Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry
2016, 5 (5): 1226-1235
(International Peer Reviewed Journal)

Inhibition Study of Caesalpinia Crista on Corrosion of Mild Steel in Sulphuric acid

Nil S. Desai[1] and G M. Malik[2*]

1. Department of chemistry, UTU, Bardoli, Gujarat, **INDIA**
2. Department of Chemistry, Navyug Science College, Surat, Gujarat, **INDIA**

Email: gmmalik2010@gmail.com

Accepted on 22nd September 2016

ABSTRACT

The inhibition effect of Caesalpinia crista (Kachko) fruit on corrosion of mild steel in sulfuric acid using weight loss measurements and electrochemical techniques has been reported in this study. The inhibition efficiency of Caesalpinia crista was found to vary with concentration, temperature and immersion time. Good inhibition efficiency I.E. % was recorded in acid solution. The adsorption study of these compounds on mild steel surface found to obey Temkin's adsorption isotherm. The activation energy values and values of free energy of adsorption indicated physical adsorption on mild steel surface. The Potentiodynamic polarization results showed that the compound studied was mixed type inhibitor.

Keywords: Mild steel, Caesalpinia crista, corrosion, inhibition effect, sulfuric acid, adsorption.

INTRODUCTION

Corrosion of metals results due to the presence of oxygen and moisture involving redox reaction. In acidic medium hydrogen evolution reaction predominates. Corrosion inhibitors reduce or prevent these reactions, they are adsorbed on the metal surface and act by forming barrier to oxygen, moisture and some of the inhibitors facilitate formation of passive film on the metal surface.

Acid inhibitors are generally used in several industrial processes to control the corrosion of metals. They find wide applications as components in pretreatment composition, in cleaning solutions for industrial equipments. Inorganic substances such as phosphates, chromates, dichromates, silicates, borates, tungstates, molybdates and arsenates have been found effective as inhibitors of metal corrosion. Anti-corrosive coatings have major disadvantage because of their toxicity and as such their use has come under severe criticism [1-6].

Corrosion control of metals is of technical, economical, environmental and aesthetical importance. The use of inhibitors is one of the best options for protecting metals and alloys against corrosion. The environmental toxicity of organic corrosion inhibitors have prompted the search for green corrosion inhibitors as they are biodegradable, do not contain heavy metals or other toxic compounds. Many researchers have reported large number of papers on eco-friendly inhibitors exhibiting good efficiency and least hazardous effect [7, 8, 9, 15]. As in addition to being environmentally friendly and ecologically acceptable, plant products are in expensive, readily available and renewable. One of the green inhibitors, photochemical plant, Caesalpinia Crista (Fevernut-Kachko) has been used for the study. Kachko is available in plenty in rural and semi urban area throughout the year.

MATERIALS AND METHODS

Very large numbers of papers have been published, which aimed to investigate the corrosion inhibition process. The following methods were used to determine the corrosion rate, weight loss and Galvanostatic polarization, the effects of temperature and concentration of the inhibitors were studied. The thermodynamic parameters for the process were computed and discussed.

Weight Loss: Weight loss method is widespread, cheap, simple and give a quantitative data. It is a valid measure of corrosion only if corrosion is perfectly uniform. Weight loss can be a meaningful measure of corrosion if specimens are of the same size and have been tested for the frequently expressed as loss in weight per unit area or loss in weight per unit area per unit time. By introducing the density of the metal into the calculations, the loss in thickness per unit time can be determined. The corrosion rate was expressed in mdd (milligram per square decimeter per day) or mpy (miliinches per year).

At any instant a fraction 'θ' of the metal surface is covered by the inhibitor molecules and uncovered fraction (1-θ) reacts with acid as it does in the absence of the inhibitor. The nature of the inhibitor interaction with the corroding surface has been deduced from the adsorption characteristics of the inhibitor. Surface coverage values are very useful in explaining the adsorption characteristics. The inhibition efficiency (η %) and degree of surface coverage (θ) at each concentration of inhibitors was calculated by comparing the corrosion loss in the absence (W_u) and presence of inhibitor (W_i) using the relationships:

$$\eta\% = \frac{W_u - W_i}{W_i} \times 100 \tag{1}$$

$$\theta = \frac{W_u - W_i}{W_i} \tag{2}$$

Effect of Temperature: The study of the effect of variation in temperature and concentration on the protective effect of corrosion inhibitors is important in the understanding of the mechanism and kinetics of their action and ultimately in the proper selection of inhibitor for particular situation. To study the effect of temperature on corrosion rate, the specimens were immersed in 230 mL in different concentrations of acid, with and without inhibitor at solution temperatures of 313, 323 and 333 K for a period of 3 h. From the results, inhibition efficiency (I.E.) (η%) and thermodynamic parameters such as energy of activation (Ea), heat of adsorption (Q_{ads}) free energy of adsorption (ΔG^0_{ads}), enthalpy of adsorption (ΔH^0_{ads}) and entropy of adsorption (ΔS^0_{ads}) were calculated using following equations:

