Corrosion Inhibition Efficiency of 3-Hydroxy-2-Methylquinazoline-4-one on Mild Steel in 1 M H_2SO_4 and 1 M HCl Acid at Different Temperatures

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Abstract

The influence of 3-hydroxy-2-methylquinazoline -4-one on the corrosion inhibition of mild steel in 1 M HCl and 1 M H_2SO_4 has been studied using weight loss, and galvanostatic polarization studies. Result obtained reveals that this organic compound is a very good inhibitor and its inhibition efficiency increases with increasing its concentration to attain 92% at 1000 ppm at 25 ℃. The potentiodynamic polarization study indicates that this compound acts as a mixed type corrosion inhibitor. The rate of corrosion of mild steel rapidly increases with temperature over the temperature range of 25 ℃ to 55 ℃, both in absence and presence of the inhibitor. Thermodynamic parameter for adsorption process has been calculated using the Langmuir's adsorption isotherm.

Keywords: corrosion, inhibition, 3-hydroxy-2-methylquinazoline -4-one, hydrochloric acid, sulfuric acid.

Introduction

Corrosion is a type of surface chemical process in which metallic material is lost as oxides, hydrides and carbonates due to its direct chemical, biochemical and electrochemical reactions with environment. There are several ways to prevent atmospheric corrosion. Hydrochloric acid and sulphuric acid are widely used for the removal of rust and scales in several industrial processes. The corrosion of steel and ferrous alloys in such environments constitutes a complex process. Among the available methods of preventing corrosion, the use of inhibitor is the

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most promising one, particularly for closed systems. The inhibitors find wide application in the industrial field. Inhibition by organic additives on metals in acids has been studied [1-10]. Organic substances contain mainly oxygen, sulphur, nitrogen, and multiple bonds in the molecules that facilitate the adsorption on the metal surface [11-14] are strongly polar. According to ref [15-16], sulphur compounds such as thiourea are very effective corrosion inhibitors for steel in acidic condition, because sulphur atom is easily protonated in acidic solution and a stronger electron donor than nitrogen. Therefore, sulphur atom is more strongly adsorbed by the metal surface. It has been observed that adsorption mainly depends on the presence of $\prod$- electrons and heteroatom, which induce greater adsorption of the inhibitor molecules on the surface of metal. All thiourea derivatives suppressed H_2 pick up by blocking the active sites on the steel surface [17].Kuzenetzov [18] studied the mechanism of action of inhibitors considering that most chemical reactions can be treated as acid-base interactions. Based in this concept, thiourea would act as a rather strong base due to its sulphur, which serves as an electron donor. On the other hand Fe^{3+}, Fe^{2+} and metallic Fe would behave like acids.

The study of corrosion of iron is a matter of tremendous theoretical and practical concern and has received a considerable amount of interest. Iron is widely used as constructional material in many industries due to its excellent mechanical properties and low cost. The highly corrosive nature of aqueous mineral acids on most metal requires degree of restraint to achieve economic maintenance and operation of equipment, minimum loss of chemical products and maximum safety conditions.

The aim of this work is to study the effect of 3-hydroxy-2-methylquinazoline -4-one as corrosion inhibitors for dissolution of mild steel in different concentrations of the inhibitor in 1 M HCl and1 M H_2SO_4 medium, by chemical and electrochemical techniques. The effect of temperature on the dissolution of mild steel in free and inhibited acid solution was also investigated.

Experimental procedure

Synthesis of 3-hydroxy-2-methylquinazoline-4-one

3-hydroxy-2-methylquinazoline-4-one was prepared in three steps, starting from isatoic anhydride. The reaction of o-benzaylhydroxylamine with isatoic anhydride in aqueous solution gave the corresponding hydroxamate (2-amino-N-benzaloxybenzamide). Cyclization with acetic anhydride gave the compound 3-hydroxy-2-methylquinazoline-4-one, o-protected by a benzyl group, debenzylation was then performed by catalytic hydrogenation. 10% pd/c (60 mg) suspended in MeOH (10 mL) was prehydrogenated with H_2 for 30 minutes. To the suspension was then added a solution of previous O-benzyl protected compound (0.429 g , 1.61 mmol) in MeOH (15 mL) . After hydrogenation at room temperature with H_2 under atmospheric pressure for 15 minutes, the mixture was filtrate through a celite pad. The filtered was evaporated to give a

solid residue which was purified by recrystallization from a MeOH-water mixture.

