Corrosion inhibition behavior of Gum Acacia as natural occurring polymer for mild steel and synergistic effect of halide ions in H₂SO₄ medium

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Abstract

The corrosion inhibition effect of Gum Acacia (GA) as green inhibitor was investigated by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods and SEM observations for mild steel in H_2SO_4 (pH=1) medium . The results show that GA is a good inhibitor, and the adsorption of GA on metal surface obeys Temkin adsorption isotherm. The inhibitive effect of GA in addition of halide ions is found to promot at all the concentration of GA. Polarization curves show that GA acts as a mixed-type inhibitor. The results obtained from gravimetric experiments were in good agreement with the electrochemical methods results. Comprehensive adsorption of the inhibitor molecules on the mild steel surface was suggested based on the thermodynamic parameters and on the comparative FT-IR spectral analysis of pure and metal surface product. An inhibition mechanism was proposed in terms of strongly adsorption of inhibitor molecules on mild steel surface.

1. Introduction:

Mild steel is one of the most important widely used engineering materials particularly for the structural and automobile applications. However, it undergoes rusting easily in the humid atmosphere and its rate of corrosion is quite high in acidic environment. Acid solutions are widely used in industries for pickling, acid cleaning, descaling and oil well acidizing. Sulfuric acid is generally the choice in the steel surface treatment over the other acids basically due to its lower cost, minimal fumes and non-corrosive nature of the SO_4^{2-} ion[1,2]. Hence corrosion of mild steel is of fundamental academic and industrial concern that has received a considerable amount of attention. Among different corrosion protection methods, application of inhibitors is one of the most convenient methods to reduce corrosion rate of metallic materials especially in acidic media. Most of the well known acid inhibitors are organic compounds containing electron donor atoms particularly nitrogen, sulfur, oxygen in their functional groups with aromatic and heterocyclic rings[3-5]. Most of the corrosion inhibitors act by adsorption of their molecules on the metal surface. Their action depends on the nature and surface charge of the metal, nature of the medium and the chemical structure of the inhibitor.

Though many organic and inorganic compounds show good anticorrosive activity, most of them are highly toxic to both human beings and environment. The investigation of new non-toxic or low-toxic and green corrosion inhibitors is essential to overcome this problem. Among eco-friendly organic compounds, the natural occurring polymers have many advantages such as high inhibition efficiency, low price, low toxicity and easy production[6-8]. It is known that polymers are adsorbed stronger than their monomer analogs; hence polymers will be better corrosion inhibitors than the corresponding monomers[9]. The improved performances of the polymeric materials are ascribed to their multiple adsorption sites for bonding with the metal surface. The polymer displaces many water molecules from the metal surface during adsorption, thus making the process entropically favorable and the presence of multiple bonding sites slower the desorption process[10,11]. Inhibition effects of natural products and different plant extracts have been examined by many researcher[12-15].

Synergistic inhibition is an effective method to improve the inhibitive force of individual inhibitors, to decrease the amount of usage and to diversify the application of inhibitor in acidic media[16,17]. The synergistic inhibition effects of organic inhibitor/metallic ion mixture, organic inhibitor/organic inhibitor mixture and inorganic inhibitor/ inorganic inhibitor mixture on

corrosion of steel in acidic media have been studied. Investigations on synergism between organic inhibitors and halide ions on steel corrosion in acidic solution have been researched extensively by many authors[18-20].

In this present investigation Gum Acica (GA) have been tested as corrosion inhibitor for mild steel in H_2SO_4 solution (pH=1). Corrosion experiments were carried out on the variation of corrosion rate due to the metal corrodibility as functions of time, temperature and inhibitor concentration together with analyses of the metal surface products for a better understanding of the inhibition mechanism with the help of FTIR spectroscopy. Morphological study of corroded metal surface has been carried out by SEM technique. A plausible adsorption mechanism for the inhibitor molecules on the metal surface in acid solution has also been proposed.

2. Experimental:

Experiments were performed to understand the inhibition behavior of GA towards corrosion on mild Steel in pH=1 H_2SO_4 at different experimental conditions. The gravimetric experiments, potentiodynamic polarization and AC Impedance measurements at different exposure periods (6, 12, 18 and 24h) and at different temperatures (303, 313, 323 and 333K) in absence and in presence of inhibitor at different concentrations (10, 50, 75, 100, 150, 200, 250 and 300ppm) were carried out to determine the corrosion parameters. The synergistic effect of halides (KCl, KBr and KI) has been studied with the optimum concentration of GA at different exposure periods and at different temperatures. Mild steel sample used for the study was analyzed and the composition of the tested steel was given in Table 1.

Table 1 Composition of the mild steel coupons

% of C	% of S	% of P	% of Si	% of Al	% of Mn	% of W	% of Fe
0.12	0.02	0.01	0.15	0.01	0.57	0.015	Rest

The steel coupons used for the gravimetric studies were cut out of the size 4.4 cm x 2.2 cm x 0.15 cm from the mild steel sheets with a small hole ~1 mm diameter at the upper edge of the specimen. The surface of the steel coupons were cleaned by mechanical abrasion and polished with increasingly finer grades of emery papers to remove the scratches. After polishing these were degreased with acetone, washed and finally dried in a stream of warm air. In the present study, experiments were performed in pH=1 H_2SO_4 test solution which was prepared in

distilled water using Analytical grade H_2SO_4 supplied by Ranbaxy Fine Chemicals. For immersion test 500 ml of pH=1 H_2SO_4 was used and for the electrochemical experiments, test solution used was 250 ml. The potentiodynamic polarization curves were recorded in absence and in presence of the inhibitors at different concentrations with the mild steel (area 1 cm^2) as working electrode using Potentiostat at ambient temperature (25 to 30^{0}C). The details about the experimental procedures for the above study are explained elsewhere[21, 22]