Energy of activation (Ea) was calculated from the slopes of log ρ versus 1/T (ρ = corrosion rate, T = absolute temperature) and also with the help of Arrhenius equation.

$$\log\frac{\rho_2}{\rho_1} = \frac{Ea}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{3}$$

where ρ_1 and ρ_2 are the corrosion rate at temperature T_1 and T_2 respectively. The enthalpy of adsorption (ΔH^0_{ads}) and entropy of adsorption (ΔS^0_{ads}) will be calculated using the following equations (4) and (5).

$$\Delta H^0_{ads} = Ea - RT \tag{4}$$

$$\Delta S^0_{ads} = \frac{\Delta H^0_{ads} - \Delta G^0_{ads}}{T} \tag{5}$$

The values of the free energy of adsorption (ΔG^0_{ads}) were calculated with slope of the following equation.

$$\log C = \log\left(\frac{\theta}{1-\theta}\right) - \log B \tag{6}$$

where $\log B = -1.74 - \left(\frac{\Delta G^0_{ads}}{2.303RT}\right)$ and C is the inhibitor concentration. The values of heat of adsorption (Q_{ads}) calculated by the following equation (7)

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \frac{T_1T_2}{T_2 - T_1} \tag{7}$$

Corrosion potential measurements: Metal specimen having an area of 0.0675 dm^2 was immersed in acid solutions with and without inhibitor at various concentrations and the potential was measured with reference electrode till a constant potential was attained.

Polarization measurements: The first report on electrochemical nature of corrosion was made by Auguste de la Rive [13] The development of mix potential theory of Wagnar and Traud ultimately found its application in the measurement of corrosion rate by polarization resistance technique and was developed by Stern and Geary [14].

Tafel plot: This technique is used to measure the corrosion current (i_{corr}) so that the corrosion rate can be calculated. A Tafel plot can yield i_{corr} directly or it can yield the Tafel constants (βa and βc). The Tafel constants can then be used with the Rp value to calculate i_{corr}.

The values of corrosion current densities in the presence and absence of inhibitor were obtained from the graph while percentage efficiency (η %) was calculated using the equation (8).

$$\eta(\%) = \left[\frac{i_{corr}(u) - i_{corr}(i)}{i_{corr}(u)}\right] \times 100 \tag{8}$$

RESULTS AND DISCUSSION

The values of inhibition efficiency (I.E. %) and the corrosion rate (CR) obtained from the weight loss method at different concentrations of H_2SO_4 given in table-1. The effect of acid concentration and exposure time on the corrosion loss of mild steel in H_2SO_4 showed increase in corrosion with time and more in higher acid concentration, as evident from an increase in the slope of the graphs.

The corrosion loss of mild steel increased with increase in concentration of H_2SO_4. It was also observed that corrosion rate decreased with increase in inhibitor concentration. The increased inhibition efficiency and decreased corrosion rate attributed to the increased adsorption and increased surface coverage θ of inhibitor on mild steel surface with increase in concentration.

Table-1: Effect of acid H_2SO_4 concentration on corrosion loss (CL) and inhibition efficiency (I.E.) of mild steel containing kachko as inhibitor

Hours	Acid Concentration	Corrosion loss				I.E.%
		CL (g)		CL (mg/dm^2)		
		Blank	With inhibitor	Blank	With inhibitor	
24 h	1.0 M	3.224	0.2451	17889.24	1360.004	92.4
	1.5 M	3.540	0.3328	19642.66	1846.631	90.6
	2.0 M	4.009	0.5172	22245.03	2869.82	87.1
48 h	1.0 M	5.811	0.6392	32243.92	3546.77	89.0
	1.5 M	6.091	0.8223	33797.58	4562.75	86.5
	2.0 M	6.413	1.1095	35584.29	6156.36	82.7
72 h	1.0 M	6.080	0.8877	33736.54	4925.64	85.4
	1.5 M	7.129	1.2904	39557.21	7160.13	81.9
	2.0 M	8.152	1.7364	45233.60	9634.89	78.7
96 h	1.0 M	6.181	1.1560	34296.97	6414.38	81.3
	1.5 M	7.973	1.8019	44240.37	9998.33	77.4
	2.0 M	10.265	2.6539	56958.16	14725.89	74.0