Yield 16 % , Mp 218 – 219 C. Found: C, 60.88; H, 4.58; N,15.78; molecular formula $C_9H_8N_2O_2$ requires C, 61.36; H, 5.30; N, 15.90; I.R. v/cm : 2561 (OH), 1684 (C=O) and 1564 (C=C and C=N).

Electrolyte

The aggressive solutions used were made of AR grade of HCl and H_2SO_4 acids. Appropriate concentrations of acid were prepared using double distilled water. The concentration range of inhibitor employed was 100 to 1000 ppm in both acidic solutions.

Specimens

Mild steel coupons of composition (C=0.16%, Mn=0.035%, Si=0.05%, S=0.025%, P=0.25% and balance Fe) have been used for weight loss measurements. These coupons were mechanically polished with emery papers of 1/0, 2/0, 3/0 and 4/0 grade and degreased with acetone before use.

Weight loss studies

Mild steel strips of size (i.e., 1 cm × 1 cm × 3 cm) were used for weight loss measurements. All weight loss experiments were carried out at 25 ºC to 55 ºC, being 24 hours the immersion time. The experiments were performed as per ASTM G31-72 method [15]. The percentage inhibition efficiency was calculated using the following equation:

$$I\% = \frac{Wo - Wi}{Wo} \times 100$$

where Wo and Wi are weight losses in the absence and presence of inhibitor, respectively.

Electrochemical studies

For potentiodynamic polarization studies, mild steel strips of same composition were used and the experiments were carried out at different temperatures and time periods up to 6 hours in the absence and presence of inhibitor. For polarization studies a cylindrical mild steel rod (exposed area of 1cm²) of the same composition as that of weight loss, coated with araldite, was used. The electrodes were polished with emery papers and degreased with acetone before used. For accurate measurements of potential and current densities, galvanostatic polarization studies were carried out at different temperatures. A platinum foil and saturated calomel electrode were used as counter and reference electrode, respectively. Polarization was carried out in 1 M HCl and 1 M H_2SO_4 in the absence and presence of the inhibitor at various concentrations and temperatures.

Results and discussion
Weight loss measurements
Tables 1 and 2 give the values of inhibition efficiencies for different concentrations of 3-hydroxy-2-methylquinazoline-4-one in 1 M HCl and 1 M H_2SO_4 obtained from weight loss measurements. The percentage inhibition efficiency were calculated using the above mentioned equation.

Table 1. Inhibition efficiency of mild steel in presence of different concentrations of 3-hydroxy-2-methylquinazoline-4-one from weight loss measurements at various temperatures in 1 M HCl.

Temperature	Solution in ppm	Weight loss/gram	I%
25 ºC	1 M HCl	0.5701	-
	100	0.1385	75.7
	200	0.1450	74.5
	500	0.1440	74.7
	1000	0.0698	87.7
35 ºC	1 M HCl	0.8900	-
	100	0.5100	42.6
	200	0.3400	61.7
	500	0.2300	74.1
	1000	0.1700	80.8
45 ºC	1 M HCl	0.8350	-
	100	0.4280	48.7
	200	0.3320	60.2
	500	0.2550	69.4
	1000	0.2050	75.4
55 ºC	1 M HCl	0.7500	-
	100	0.6000	20.0
	200	0.5300	29.3
	500	0.3400	54.6
	1000	0.3000	60.0

Results in Tables 1 and 2 show that the inhibition efficiency increases with increasing the concentration of the inhibitor in both acids at lower temperatures. As the temperature increases the inhibition efficiency decreases. The inhibition efficiency is more than 90% in case of 1 M H_2SO_4 medium in the presence of 1000 ppm concentration of 3-hydroxy-2-methylquinazoline-4-one at 25 ºC, which is appreciably good.