The organic compound Gum Acacia selected from natural polymers and has been explored as corrosion inhibitor for mild steel in pH=1 H_2SO_4. Gum Acacia has very complex structure (Fig. 1) and is slightly acidic; pH- 4.5-5.0, MW range is from 250,000 to 1,000.0000[23,24].
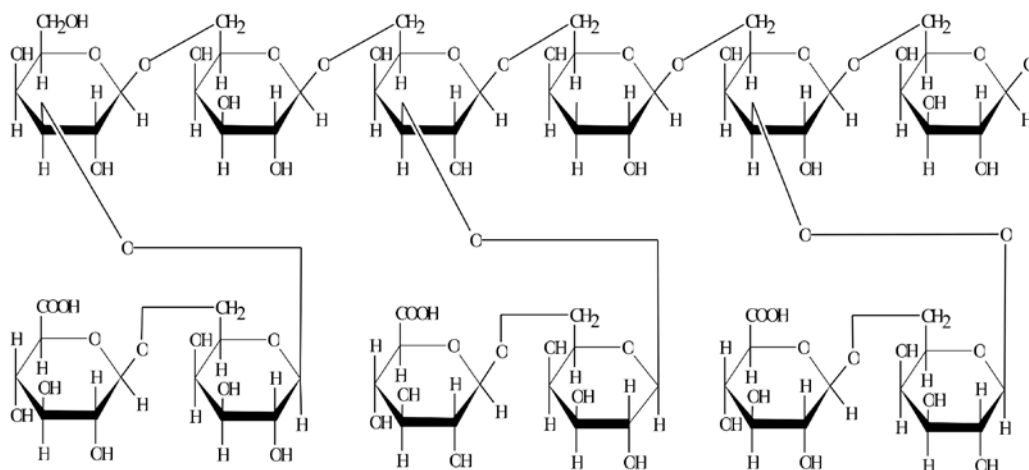

Fig. 1 Structure of Gum Acacia (GA)

3. Results and discussion:

The inhibition efficiency increases with the inhibitor concentration up to 250 ppm (70.02%) and then tends to a constant value for 6h exposure at room temperature has been shown in Fig 2. The inhibition efficiency of GA was 39% at 10 ppm. In the present study degree of surface coverage (θ) was tested graphically for fitting a suitable adsorption isotherm. The best fit
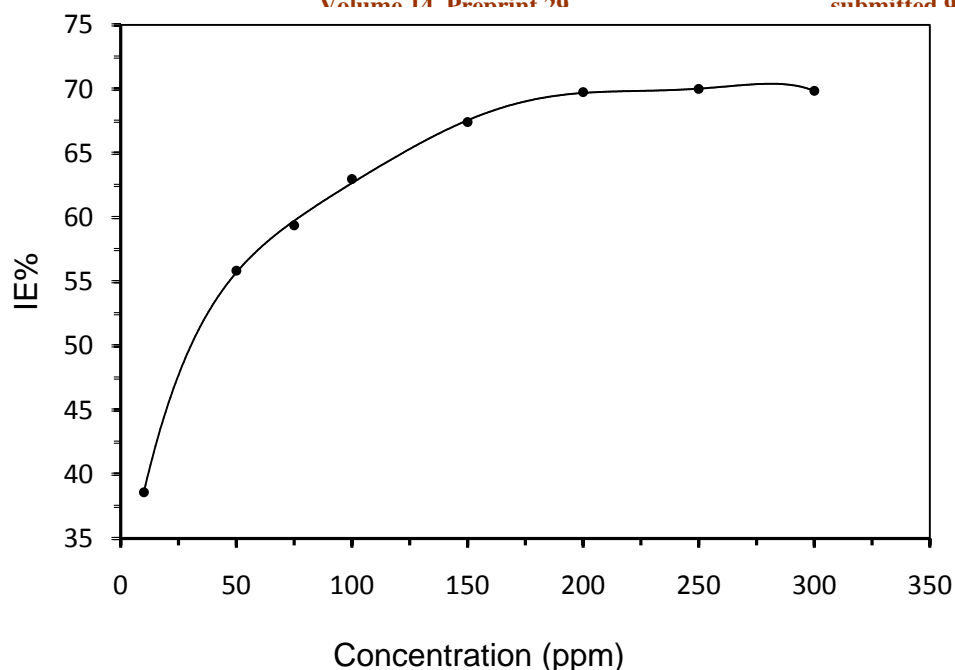
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Fig. 2 Variation of inhibition efficiency with the inhibitor concentration

was obtained with Temkin adsorption isotherm in which a straight line was obtained from the plot of Log C against θ. The corrosion parameters for individual and combination of GA with halides have been given in Table 2. Further it is found that, in addition of halide ions, the

Table 2 Corrosion parameters in presence of GA at different inhibitor concentration

Concentration (ppm)				CR (mpy)	IE%	Surface Coverage (θ)	S
Gum Acacia	Chloride	Bromide	Iodide				
0	0	0	0	359.70	-	-	-
100	0	0	0	133.02	63.00	0.63	-
100	700	0	0	113.45	68.46	0.68	1.84
100	0	700	0	92.41	74.31	0.74	1.57
100	0	0	700	65.61	81.76	0.82	1.40
250	0	0	0	107.59	70.09	0.70	-
250	700	0	0	104.06	71.07	0.71	1.79
250	0	700	0	84.93	76.39	0.76	1.16
250	0	0	700	46.87	86.97	0.87	1.38

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inhibitive effect of GA is promoted at all the concentration of GA (Table 3). The highest efficiency (~ 87%) was obtained in case of 250 ppm GA with 700 ppm iodide. The combined inhibition behavior of GA with halides can be explained in more details with the synergism parameter (s). The highest value of synergism parameter (1.84) was obtained for 700 ppm chloride with 100 ppm GA. The synergistic behavior of halides with GA might be due to the preferential adsorption of halide ions (Cl^-, Br^-, I^-) on the metal surface and makes the negatively charged surface which facilitate further adsorption of inhibitor molecules[25,26]. Therefore halide ions enhance the adsorption of GA and improve the inhibitive effect to a considerable extent.

