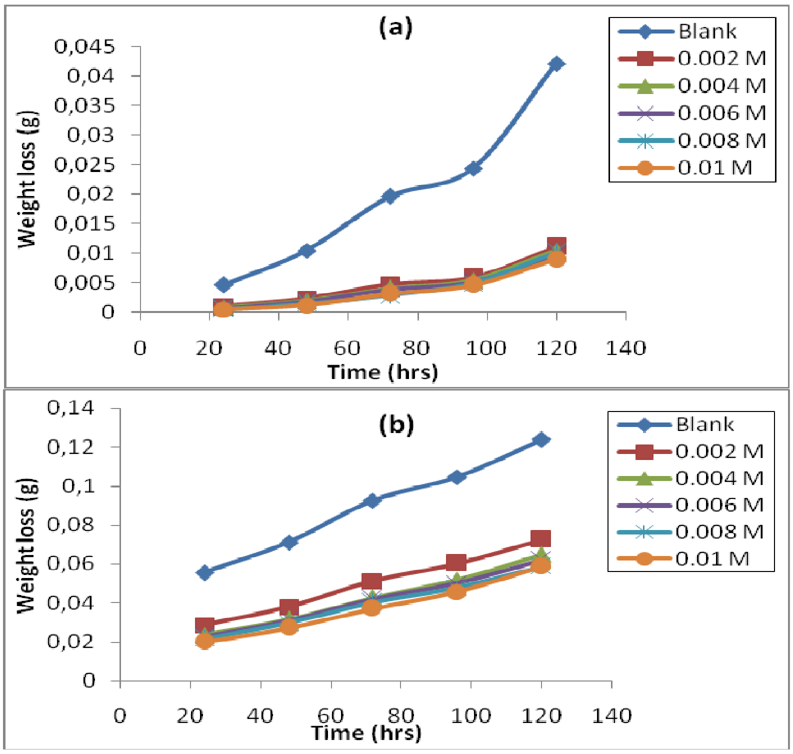

Figure 2: Variation of weight loss (g) with time (hrs) for the corrosion of (a). aluminium and (b). mild steel in 0.1 M H_2SO_4 containing various concentrations of hypoxanthine (HYP) at 303 K.

Table 1: Corrosion rates and inhibition efficiencies of aluminium and mild steel in the presence of various concentrations of hypoxanthine (HYP) in 0.1 M H_2SO_4.

Metal	**C (M)**	**Corrosion rate X 10^{-4} ($gh^{-1}cm^{2}$)**		**Inhibition efficiency (IE %)**	
		303 K	**333 K**	**303 K**	**333 K**
Aluminium	Blank	0.421	2.56	-	-
	0.002	0.101	1.26	76.23(0.76)	50.69(0.51)
	0.004	0.092	1.16	78.21(0.78)	54.91(0.55)
	0.006	0.085	1.09	79.70(0.80)	57.35(0.57)
	0.008	0.081	1.03	80.69(0.81)	59.79(0.60)
	0.01	0.075	0.99	82.18(0.82)	61.49(0.62)
Mild steel	Blank	1.86	6.46	-	-
	0.002	1.04	2.98	44.02(0.44)	53.98(0.54)
	0.004	0.892	2.66	52.18(0.52)	58.81(0.59)
	0.006	0.867	2.64	53.52(0.54)	59.23(0.59)
	0.008	0.827	2.59	55.64(0.56)	60.00(0.60)
	0.01	0.785	2.46	57.88(0.58)	61.94(0.62)

3.2.2 Electrochemical impedance spectroscopy

Impedance experiments were undertaken to afford insight into the characteristics and kinetics of electrochemical processes occurring at the metal/acid interface and how these were modified by the presence of HYP. The impedance responses of these systems are given in Figure 3 as Nyquist plots. The Nyquist plots generally have the form of only one depressed semicircle in the high frequency region, which denotes that the process is under charge-transfer control and corresponds to one time constant in the Bode plots. The single time constant may be attributed to the short exposure time in the corrodent, which is insufficient to reveal degradation of the substrate [13, 14]. The depression of the Nyquist semicircle with center under the real axis is typical for solid metal electrodes that show frequency dispersion of the impedance data.