Galvanostatic polarization measurements
Tables 3 and 4 give the electrochemical parameters such as corrosion potential (E_{corr}), Tafel's slopes (b_a and b_c), corrosion current (i_{corr}), and inhibition efficiency (I%) for corrosion of mild steel in 1 M HCl and 1 M H_2SO_4 in absence

and presence of 3-hydroxy-2-methylquinazoline-4-one inhibitor at different concentrations and temperatures.

Table 2. Inhibition efficiency of mild steel in presence of different concentrations of 3-hydroxy-2-methylquinazoline-4-one from weight loss measurements at various temperatures in 1 M H_2SO_4.

Temperature	Solution/mol (L^{-1})	Weight loss/gram	I%
25 °C	1 M H_2SO_4	0.0786	-
	100	0.0384	56.10
	200	0.0275	65.01
	500	0.0231	70.61
	1000	0.0074	90.58
35 °C	1 M H_2SO_4	0.1568	-
	100	0.0728	53.57
	200	0.0658	58.03
	500	0.0518	66.96
	1000	0.0189	87.94
45 °C	1 M H_2SO_4	0.5467	-
	100	0.3091	43.46
	200	0.2394	56.20
	500	0.2075	62.04
	1000	0.1374	74.86
55 °C	1 M H_2SO_4	1.1891	-
	100	0.9105	23.42
	200	0.6113	48.59
	500	0.5913	50.27
	1000	0.4692	60.54

Figs. 1 to 4 show the effect of compound concentration on the current potential curves for both the cathodic and anodic reactions at different temperatures in 1 M HCl. The potential curves for the same temperature and concentration in 1 M H_2SO_4 acid medium are shown in Figs. 5 to 8. As the concentration increases there is an increase in the values of both the Tafel's slopes in both acids. Values of Tafel's slopes (cathodic and anodic) are larger in the case of 1 M H_2SO_4 in comparison to 1 M HCl. But in 1 M H_2SO_4 the values of cathodic Tafel's slopes are larger than those of anodic values. So inhibition of corrosion of mild steel in 1 M H_2SO_4 is under mixed control but predominantly under anodic control. The percentage inhibition curve of 3-hydroxy-2-methylquinazoline-4-one on mild steel in 1 M H_2SO_4 solution shows that the corrosion inhibition efficiency reached about 90% with solution containing 1000 ppm inhibition, whereas at the lower concentration of 100 ppm, the percentage inhibition was about 55.33% at 25 °C. The percentage inhibition of 3-hydroxy-2-methylquinazoline-4-one in 1 M HCl is about 87% having concentration 1000 ppm, while at lower concentration 100 ppm the percentage inhibition was about 66.1% at 25 °C. At lower concentrations the inhibition efficiency is larger in the case of 1 M HCl at all temperatures, except for 55 °C.

Table 3. Electrochemical parameters of mild steel in 1 M HCl in presence of 3-hydroxy-2-methylquinazoline-4-one as additive.

Temp.	Solution/mol (L^{-1})	E_{corr} mV	Log i_{corr} $\mu A/cm^2$	b_c mV/dec	b_a mV/dec	I%
25 °C	1 M HCl	410	3.57	29	40	-
	100	451	3.10	21	29	66.1
	200	439	2.99	30	32	73.6
	500	390	2.80	20	20	83.0
	1000	407	2.68	75	45	87.1
35 °C	1 M HCl	474	3.40	21	22	-
	100	427	3.06	18	18	54.2
	200	437	3.04	16	17	56.3
	500	420	2.88	13	20	69.8
	1000	442	2.59	22	24	84.5
45 °C	1 M HCl	478	3.39	28	28	-
	100	451	3.19	14	16	36.9
	200	431	3.00	16	16	59.2
	500	420	2.90	20	20	67.6
	1000	450	2.80	25	20	74.2
55 °C	1 M HCl	493	3.37	20	11	-
	100	442	3.19	17	16	33.9
	200	441	3.09	12	12	47.5
	500	457	3.01	18	08	56.3
	1000	440	2.90	31	32	66.1

The value of I_{corr} is found to be a little larger in the case of lowest concentrations of the compound in both the acids. As the concentration increases, the values of I_{corr} decrease. The inhibition efficiency of 3-hydroxy-2-methylquinazoline-4-one depends on many factors, including number of adsorption active center in the molecule and their charge density, which are affected by hydroxy (–OH) group. The values of inhibition efficiency obtained by weight loss method and galvanostatic polarization studies show fairly good agreement in both acids. It is also found that the compound performs better in 1 M H_2SO_4.