Table 3 Corrosion parameters in presence of GA and GA + Halides at different exposure period

Exposure Period (h)	Concentration (ppm)				CR (mpy)	PI
	Gum Acacia	Chloride	Bromide	Iodide		
6	0	0	0	0	359.70	-
	250	0	0	0	107.59	70.09
	250	700	0	0	104.06	71.07
	250	0	700	0	84.93	76.39
	250	0	0	700	46.87	86.97
12	0	0	0	0	370.61	-
	250	0	0	0	102.46	72.34
	250	700	0	0	96.03	74.09
	250	0	700	0	77.98	78.96
	250	0	0	700	46.18	87.54
18	0	0	0	0	392.42	-
	250	0	0	0	97.46	75.43
	250	700	0	0	90.37	76.97
	250	0	700	0	79.31	79.79
	250	0	0	700	39.56	89.92
24	0	0	0	0	421.27	-
	250	0	0	0	91.82	78.24
	250	700	0	0	82.91	80.32
	250	0	700	0	69.68	83.46
	250	0	0	700	39.77	90.56

Inhibition efficiency obtained increases in the order

GA + Iodide > GA + Bromide > GA + Chloride > GA

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It might be due to the radii and the electronegativity of the halide ions play a significant role in the adsorption process[20]. The corrosion rate and percentage inhibition in presence of optimum inhibitors concentration for the tested exposure periods have been listed in Table 3. The corrosion rate increases with the exposure period up to 24h in case of the free acid whereas corrosion rate decreases with the exposure period up to 24h in case of the inhibited acid. The inhibition efficiency for all the inhibitors increases (Fig 3) with time and the combination of GA and Iodide anion offered maximum inhibition (~ 91%) at 24h exposure.
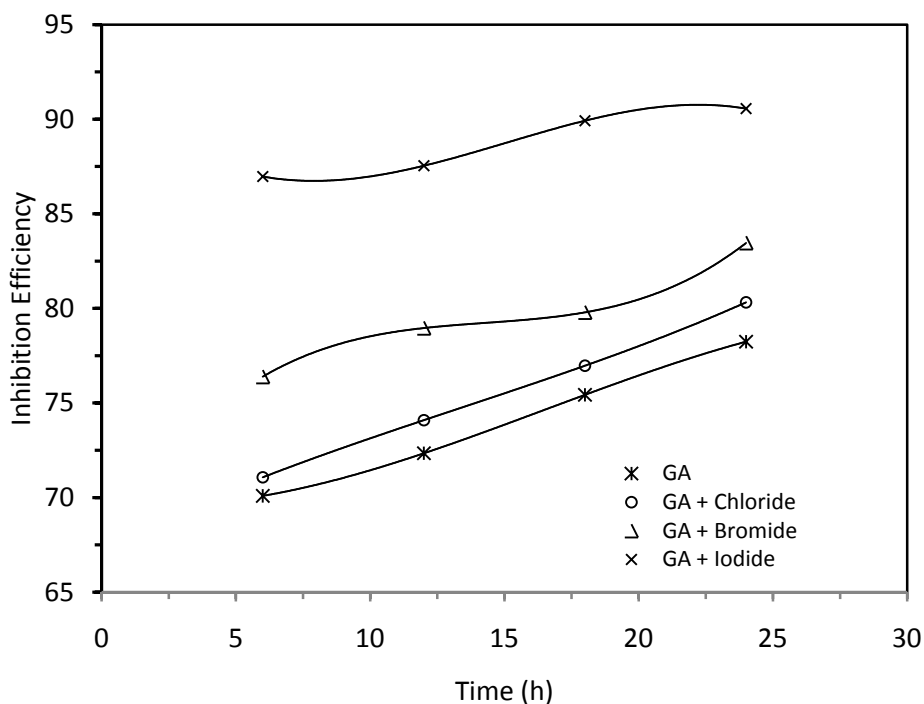

Fig. 3 Variation of inhibition efficiency in presence of the inhibitors at different exposure period

Temperature dependence of the corrosion parameters of the corrosion process both in the absence and in the presence of inhibitors lead to some conclusions concerning the mechanism of the inhibiting action. The corrosion experiments were carried out at high temperatures with the optimum inhibitor concentration to understand the effect of temperature. The corrosion rate in absence of the inhibitors has been found to increase steeply from 303 K to 333 K whereas in presence of the inhibitor the corrosion rate increased slowly. The corrosion parameters in absence and in presence of the inhibitor in the temperature range 303 K to 333 K have been summarized in Table 4. The inhibition efficiency for all the inhibitors decreases (Fig 4) with

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temperature and the combination of GA and Iodide anion offered maximum inhibition (~ 71%) at 333K. The lower inhibition efficiency at higher temperature in case of the inhibitor might be

Table 4 Corrosion parameters in presence of GA and GA + Halides at different exposure period