The corresponding impedance parameters are presented on Table 2. The increase in R_{ct} values in inhibited systems which signifies an increase in the diameters of the Nyquist semicircles with a corresponding decrease in the double layer capacitance (C_{dl}), confirms the corrosion inhibiting effect of HYP. The observed decrease in C_{dl} values, which normally corresponds to alteration of the double-layer thickness can be attributed to the adsorption of HYP (with lower dielectric constant compared to the displaced adsorbed water molecules) onto the metal/acid interface, thereby protecting the metals from the corrosive effect of the aggressive acid.

The magnitude and trend of the obtained values presented agreed with those determined from gravimetric measurements.

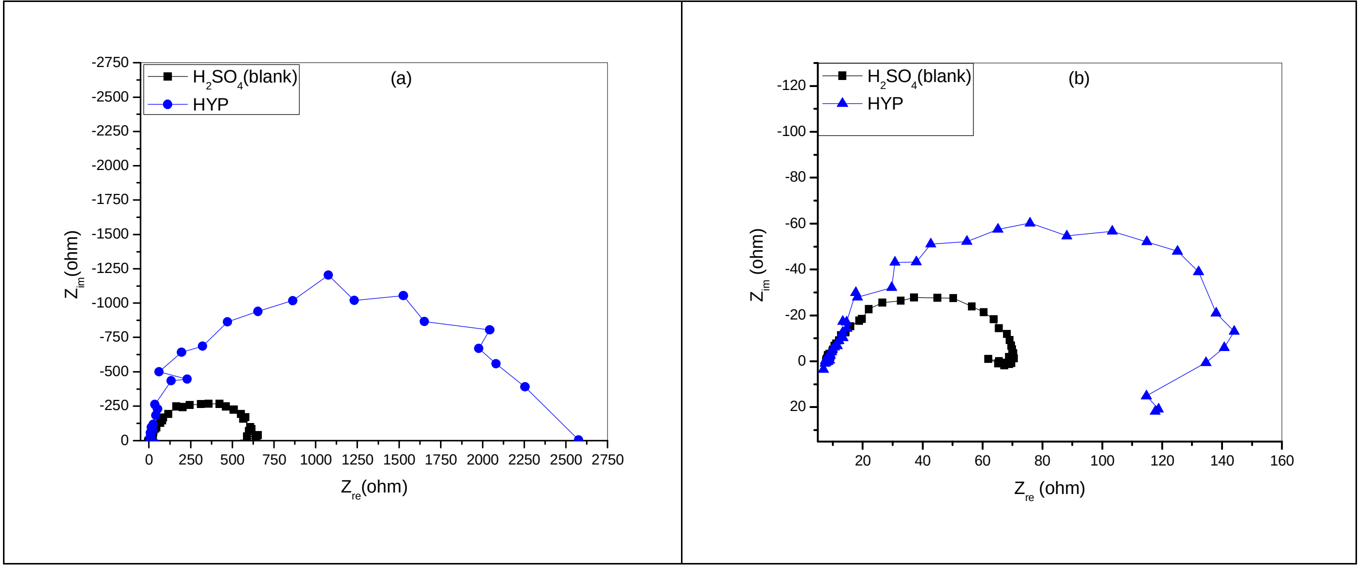

Figure 3: Impedance spectra for (a) aluminium and (b) mild steel in 0.1 M H_2SO_4 in the absence and presence of 0.01 M hypoxanthine (HYP) at 303 K.

Table 2. Impedance data for aluminium (Al) and mild steel (MS) in 0.1 M H_2SO_4 in the absence and presence of 0.01 M hypoxanthine (HYP) at 303 K.

System	**R_{ct} (Ω cm^2)**	**C_{dl}($\mu\Omega^{-1}S^n cm^{-2}$)**	**N**	**IE%**
H_2SO_4 (Blank)	591.7	14.90	0.96	
HYP + Al	2301	3.00	0.93	74.29
HYP + MS	137	2.00	0.85	54.33

3.2.3 Potentiodynamic polarization measurements

The corrosion current is a function of the reactivity of a metal in an aqueous environment. The higher the values of i_{corr}, the higher the dissolution of the metal and vice versa. Typical potentiodynamic polarization curves for aluminium and mild steel in 0.1 M H_2SO_4 in the absence and presence of 0.01 M HYP are shown in Figure 4 while the electrochemical parameters derived from the polarization curves and inhibition efficiency values are summarized on Table 3.