Adsorption kinetics
From polarization measurements, surface coverage θ values have been obtained for various concentrations of the inhibitor 3-hydroxy-2-methylquinazoline-4-one. Data were tested graphically for fitting a suitable adsorption isotherm. A straight line is obtained by plotting a graph between log θ/1- θ vs. 1/T in both the acids (Figs. 9 and 10). This clearly proves that the adsorption of 3-hydroxy-2-methylquinazoline-4-one on mild steel surface from both the acids obeys Langmuir's adsorption isotherm.

Table 4. Electrochemical parameters of mild steel in 1 M H_2SO_4 in presence of 3-hydroxy-2-methylquinazoline-4-one as additive.

Temp.	Solution/mol (L^{-1})	E_{corr} mV	Log i_{corr} $\mu A/cm^2$	b_c mV/dec	b_a mV/dec	I%
25 ºC	1 M H_2SO_4	512	3.45	99	141	-
	100	471	3.10	53	72	55.33
	200	453	3.00	36	97	64.51
	500	481	2.90	36	52	71.81
	1000	483	2.42	163	297	90.66
35 ºC	1 M H_2SO_4	522	3.38	111	151	-
	100	478	3.05	59	72	53.22
	200	481	3.00	49	48	58.31
	500	472	2.89	49	73	67.59
	1000	485	2.48	123	170	87.41
45 ºC	1 M H_2SO_4	500	3.35	75	73	-