Exposure Period (h)	Concentration (ppm)				CR (mpy)	PI
	Gum Acacia	Chloride	Bromide	Iodide		
303	0	0	0	0	603.80	-
	250	0	0	0	190.55	68.45
	250	700	0	0	186.63	69.09
	250	0	700	0	140.93	76.66
	250	0	0	700	111.34	81.56
313	0	0	0	0	1215.89	-
	250	0	0	0	433.31	64.37
	250	700	0	0	384.71	68.36
	250	0	700	0	346.89	71.47
	250	0	0	700	305.31	74.89
323	0	0	0	0	2111.95	-
	250	0	0	0	801.05	62.06
	250	700	0	0	761.15	63.96
	250	0	700	0	654.45	69.01
	250	0	0	700	552.91	73.82
333	0	0	0	0	2900.68	-
	250	0	0	0	1115.02	61.56
	250	700	0	0	1087.6	62.52
	250	0	700	0	928.21	68.00
	250	0	0	700	844.39	70.89

due to decrease in hydrogen evolution overpotential and also the higher desorption rate than the adsorption at high temperature[27,28]. Thermodynamic parameters (Table 5) in presence of the inhibitor have been calculated from the well known equations.
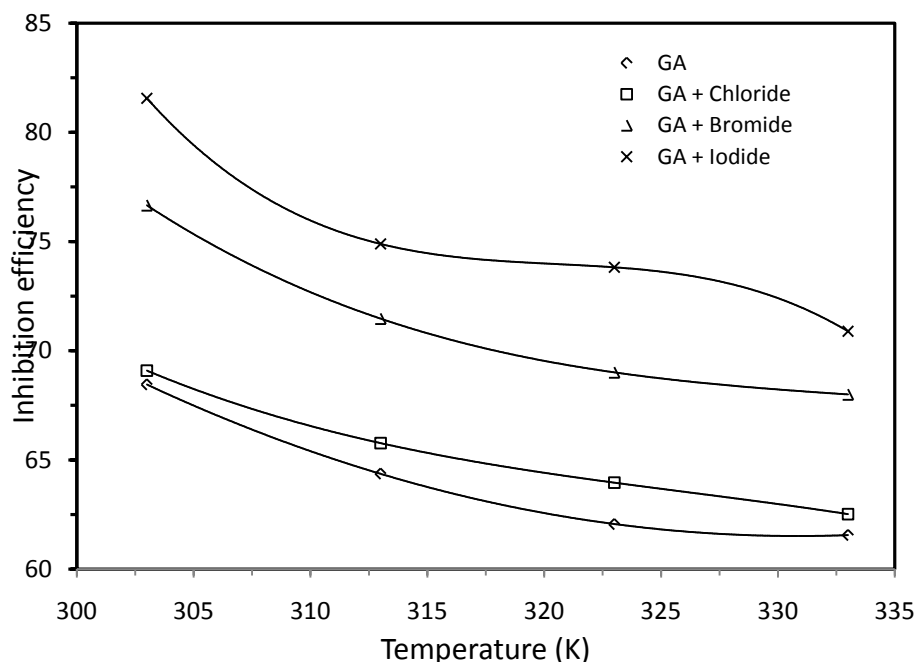
Fig. 4 Variation of percentage inhibition with temperature in presence of GA

Table 5 Thermodynamic parameters in absence and in presence GA

Thermodynamic parameters (kJ/mol)	Blank	GA	GA + Chloride (250 + 700)ppm	GA+ Bromide (250 + 700) ppm	GA + Iodide (250 + 700) ppm
Heat of adsorption	-	-55.891	-54.589	-59.969	-62.764
Activation energy	44.306	49.821	50.223	52.998	56.11
Average Free energy		- 8.750	-8.443	-12.158	-16.696
Entropy of adsorption		0.154	0.137	0.165	0.173

The E_a value for dissolution of mild steel in sulphuric acid (pH=1) in absence of inhibitor has been reported[29] as ~44 kJ/mol. Higher values of E_a were obtained in presence of the studied inhibitor combinations indicated the formation of an adsorptive film of an electrostatic character. The lower negative values of ΔG_{ads} suggested the spontaneous adsorption of the inhibitors on the metal surface. The negative values of ΔH_{ads} revealed the exothermic and physical adsorption of the inhibitors on the metal surface causes the dissolution of steel is difficult. Positive values of

ΔS_{ads} were observed for the inhibitors may be due to involvement of less ordered transition state in the adsorption process. The adsorption of the inhibitor molecules occur after desorption of water molecules initially adsorbed on metal surface due to stronger attraction between the metal surface and inhibitors molecules compared to water [30].

The electrochemical parameters for corrosion of the experimental steel in the acid containing GA are summarized in Table 6. The E_0 value in presence of the inhibitors was found to shift slightly towards less negative side compared to that of the free acid (-0.5518V) for the higher concentration of GA and halides. The significant reduction in corrosion current (I_{corr}) at

Table 6 Electrochemical corrosion parameters in absence and in presence of GA

Concentration of Inhibitor	E_0 (V)	I_0 (μ amp/ cm^2)	Tafel Slopes (mV)		PI
			Anodic (β_a)	Cathodic (β_c)	
Blank	-0.5518	423.0	124.16	191.93	-
GA					
50 ppm	-0.5451	184.1	99.16	148.13	56.50
100 ppm	-0.5485	153.8	93.01	163.21	63.60
250 ppm	-0.5478	126.1	86.28	168.83	70.21
GA + Chloride					
100 + 700 ppm	-0.5818	141.1	111.96	130.96	66.67
250 + 700 ppm	-0.5417	124.9	86.76	164.85	70.47
GA + Bromide					
100 + 700 ppm	-0.5718	104.2	98.49	125.58	75.37
250 + 700 ppm	-0.5618	94.73	93.55	121.95	77.60
GA + Iodide					
100 + 700 ppm	-0.5748	81.74	99.03	120.89	80.67
250 + 700 ppm	-0.5358	50.88	55.58	167.20	87.97