Addition of HYP is seen to affect the anodic as well as the cathodic partial reactions, shifting the corrosion potential (E_{corr}) toward more positive (anodic) values (especially for mild steel corrosion) and reducing the anodic and cathodic current densities and the corresponding corrosion current density (i_{corr}). This indicates that the HYP functioned as a mixed-type inhibitor in H_2SO_4 for the corrosion of aluminium and mild steel.

The obtained values presented on Table 3 follow the same trend as the gravimetric and impedance data indicating the corrosion inhibiting efficacy of hypoxanthine.

Table 3: Polarization data for aluminium (Al) and mild steel (MS) in 0.1 M H_2SO_4 in the absence and presence of 0.01 M hypoxanthine (HYP) at 303 K.

System	**E_{corr} (mV vs SCE)**	**i_{corr} (μA cm^{-2})**	**IE%**
H_2SO_4 (Blank)	-661.12	109.13	
HYP + Al	-703.11	27.42	74.87
HYP + MS	-482.4	97.45	54.11

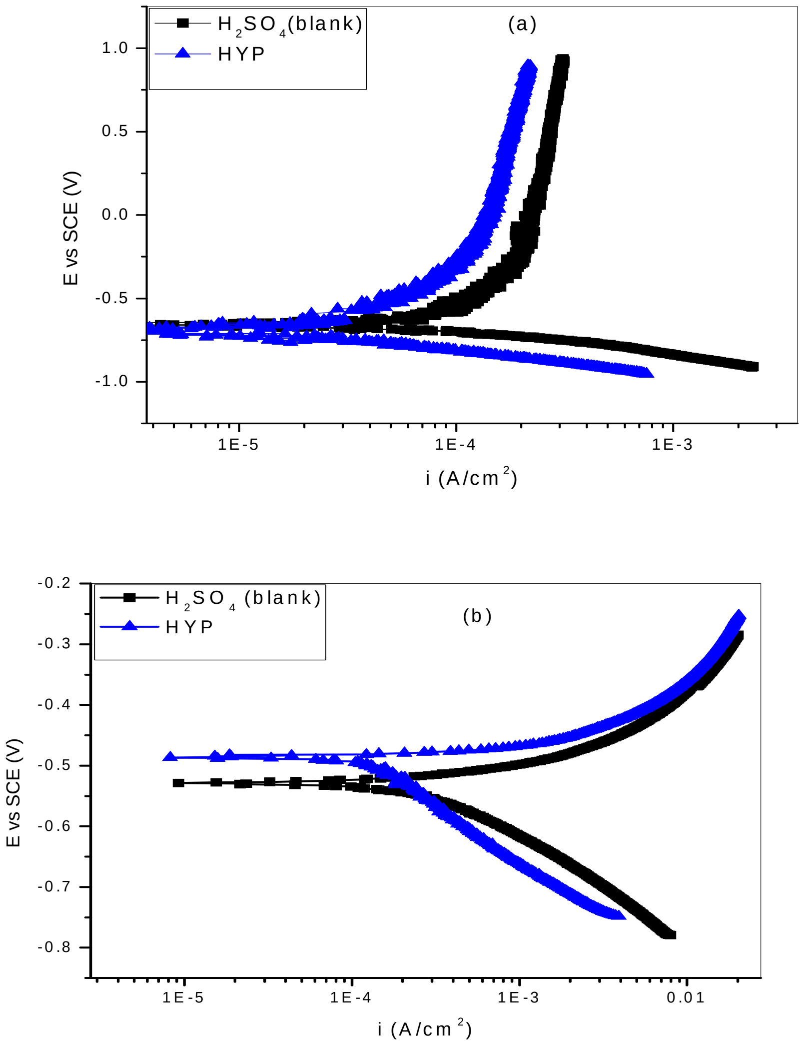

Figure 4: Polarisation curves for (a) aluminium and (b) mild steel in 0.1 M H_2SO_4 in the absence and presence of 0.01 M hypoxanthine (HYP) at 303 K.

3.3 Effect of Temperature/ thermodynamics Study

The adsorption mechanism of HYP on aluminium and mild steel were also investigated by changing the temperature of the systems from 303 to 333 K. The trend in inhibition efficiency against temperature is shown in Table 4.