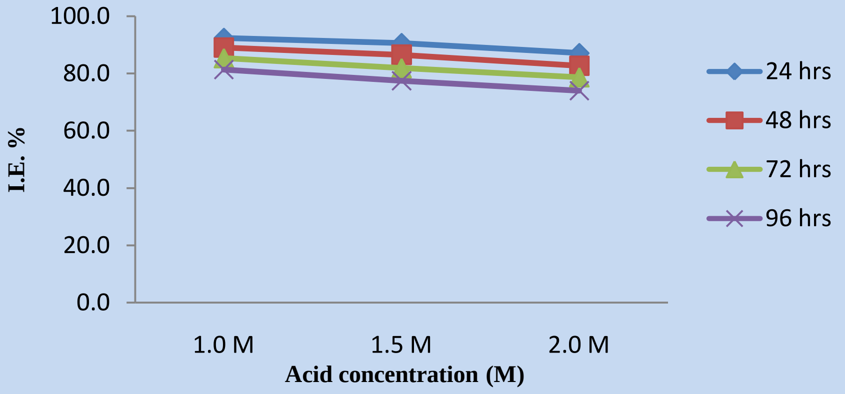


Figure-1: Effect of H_2SO_4 concentration on inhibition efficiency of kachko for mild steel in 5mM inhibitor concentration at different time interval.

Effect of temperature: The effect of temperature was studied in 1.0 M H_2SO_4 containing 5mM of inhibitor concentration at 313, 323 and 333 K temperature. The results of table2 showed that corrosion loss increased with increase in temperature. Inhibition efficiency of inhibitors decreased with the increase in temperature. In 1.0 M H_2SO_4 at 5mM inhibitor concentration, the inhibition efficiency for Kachko was 88%, 86%, 78% at 313, 323 and 333 K respectively.

Activation energy calculated from the slopes of plots of log ρ vs 1/T (ρ=corrosion rate and T=absolute temperature) and also using the Arrhenius equation. The Ea values are given in table-3 show that the energy of activation for the corrosion of mild steel in 1.0 M H_2SO_4 decreases in acid containing inhibitor. The higher value of Ea indicates physical adsorption of the inhibitors of metal surface. The Ea calculated from the slopes of Arrhenius plot and by using equation (8) are almost similar.

The values of heat of adsorption (Q_{ads}) and free energy of adsorption ($\Delta G^0{}_a$) were calculated from the equation (7). From table-4 it is evident that in all the cases, the Q values are negative. The negative Q values show that the adsorption and hence the inhibitive efficiency decreases with rise in temperature. The values of $\Delta G^0{}_{ads}$ are given in table-4. In all the cases mean $\Delta G^0{}_{ads}$ values are negative. The results are shown in figs- 2-4.

Table-2: Corrosion loss (CL) of mild steel in H_2SO_4 and effect of inhibitor (kachko)
Effective area of specimen: 0.3074 dm^2; Immersion period: 2 h

Temp.	Acid Concentration	CL mg/dm^2 Blank	CL mg/dm^2 With inhibitor(ρ)	log ρ	I.E %	Surface coverge (θ)	1-θ	log (θ/1-θ)
313 K	1.0 M	3157.25	371.76	2.5703	88%	0.8823	0.1177	0.8748
	1.5 M	5310.17	826.74	2.9174	84%	0.8443	0.1557	0.7342
	2.0 M	7723.89	1342.8	3.1280	82%	0.8261	0.1739	0.6767
323 K	1.0 M	4272.55	610.36	2.7856	86%	0.8571	0.1429	0.7780
	1.5 M	6558.65	1242.92	3.0944	81%	0.8105	0.1895	0.6311
	2.0 M	9394.07	2263.89	3.3549	76%	0.7590	0.241	0.4982
333 K	1.0 M	8467.42	1808.9	3.2574	78%	0.7864	0.2136	0.5660
	1.5 M	13139.49	3628.89	3.5598	72%	0.7238	0.2762	0.4184
	2.0 M	18987.9	6159.13	3.7895	67%	0.6756	0.3244	0.3186

Table-3: Effect of temperature on the corrosion lose (CL), energy of activation (Ea) for the corrosion of mlid steel in H_2SO_4 (kachko) at inhibitor concentration
Effective area of specimen: 0.3074 $dm^{2:}$:Inhibitor concentration: 5mM, Immersion period: 2 h