	100	480	3.10	50	59	43.76
	200	464	2.98	30	78	57.34
	500	470	2.93	30	71	61.98
	1000	470	2.75	55	121	74.88
55 ºC	1 M H_2SO_4	480	3.29	41	93	-
	100	471	3.17	46	32	24.14
	200	470	3.00	50	39	48.71
	500	472	2.99	47	88	49.88
	1000	476	2.89	35	59	60.18
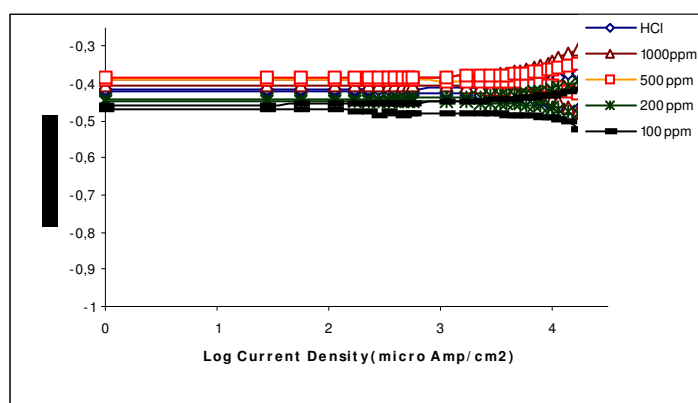
Figure 1. Galvanostatic polarization curves of mild steel in 1 M HCl containing different concentrations of 3-hydroxy-2-methylquinazoline-4-one at 25 ºC.
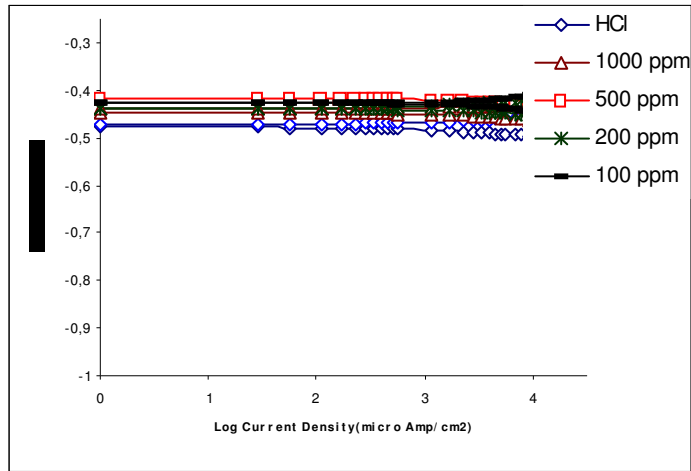
Figure 2. Galvanostatic polarization curves of mild steel in 1 M HCl solution containing different concentrations of 3-hydroxy-2-methylquinazoline-4-one at 35 ºC.
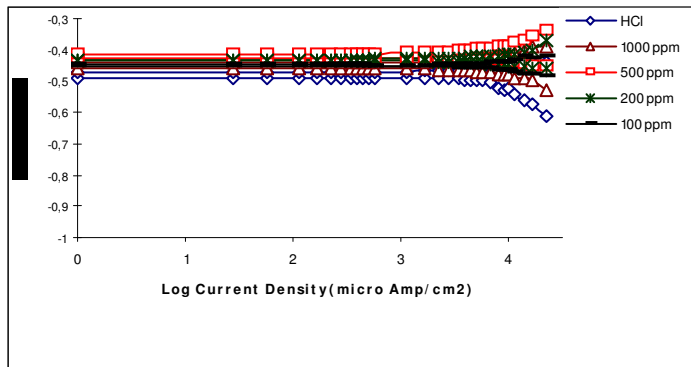
Figure 3. Galvanostatic polarization curves of mild steel in 1 M HCl solution containing different concentrations of 3-hydroxy-2-methylquinazoline-4-one at 45 ºC.
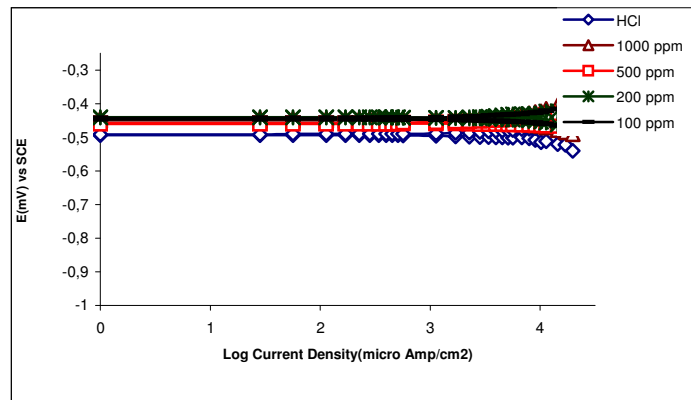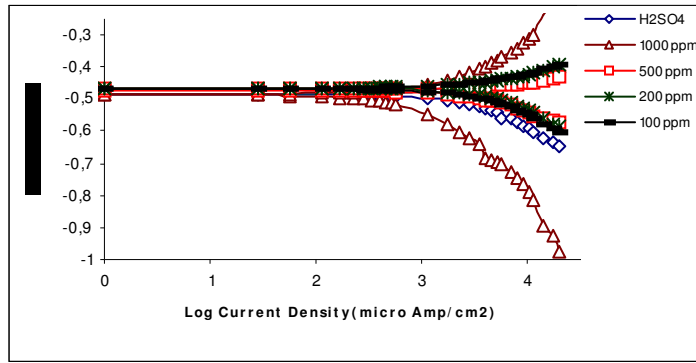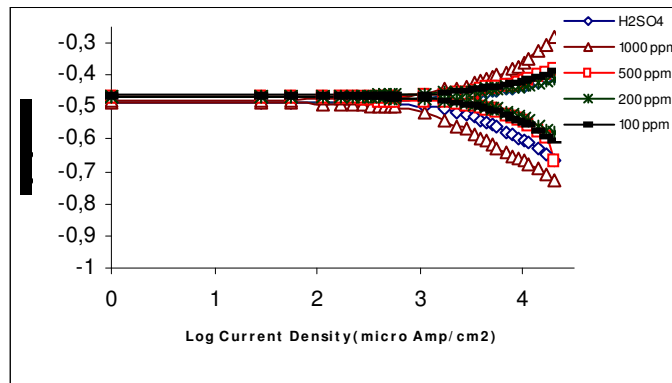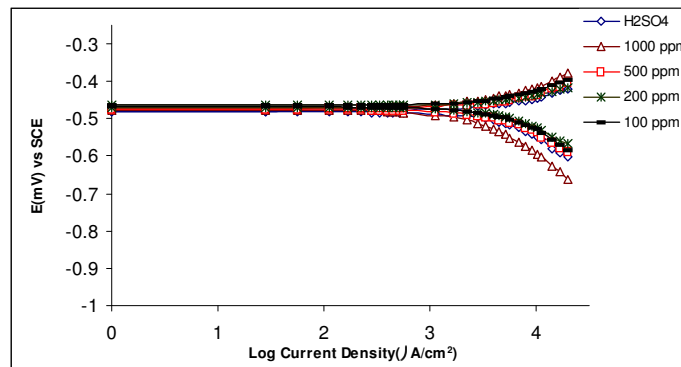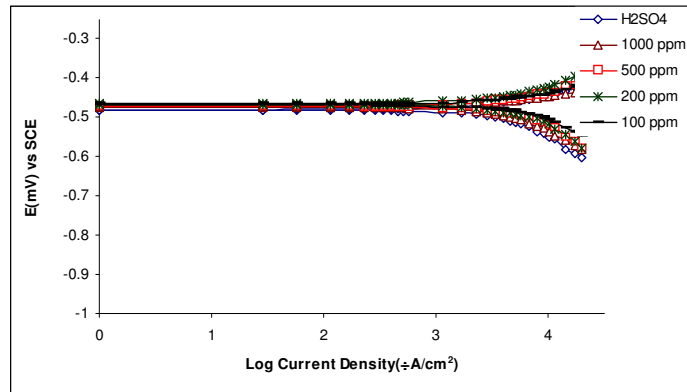