The apparent activation energies (E_a) for the corrosion process in the absence and presence of HYP were calculated using a modified form of the Arrhenius equation:

$$\log\frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (1)$$

where ρ_1 and ρ_2 are the corrosion rates at temperatures T_1 and T_2, respectively. The heats of adsorption (Q_{ads}) was quantified from the trend of surface coverage with temperature as follows [6]:

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \frac{T_1T_2}{T_2-T_1} \qquad (2)$$

where θ_1 and θ_2 are the degrees of surface coverage at temperatures T_1 and T_2, and R is the gas constant. The calculated values for both parameters are given in Table 4. The values reveal that while inhibition efficiency of HYP decreased with rise in temperature for aluminium in 0.1 M H_2SO_4, IE% increased with rise in temperature in 0.1 M H_2SO_4 for mild steel. The occurence of decreasing and increasing inhibition efficiencies at higher temperatures are evidence of specific physisorptive and chemisorptive interactions respectively, between HYP species and the metal surfaces [5, 15, 16]. The decrease in inhibition efficiency of HYP with increase in temperature for aluminium in H_2SO_4 as well as negative Q_{ads} values suggests physisorption and also signifies that the degree of surface coverage decreased with rise in temperature, E_a tend to decrease on addition of HYP to aluminium in H_2SO_4 solution. For mild steel systems, E_a in the presence of HYP was lower than that in the uninhibited acid, the positive values of Q_{ads} implies an increase in degree of surface coverage with rise in temperature, which is indicative of chemisorption. The reason for this, as suggested by Oguzie [17] may be that equilibrium is rapidly attained in physical adsorption resulting in desorption whereas in chemisorptions, the process is relatively slow and not readily reversible.

Table 4: Calculated values of activation energies (E_a) and heats of adsorption (Q_{ads}) for the corrosion of aluminium (Al) and mild steel (MS) in 0.1 M H_2SO_4 in the absence and presence of various concentrations of hypoxanthine (HYP).

System	**Concentration (M)**	**Activation Energy E_a (kJ mol^{-1})**	**Heat of adsorption Q_{ads} (kJ mol^{-1})**
	Blank	**50.54**	
HYP (Al)	0.002	70.94	-12.03
	0.004	71.05	-11.43
	0.006	71.30	-11.33
	0.008	71.09	-10.93
	0.01	72.19	-11.21
HYP (MS)	0.002	29.47	3.98
	0.004	30.59	2.50
	0.006	31.18	1.68
	0.008	31.96	3.88
	0.01	31.05	3.86

3.4 Adsorption study

The surface coverage data obtained from IE% values best fitted the adsorption models of Langmuir (eqn. 3) and Temkin (eqn. 4) isotherms taking into cognizance that the values of the regression coefficient, R^2, were greater than 0.9 [18]. Thermodynamic parameters associated with the adsorption process were deducted using the relationship between the adsorption equilibrium constant (k_{ads}) (eqn. 5) and the standard free energy of adsorption, $\Delta G_{ads}°$ [19];

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (3)$$

$$-2 \propto \theta = 2.303(\log k + \log C) \qquad (4)$$

$$\log K_{ads} = -1.744 - \frac{\Delta G^{\circ}_{ads}}{2.303RT} \qquad (5)$$

The evaluated values of the adsorption equilibrium constant, k_{ads}, were all quite high especially in the case of Temkin isotherm reflecting the high adsorption ability of the HYP onto the metal surfaces. Table 6 shows the parameters of linearisation for each adsorption model.