higher concentration level indicated more adsorption of the inhibitors and better inhibition performance. Variations in values of both the Tafel slopes were observed in the presence of these inhibitors. Significant decrease in the values of anodic Tafel slopes (β_a) (38 mV). The potentiodynamic polarization curves in absence and presence GA along with halides are given in
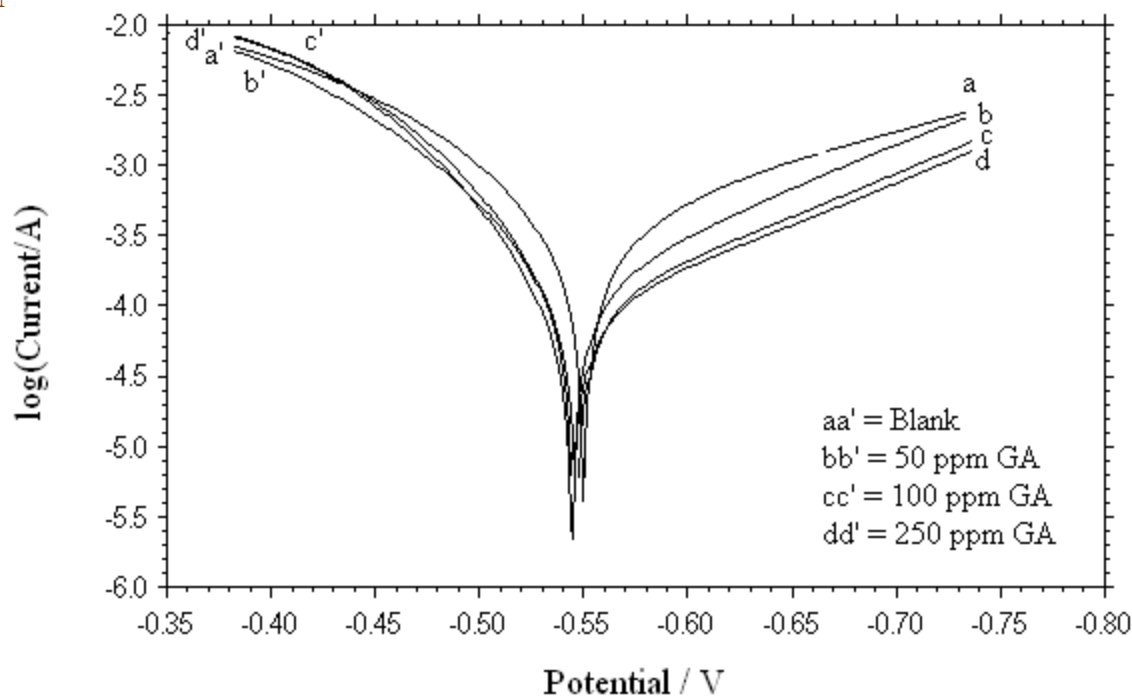
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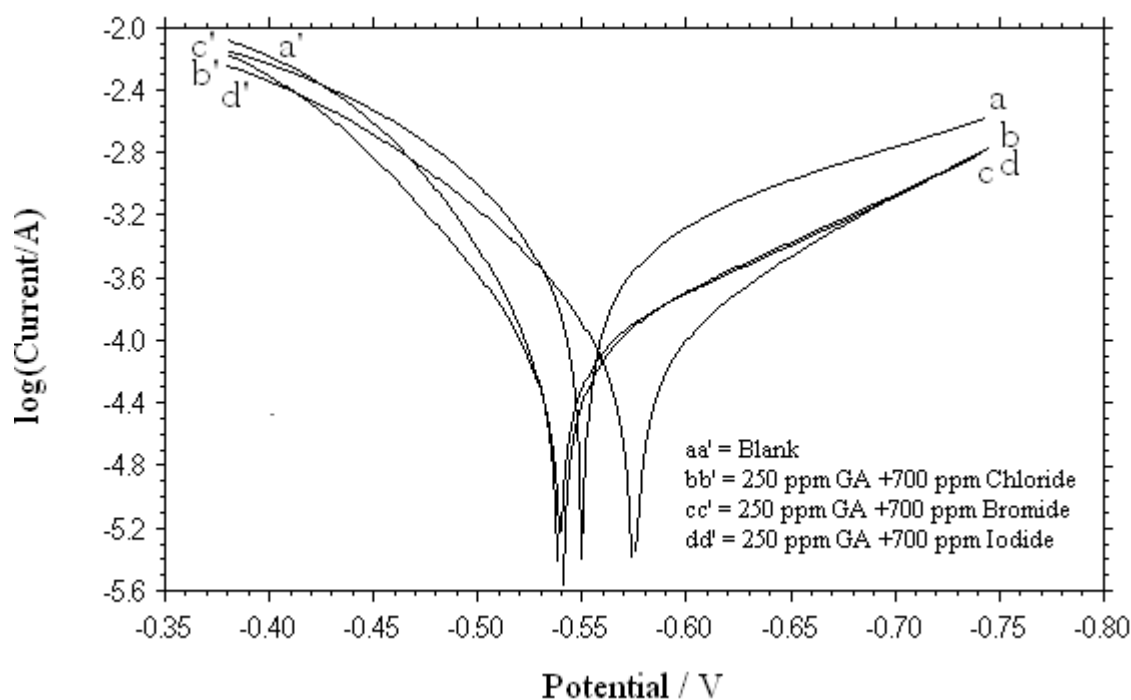Fig. 5 Potentiodynamic polarization curves in presence of the GA

Fig. 6 Potentiodynamic polarization curves in presence of the GA and halides

Fig 5 and Fig 6. It is clear from the Tafel slopes that the anode is more polarized ($\beta_a > \beta_c$) when external current is applied for the inhibitor indicated anodic control in presence of the inhibitor[31,32]. The inhibition efficiencies calculated from potentiodynamic polarization study

were slightly different from that of the weight loss study. This may be explain as the results obtained from the weight loss measurement were average values, while the results obtained from potentiodynamic measurement were instantaneous values.