Acid Conc.	Temperature									Activation Energy (Ea) KJ/mol			Ea from Arrhenius Plot
	313 K			323 K			333 K						
	CL mg/dm2		I.E %	CL mg/dm2		I.E %	CL mg/dm2		I.E %	313K - 323K	323K - 333K	Mean	
	Blank	With inhibitor		Blank	With inhibitor		Blank	With inhibitor					
1.0 M	3157.25	371.76	88	4272.55	610.36	86	8467.42	1808.90	78	41.68	97.17	69.43	68.26
1.5 M	5310.17	826.74	84	6558.65	1242.92	81	13139.49	3628.89	72	34.28	95.83	65.05	63.77
2.0 M	7723.89	1342.80	82	9394.07	2263.89	76	18987.90	6159.13	67	43.91	89.52	66.71	65.76

Table-4: Effect of temperature on heat of adsorption Q_{ads} and free energy of adsorption ($\Delta G^0{}_a$) of mild steel in H_2SO_4 in presence of inhibitor (kachko)

Acid (H_2SO_4) Conc.	Heat of adsorption Q_{ads} KJ/mol			Free Energy of Adsorption ($\Delta G^0{}_a$) kJ/mol			
	313K - 323K	323K - 333K	Mean	313 K	323 K	333 K	Mean
1.0 M	-18.76	-43.64	-31.20	-32.3695	-33.4615	-35.14	-33.6586
1.5 M	-19.96	-43.80	-31.88	-32.4946	-33.8313	-36.24	-34.1899
2.0 M	-34.55	-36.99	-35.77	-32.6324	-34.5459	-37.38	-34.853

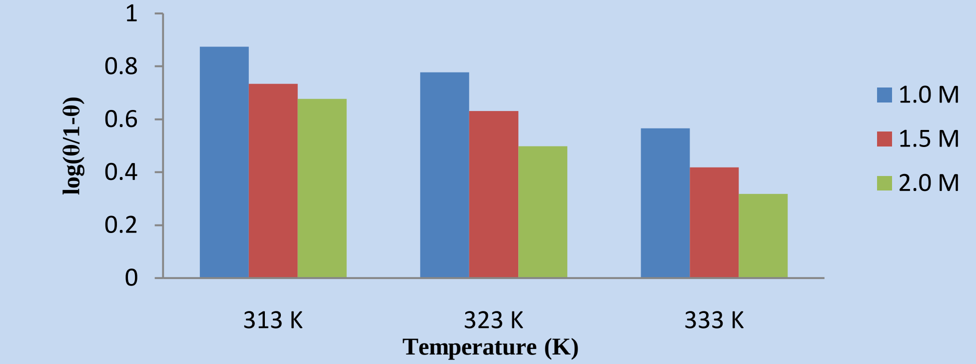


Figure-2:Corrosion loss of mild steel in H_2SO_4 and effect of inhibitor (kachko)

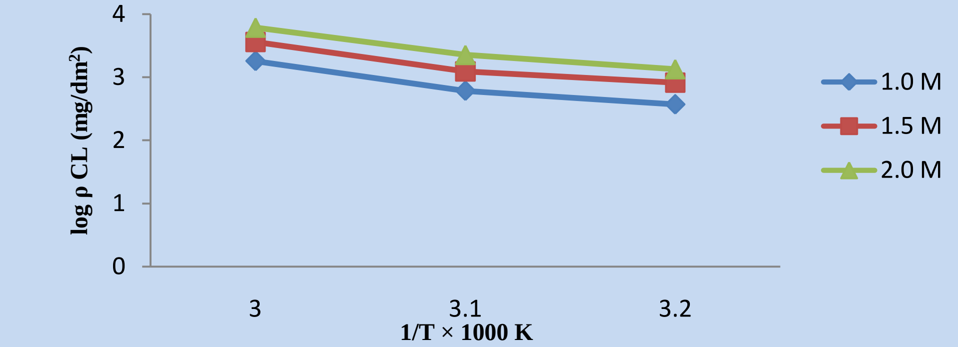


Figure-3:Arrhenius plots for corrosion of mild steel in H_2SO_4 in presence of 5mM (kachko) ininhibitor concentration.