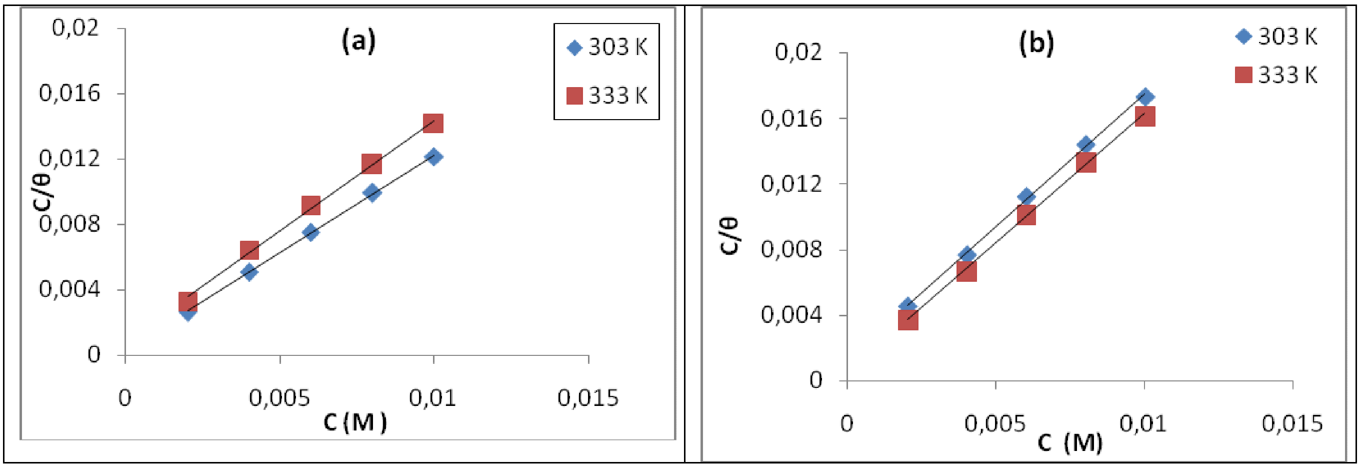

Figure 5: Langmuir isotherm for the adsorption of hypoxanthine (HYP) onto (a) aluminium (b) mild steel surface in 0.1 M H_2SO_4 at 303 and 333 K respectively.

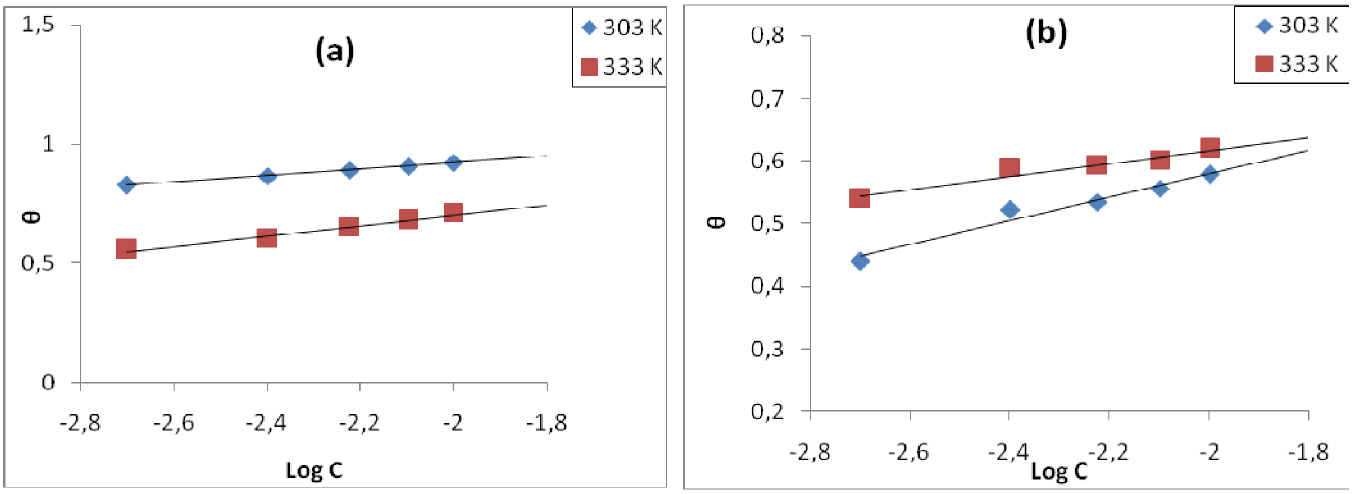

Figure 6. Temkin isotherm for the adsorption of hypoxanthine (HYP) onto (a) aluminium (b) mild steel surface in 0.1 M H_2SO_4 at 303 and 333 K respectively.

Table 5: Langmuir and Temkin isotherm parameters obtained from the corrosion data for aluminium (Al) and mild steel (MS) in 0.1 M H_2SO_4 in the presence of hypoxanthine (HYP).