Electrochemical impedance spectra for mild steel/H_2SO_4 interface in absence and presence of GA alone (Fig. 7) and GA with halides (Fig. 8) were recorded as Nyquist plot and the impedance data obtained were summarized in Table 7.

Table 7 Electrochemical impedance parameters in absence and in presence of the inhibitors

Inhibitor Concentration	R_t (Ω cm^2)	C_{dl} (μFcm^{-2})	% IE
Blank	58	121.32	-
50 ppm GA	118	29.39	51.67
100 ppm GA	140	21.11	58.57
250 ppm GA	160	16.13	63.75
100 ppm GA + 700 ppm Chloride	154	17.45	62.34
100 ppm GA + 700 ppm Bromide	213	8.74	72.77
100 ppm GA + 700 ppm Iodide	330	4.24	82.42
250 ppm GA + 700 ppm Chloride	202	10.01	71.28
250 ppm GA + 700 ppm Bromide	223	8.22	73.99
250 ppm GA + 700 ppm Iodide	378	2.89	84.49

The R_t values increases with inhibitor concentration and this in turn leads to an increase in IE% and may be attributed to the formation of protective film on the metal–solution interface. The addition of inhibitor lowers the C_{dl} value, suggesting that the inhibition can be attributed to surface adsorption[15, 33]. Similar trend have observed with the addition of halides. The maximum R_t (378 Ω cm^2) and minimum C_{dl} (2.89 μFcm^{-2}) have been obtained for the combination of 250 ppm GA with 700 ppm Iodide which is in accordance with the gravimetric and potentioostatic corrosion experiments.
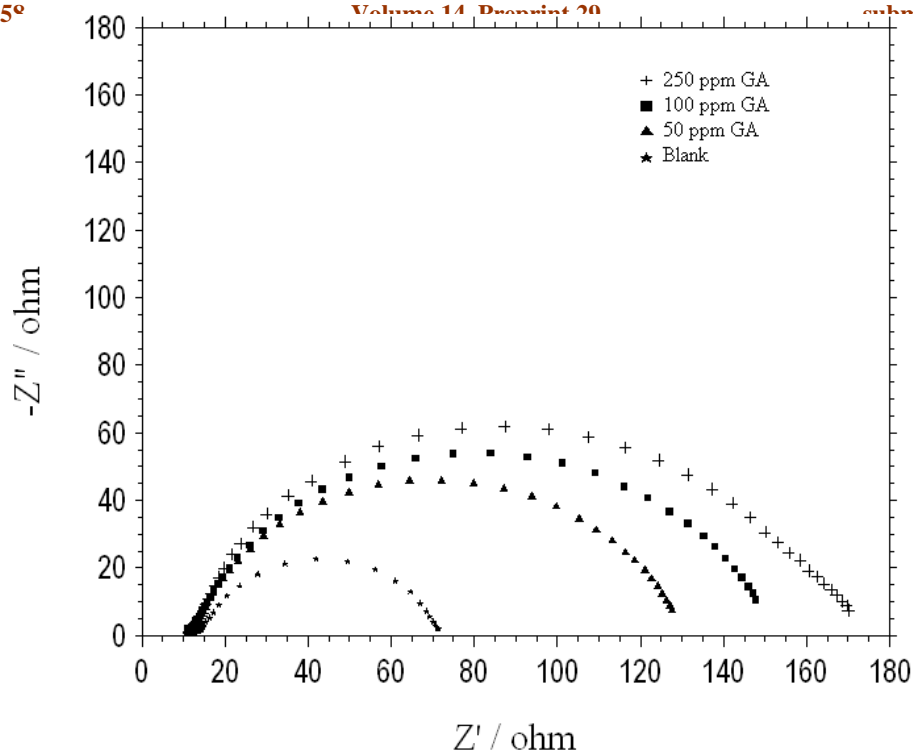
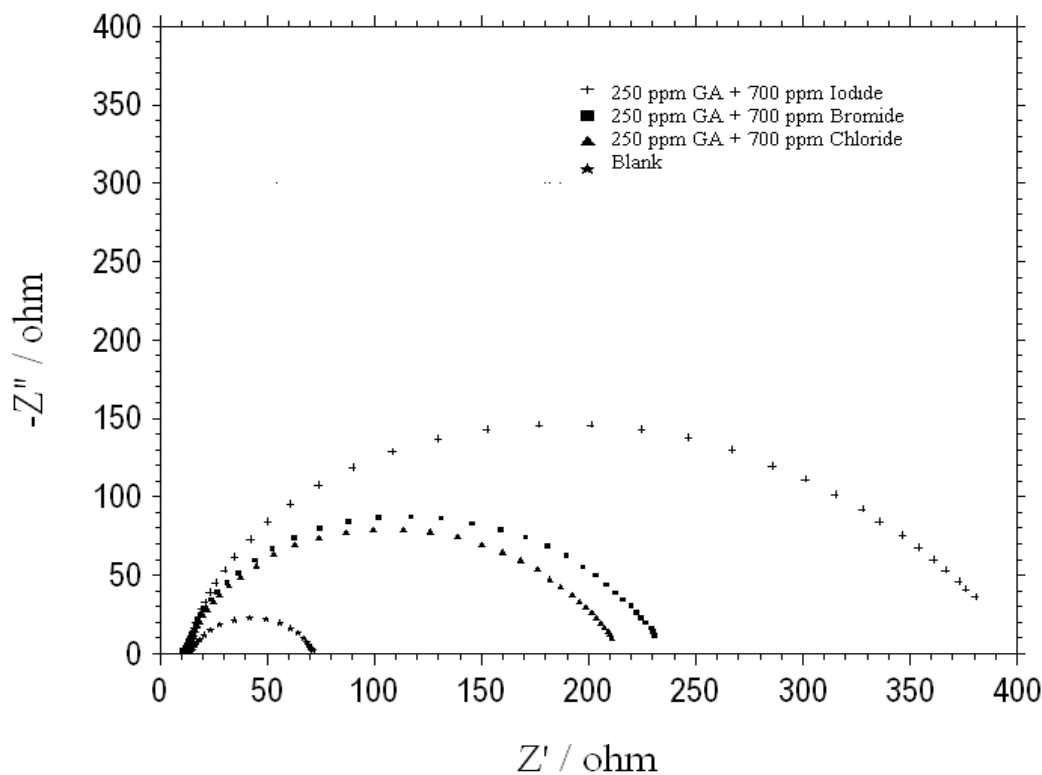Fig. 7 Electrochemical impedance plots in absence and in presence of GA