Figure 4. Galvanostatic polarization curves of mild steel in 1 M HCl solution containing different concentrations of 3-hydroxy-2-methylquinazoline-4-one at 55 ºC.

Figure 5. Galvanostatic polarization curves of mild steel in 1 M H_2SO_4 solution containing different concentrations of 3-hydroxy-2-methylquinazoline-4-one at 25 ºC.

Figure 6. Galvanostatic polarization curves of mild steel in 1 M H_2SO_4 solution containing different concentrations of 3-hydroxy-2-methylquinazoline-4-one at 35 ºC.

Figure 7. Galvanostatic polarization curves of mild steel in 1 M H_2SO_4 solution containing different concentrations of 3-hydroxy-2-methylquinazoline-4-one at 45 ºC.

Figure 8. Galvanostatic polarization curves of mild steel in 1 M H_2SO_4 solution containing different concentration of 3-hydroxy-2-methylquinazoline-4-one at 55 °C.

To calculate the activation energy of corrosion process, corrosion current densities at various temperatures in the absence and presence of various concentrations of inhibitor were put in Arrhenius equation,

$$\log K = \log A - \frac{E_a}{2.303 R T}$$

where, K is the specific corrosion rate constant, Ea is the activation energy, T is the absolute temperature, and A is the exponential factor. Plotting of log K against 1/T in absence and presence of the inhibitor gives straight line, as shown in Figs.11 and 12. The activation energy, calculated from this graph, is 72.18 Kcal/mol in 1 M HCl solution, while it is 74.11 Kcal/mol in the case of H_2SO_4. The results show that the rate of corrosion increases as the temperature increases. This indicates that corrosion inhibition takes place by adsorption of the inhibitor at the electrode surface.
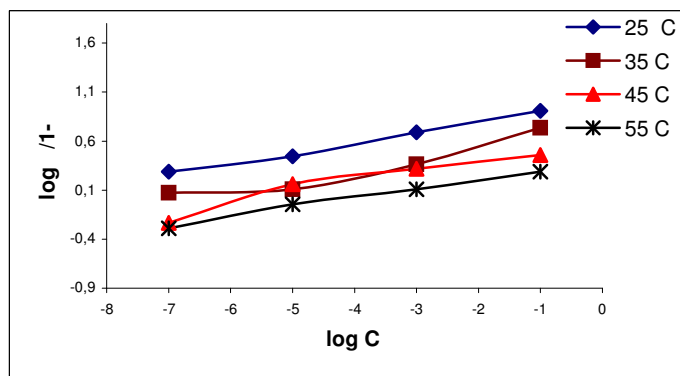