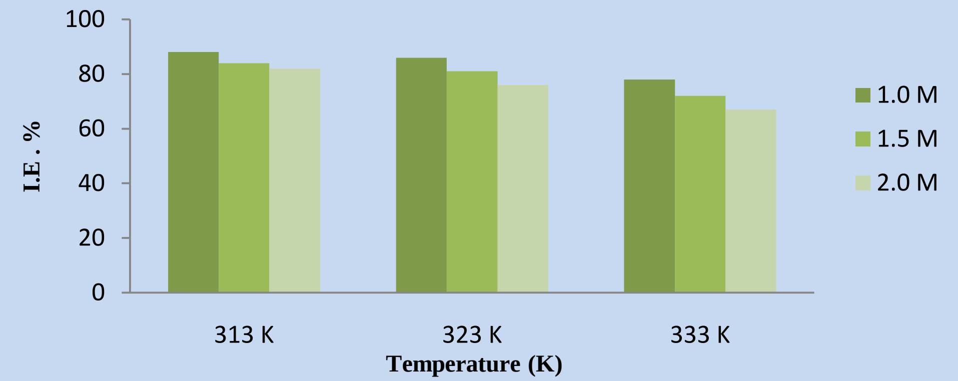


Figure-4: Effect of temperature on inhibition efficiency of kachko for mild steel at different H_2SO_4 concentration.

Potential measurement: In 1.0 M H_2SO_4 the potential shifted to the negative direction from its initial value (-0.540mV) and settled at (-0.529 mV) within 30 min (Table- 5, Fig-5). On addition of 5mM of the inhibitor (Kachko) in 1.0 M H_2SO_4 the initial value of the OCP (open circuit potential) increased (become less negative) (-0.501 mV) and settled at (-0.523mV) within 30 min.

Table-5: Electrode potential (mv) of mild steel in H_2SO_4 containing the inhibitor (kachko) at different exposure period

Acid Concentration: 1.0 M: Inhibitor Concentration: 5 mM

Time (in min)	Electrode Potential (mV)		Time (in min)	Electrode Potential (mV)	
	Blank	With inhibitor		Blank	With inhibitor
0	-0.54	-0.501	24	-0.533	-0.522
2	-0.539	-0.508	26	-0.531	-0.522
4	-0.538	-0.51	28	-0.529	-0.523
6	-0.537	-0.512	30	-0.529	-0.523
8	-0.536	-0.515	32	-0.529	-0.523
10	-0.535	-0.517	34	-0.529	-0.523
12	-0.535	-0.518	36	-0.529	-0.523
14	-0.535	-0.519	38	-0.529	-0.523
16	-0.534	-0.52	40	-0.529	-0.523
18	-0.534	-0.52	42	-0.529	-0.523
20	-0.534	-0.521	44	-0.529	-0.523
22	-0.533	-0.521	46	-0.529	-0.523

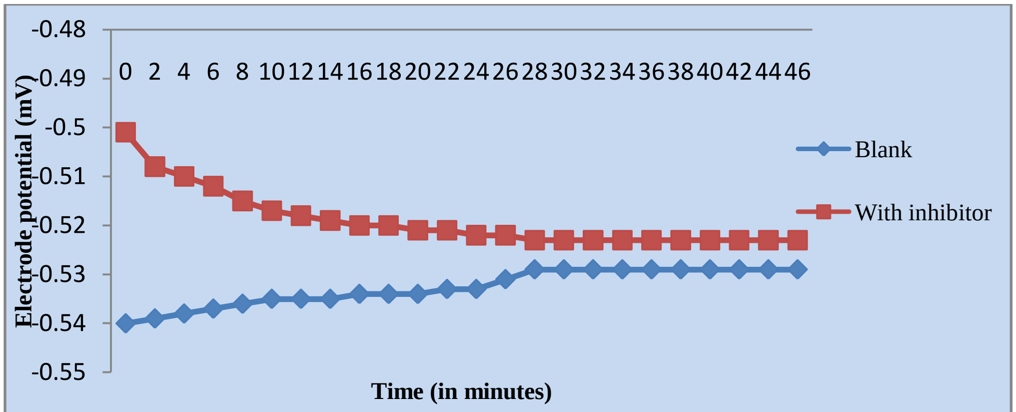
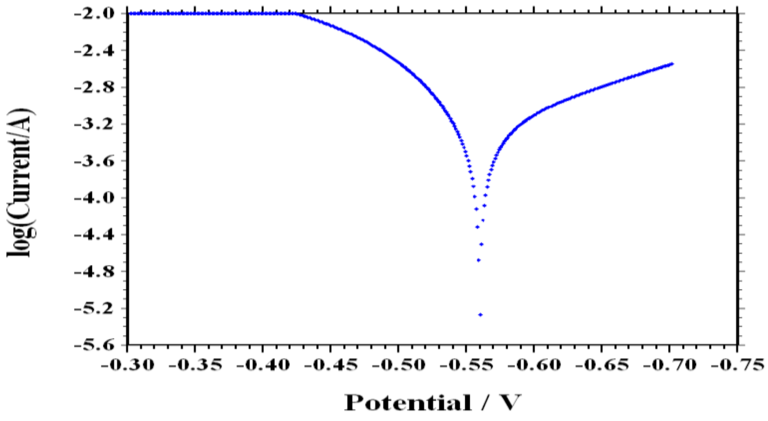


Figure-5: Variation in open circuit Potential with time for mild steel in 1.0 M H_2SO_4 without and with inhibitor Caesalpinia crista conc.