Fig. 8 Electrochemical impedance plots in absence and in presence of GA + Halide ions

GA showed typical bands of the -OH bond at 3425 cm^{-1} and it was obtained at 3422 cm^{-1} in case of the metal surface product (Fig 9). Two strong bands at 1616 and 1423 cm^{-1} are due to asymmetric and symmetric stretching vibration of the carboxylic acid for pure GA and these were at 1561 and 1401 cm^{-1} respectively in the metal surface product[34-36]. The band obtained at 1042 cm^{-1} due to the stretching of the CO bond and it was at 1023 cm^{-1} for metal surface product. The peaks arise due to ring breathing vibrations were obtained at 641 cm^{-1} for GA and at 1673 cm^{-1} for metal surface product. FT-IR spectra revealed the presence of GA in the metal surface product after corrosion experiments in the inhibited acid solution. The slight difference in the peak or band position might be due to adsorption of the inhibitor molecules on the metal surface.
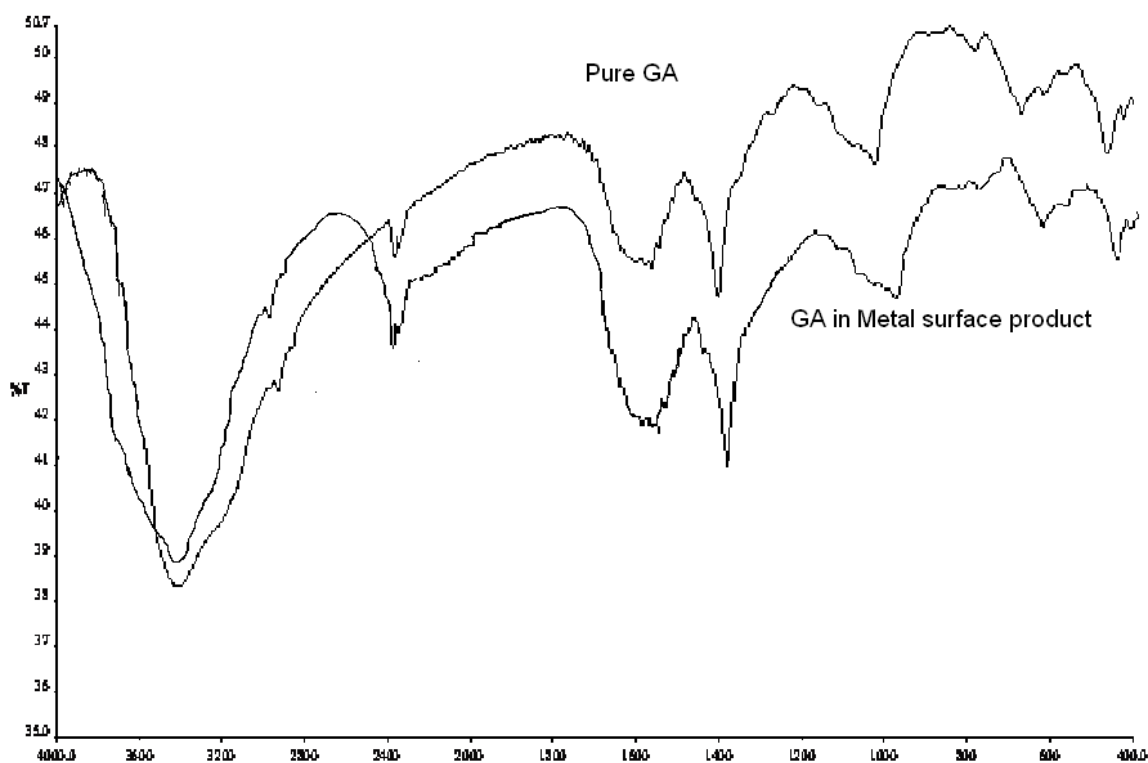