Isotherm	Temperature (K)	System	Intercept	Slope	Log K_{ads}	R^2	ΔG_{ads} (kJmol$^-$)
Langmuir	303	HYP (Al)	0.000	1.194	0.0	0.999	-10.12
		HYP(MS)	0.001	1.609	3.0	0.999	-27.52
	333	HYP (Al)	0.000	1.348	0.0	0.997	-11.12
		HYP(MS)	0.000	1.575	0.0	0.997	-11.12
Temkin	303	HYP (Al)	0.981	0.081	12.110	0.979	-80.370
		HYP(MS)	1.530	0.410	3.734	0.991	-31.780
	333	HYP (Al)	0.918	0.153	6.000	0.994	-49.380
		HYP(MS)	1.088	0.291	3.739	0.994	34.960

Negative ΔG_{ads} values indicate spontaneity of the adsorption process [20, 21]. Generally, ΔG_{ads} values with magnitude much less than 40 kJ mol^{-1} have typically been correlated with the electrostatic interactions between organic molecules and charged metal surface (physisorption), whilst those of magnitude in the order of 40 kJ mol^{-1} and above are associated with charge sharing or transfer from the organic molecules to the metal surface (chemisorption) [22].

3.5. Synergistic considerations

The influence of 0.005 M KI on the corrosion of aluminium and mild steel in 0.1M H_2SO_4 containing 0.01 M HYP , corresponding to [KI]/[INH] ratio of 0.2, is depicted in Figure 7 by weight loss measurements. Corrosion inhibition synergism results from increased surface coverage arising from ion-pair interactions between the organic purine as cations and the iodide ions [17]. From the results obtained in Figure 7, it is obvious that I^- ions promoted the adsorption of HYP only on the mild steel surfaces.

Conclusion

Results obtained from the study showed that HYP inhibited the corrosion of aluminium and mild steel in 0.1 M H_2SO_4. The presence of iodide ions enhanced the inhibitive behaviour of HYP only for the corrosion of mild steel in H_2SO_4. Polarization measurements suggest a mixed-inhibition mechanism, which the impedance data indicated was achieved via adsorption of HYP species on the aluminium and mild steel surfaces.

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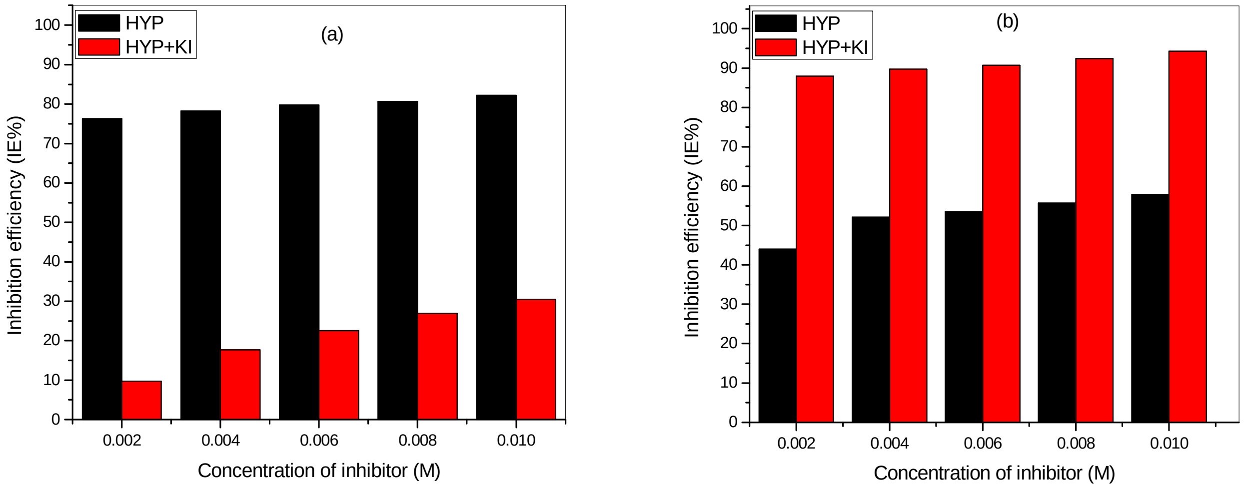

Figure 7: Synergistic effect of iodide ions on the inhibition efficiency of HYP on the corrosion of (a) aluminium and (b) mild steel in 0. 1 M H_2SO_4 at 303 K.

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