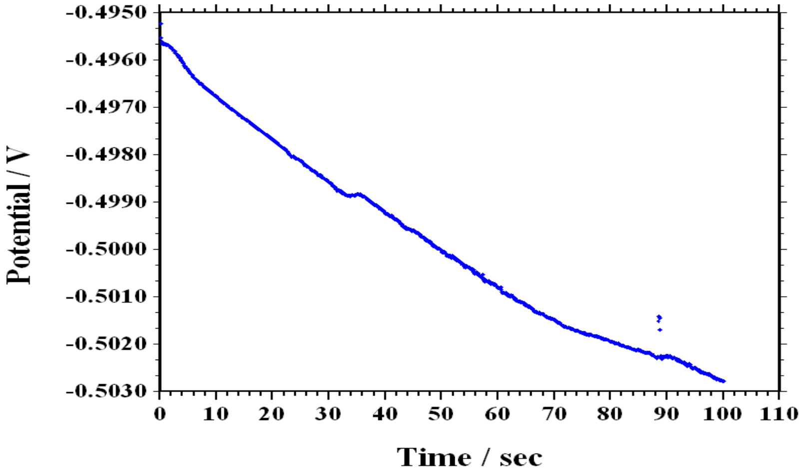
Polarization Measurements: Anodic and cathodic polarization curves for mild steel in 1 M H_2SO_4 at 5 mM inhibitor concentration in the presence and absence of inhibitors are shown in figures 6 and 9. The values of the corrosion potential with inhibitors were found more positive than without inhibitors as shown in figures 7 and 10. Polarization study reveals that the inhibitor functions as little anodic, but significant cathodic inhibitor, inhibitor functions as a mixed inhibitor. It is evident from the figures that cathodic Tafel slopes (β_c) remain almost unchanged with increasing inhibitor concentration. This indicates that hydrogen evolution is active controlled and the addition of inhibitor did not change the mechanism of cathodic hydrogen evolution reaction. It is observed from figure 8 and figure 11 that the electrochemical impedance diagrams are almost semicircular in appearance, but not perfect semicircle. The difference has been attributed to frequency dispersion. The semicircular nature of the plots indicates that the corrosion of mild steel is mainly controlled by charge transfer process.



Sept. 14, 2015 15:29:21
Tech: TAFEL
File: TAFEL.bin

Init E (V) = -0.302
Final E (V) = -0.702
Segment = 1
Hold Time at Ef (s) = 0
Scan Rate (V/s) = 0.01
Quiet Time (s) = 2

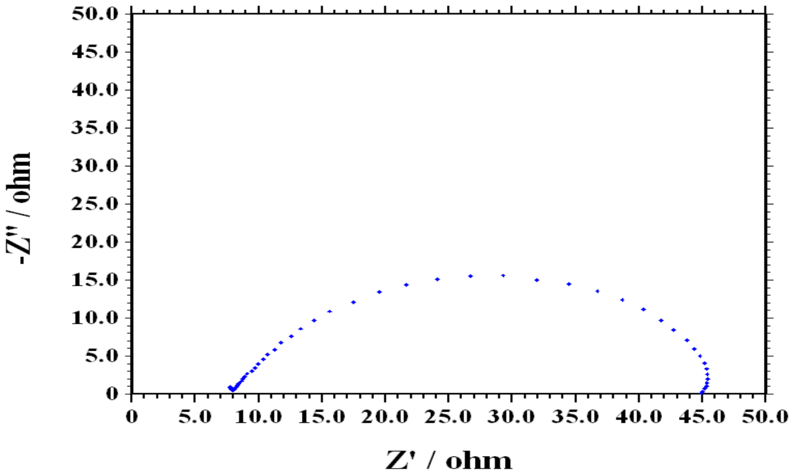
Figure-6: Polarization curve for corrosion of mild steel in 1 M H_2SO_4 without inhibitor.