Figure 9. Variation of surface coverage vs. concentration at different temperatures of 3-hydroxy-2-methylquinazoline-4-one in 1 M HCl.
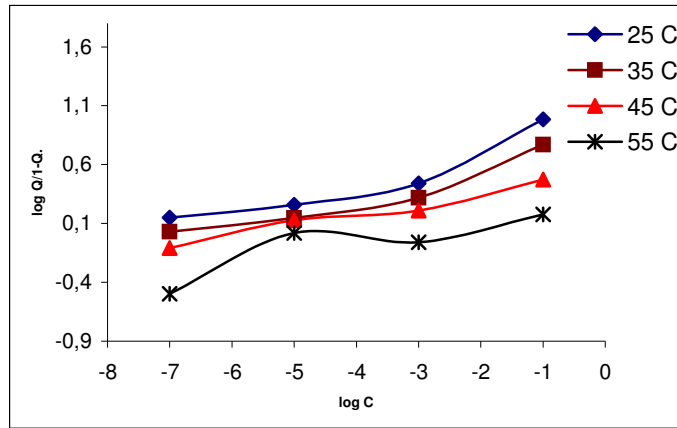
Figure 10. Variation of surface coverage vs. concentration at different temperatures of 3-hydroxy-2-methylquinazoline-4-one in 1 M H_2SO_4.
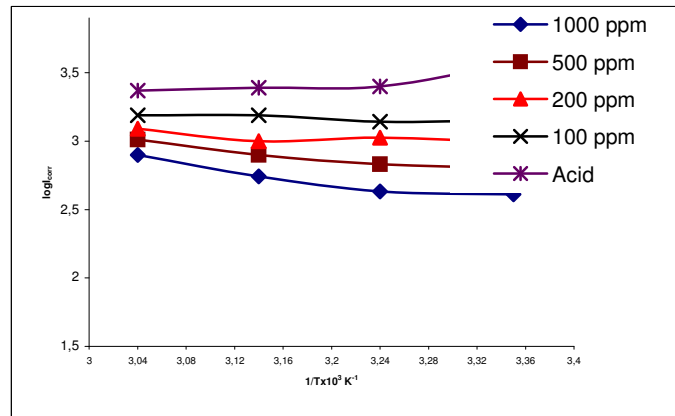

Figure 11. Variation of corrosion current vs. reciprocal of temperature at different concentrations of 3-hydroxy-2-methylquinazoline-4-one in 1 M HCl.
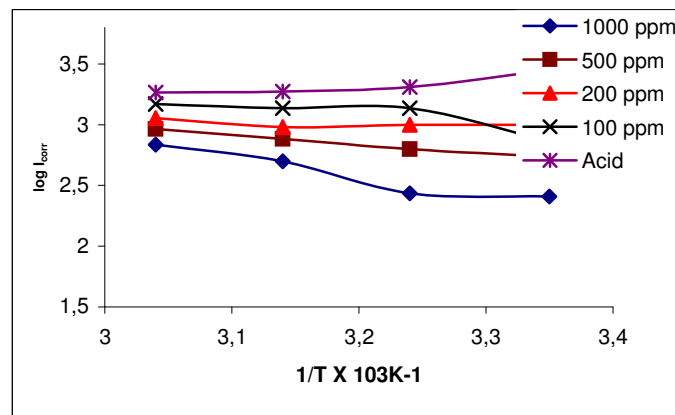

Figure 12. Variation of corrosion current vs. reciprocal of temperature at different concentrations of 3-hydroxy-2-methylquinazoline-4-one in 1 M H_2SO_4.

Conclusions

1. 3-hydroxy-2-methylquinazoline-4-one inhibits the corrosion of mild steel in both the acids (1 M HCl and 1 M H_2SO_4).
2. The performance of this compound as an inhibitor in both the acids is very much encouraging.
3. The inhibition efficiency increases with increasing the concentration of the inhibitor in both the acids.

4. The inhibition efficiency decreases with increasing the temperature in both the acids.
5. The inhibition of corrosion of mild steel by 3-hydroxy-2-methylquinazoline-4-one in both the acids is of the mixed type.
6. The adsorption of 3-hydroxy-2-methylquinazoline-4-one on mild steel surfaces from both the acids obeys Langmuir's adsorption isotherm.

Acknowledgements

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