Fig. 9 FT-IR spectra of GA both as pure form and in metal surface product

A uniform flake type corrosion product was seen in case of the free acid (Fig. 10 B). SEM study revealed that the metal surface was partially covered with the quasi globular inhibitor products along with flake type deposition may be of metal oxides and metal hydroxides [37] in presence of all the inhibitors. A more compact layer has been observed in case of the mixture of GA with bromide and iodide (Fig. 10 E and 10 F).
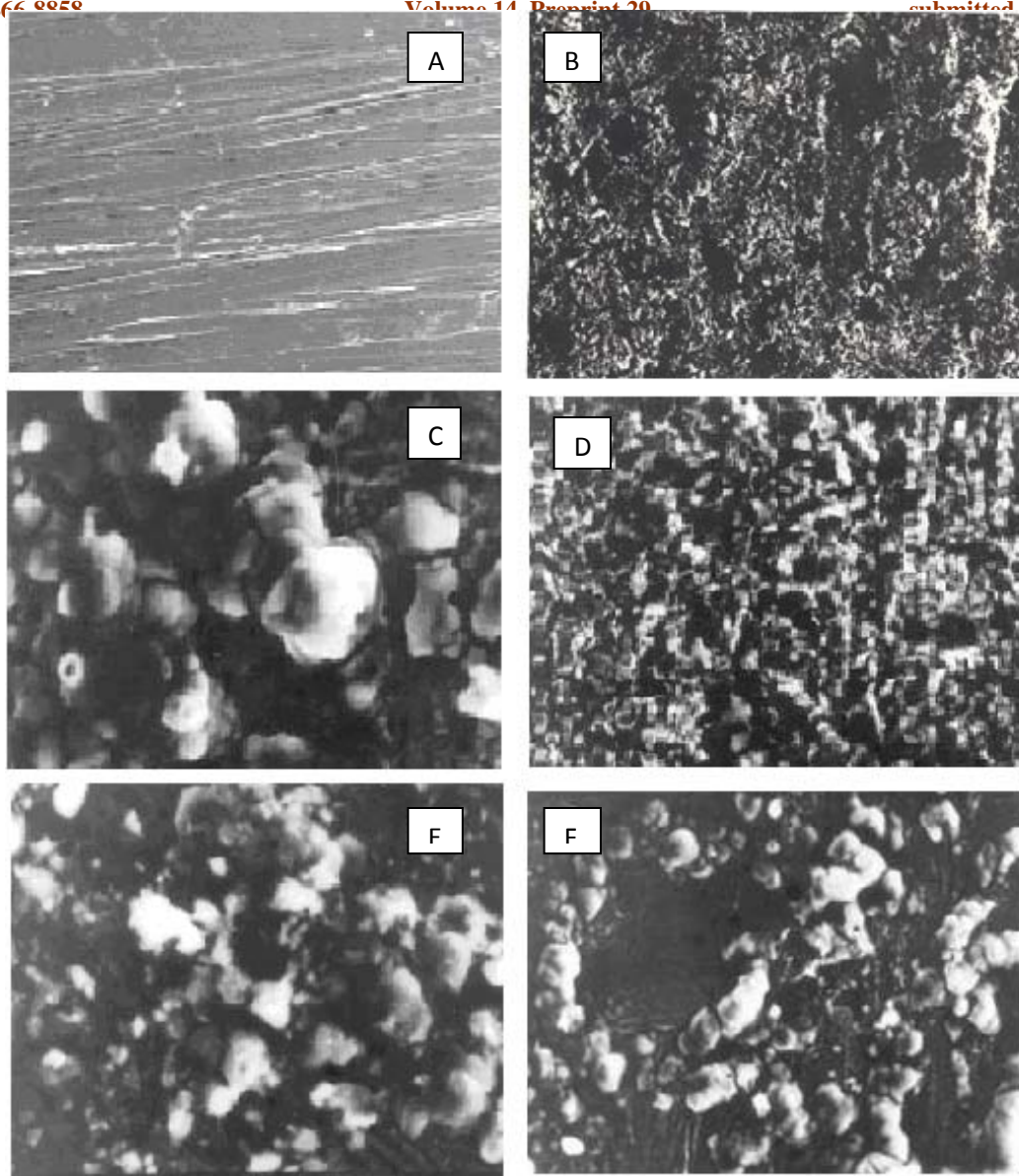
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Fig. 10 SEM Micrographs of the metal surface in absence and in presence of the inhibitors (A) Before exposure, (B) Blank, (C) 250 ppm GA, (D) 250 ppm GA + 700 ppm chloride, (E) 250 ppm GA + 700 ppm bromide (F) 250 ppm GA + 700 ppm iodide

The strong chemisorption of halide ions on the metal surface is responsible for the synergistic effect in combination with inhibitor in their cationic form[38,39]. The inhibitors are then adsorbed by coulombic attraction on the metal surface where halide ions are already adsorbed by chemisorption. Stabilization of adsorbed halide ions with inhibitors in forms cations leads to greater surface coverage and thereby greater inhibition.

5. 1. Conclusion

(1) Gum Acacia acts as inhibitors for the corrosion of mild steel in H_2SO_4 (pH = 1) medium. The maximum inhibition efficiency for the inhibitors was obtained for the combination of 250 ppm GA and 700 ppm Iodide (~87%) for 6h exposure period.

(2) The adsorption of GA on mild steel surface in acidic medium follows Temkin adsorption isotherm.

(3) The spontaneous physisorption of the inhibitors on the metal surface revealed from the negative values of ΔG_{ads} and lower negative ΔH_{ads}.

(4) Synergistic effect was observed (s>1) between GA and the halides; inhibition efficiency of the combinations follow the trend Iodide > Bromide > Chloride might be due to the size and the electronegativity of the halide ions.

(5) The potentiodynamic study suggested the mixed type inhibition and preferentially anodic control for all the inhibitors. In strong acid the protonated polymer molecules were responsible for the adsorption on the metal surface preferentially on anodic sites or on the negatively charged surface resulted from preadsorption of halide ions.

(6) The comparative FT-IR spectral analysis revealed the presence of GA in the metal surface product and the slight difference in the peak or band position might be due to interaction of adsorbed inhibitor molecules with the metal surface.

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