Sept. 14, 2015 15:25:19
Tech: OCPT
File: OCP.bin

Run Time (s) = 100

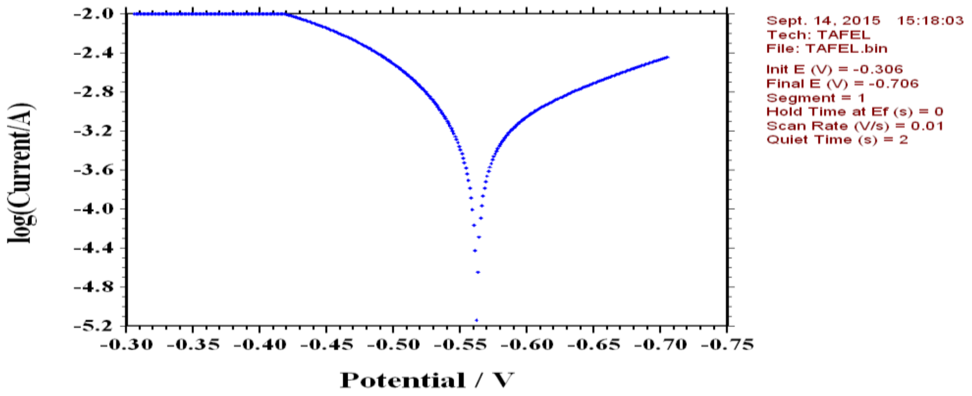
Figure-7: Polarization curve for corrosion of mild steel in 1 M H_2SO_4 without inhibitor.



Sept. 14, 2015 15:16:42
Tech: IMP
File: IMPEDENCE.bin

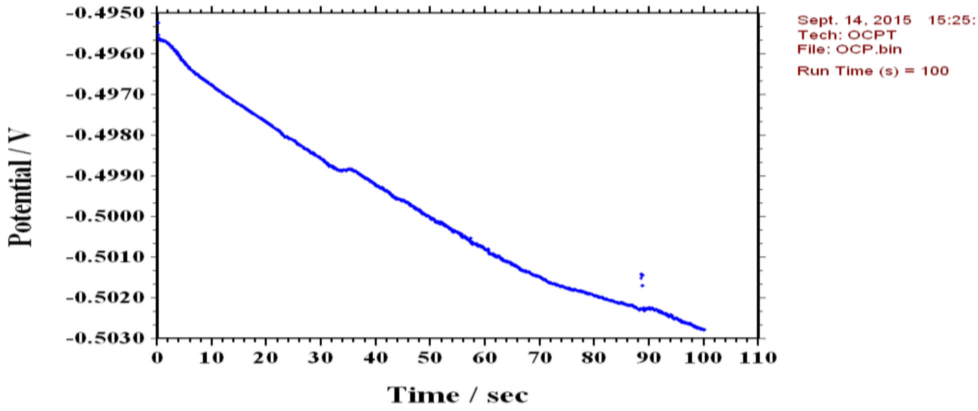
Init E (V) = -0.506
High Freq (Hz) = 1e+5
Low Freq (Hz) = 1
Amplitude (V) = 0.005
Quiet Time (s) = 2

Figure-8: Polarization curve for corrosion of mild steel in 1 M H_2SO_4 without inhibitor.



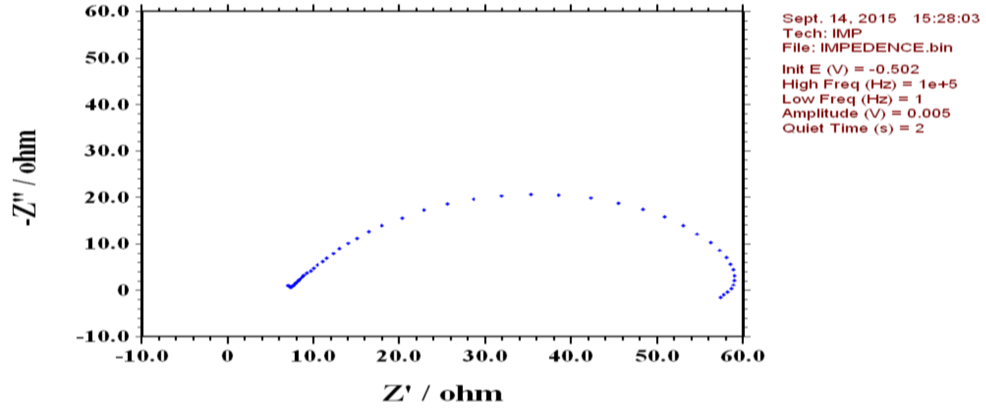
Sept. 14, 2015 15:18:03
Tech: TAFEL
File: TAFEL.bin
Init E (V) = -0.306
Final E (V) = -0.706
Segment = 1
Hold Time at Ef (s) = 0
Scan Rate (V/s) = 0.01
Quiet Time (s) = 2

Figure-9: Polarization curve for corrosion of mild steel in 1 M H_2SO_4 containing 5 mM inhibitor concentration (Kachko).



Sept. 14, 2015 15:25:19
Tech: OCPT
File: OCP.bin
Run Time (s) = 100

Figure-10: Polarization curve for corrosion of mild steel in 1 M H_2SO_4 containing 5 mM inhibitor concentration (Kachko).



Sept. 14, 2015 15:28:03
Tech: IMP
File: IMPEDENCE.bin
Init E (V) = -0.502
High Freq (Hz) = 1e+5
Low Freq (Hz) = 1
Amplitude (V) = 0.005
Quiet Time (s) = 2

Figure-11: Polarization curve for corrosion of mild steel in 1 M H_2SO_4 containing 5 mM inhibitor concentration (Kachko).

APPLICATIONS

The corrosion inhibition behavior of Caesalpinia crista on mild steel in sulphuric acid medium has been investigated using weight loss method, potential measurement technique and polarization technique. This compound is eco friendly, very effective and low cost. It is applicable as a mixed type corrosion inhibitor.

CONCLUSIONS

Caesalpinia crista has been found to be a good eco-friendly inhibitor for the corrosion control of mild steel in H_2SO_4 solution. The inhibition efficiency increases with increase in caesalpinia crista concentration. Caesalpinia crista adsorbed on metal surface follows Langmuir adsorption isotherm. Tafel plots indicate that caesalpinia crista acts as a mixed type inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. All three techniques gave almost identical values of inhibition efficiency for mild steel in H_2SO_4.

ACKNOWLEDGEMENTS

The authors are thankful to the Principal, Navyug Science College, Surat and Department of Chemistry, UTU, Bardoli for providing laboratory facilities.

REFERENCES

[1] S.L. Granese, B.M. Rosales, C. Oviedo, J.O. Zerbino, *Corrosion Science*, **1992**, 33, 1439-1453.
[2] L.D. Skryler, E.A. Streltsova, T.L. Skrylevo, *Protection metals USSR*, **1991**, 27**,** 755-758.
[3] A. Swift, A.J. Paul, J.C. Vickerman, *Surface interface analysis*, **1993**, 20, 27-35.
[4] A. Frignani, M. Tassinari, L. Meszaros, G. Trabanelli, *Corrosion Science*, **1991**, 32, 903-911.
[5] G. Moretti, F. Guidi, G. Grion, *Corrosion Science*, **2004**, 46, 387-403.
[6] S.N. Raicheva, B.V. Aleksiev, E.I. Sokolova, *Corrosion Science*, **1993**, 34, 343-350.
[7] C. Ejieh, R. A. Dr. Ejimofor, Inhibition of corrosion on mild steel using piper guineense (uziza) extract in sulphuric acid medium of varying pH value,.
[8] R. T. Vashi, K. K. Patel, Azadirachta indica extract as corrosion inhibitor for copper in nitric acid, **2015**.
[9] Hassen Challouf et al, Origanum majorana extracts as mild steel corrosion green inhibitors in aqueous chloride medium, **2016**.
[10] A.M.S. Abedel, A.E.L. Saicd, *Trans SAEST*, **1981**, 16, 197.
[11] N. Subramanian, K. Ramakrishnaiah, *Indian J Tech*, **1970**, 8**,** 369.
[12] H.M. Bhajiwala, R.T.Vashi, *Bul of Electroche.*, **2001**, 17, 441.
[13] Auguste de La Rive. A treatise on electricity, in theory and practice, **1853**.
[14] M. Stern, A.L. Geary, *Electrochem. Soc.*, **1957**,104, 56,
[15] Alpana Soni et al, *Journal of Applicable Chemistry*, **2016**, 5(1), 281-290.

AUTHORS' ADDRESSES

1. **Nil S. Desai**
Research Scholar, Department of Chemistry,
Uka Tarsadia University, Bardoli, Gujarat, India.
E-mail: falgunidabhade@yahoo.com, Mobile No. 0982533157
2. **G. M. Malik**
Head, Department of Chemistry,
Navyug Science College, Rander Road, Surat, Gujarat, India.
E mail: gmmalik2010@gmail.com, Mobile No. 09824339606