

Research Article

Corrosion Inhibition of Mild Steel in 1 mol L⁻¹ HCl Using Gum Exudates of *Azadirachta indica*

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Received 7 July 2016; Revised 22 September 2016; Accepted 13 November 2016

Academic Editor: Ali Eftekhari

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The ability of gum exudates of *Azadirachta indica* (GAI) to inhibit corrosion on mild steel in 1 mol L⁻¹ HCl has been studied using mass loss, polarization, and impedance measurements. The effect of temperature (303–323 K) and immersion time of 1, 2, 4, 6, and 12 hours on corrosion behavior of mild steel was examined. Gum exudates decrease the corrosion rate up to a concentration of 80 ppm and at 323 K temperature. GAI adsorb chemically onto the surface of the mild steel while it obeys Langmuir adsorption isotherms. Polarization studies show GAI as mixed mode inhibitor. Surface studies ascertain that a shielding layer was formed on the mild steel surface.

1. Introduction

Mild steel corrosion is a subject of incredible theoretical and practical interest and as such has received extensive attention. Researchers strive to control the scaling process through various methods. The use of inhibitors is an exceptionally indispensable means to forestall and restrain corrosion attack of aggressive solutions on metallic materials. Enforcement of strict environmental regulations forces investigators to find naturally occurring and biodegradable substances to be used as corrosion inhibitors. Accordingly, plant origin substances form an excellent kind of inhibitors because of their wide abundance, easy availability, low toxicity, biodegradability, and cost-effective nature. They generally contain a variety of natural products rich in conjugated aromatic structures and long aliphatic chains having nitrogen, sulfur, and oxygen heteroatoms with free electron pairs that are available to form bonds with the metal surface. Extracts from plant leaves, roots, and stems were reported as quality inhibitors for metals and alloys in acidic medium [1–5]. Exudates of some trees were found to be good inhibitors towards metal corrosion in

acid solutions. Eddy et al. reported the following reasons to consider gums as good inhibitors [6]:

- (i) Complex formation of gums occurs with metal ions.
- (ii) A large surface area is occupied, thereby protecting metals' surfaces from corrosion.
- (iii) Arabinogalactan, sucrose, oligosaccharides, polysaccharides, and glucoproteins compounds present in the gum act as centers of adsorption.
- (iv) Natural gums are nontoxic, green, and ecofriendly.

Several investigations were made using Gum Arabic [7], Locust Bean gum [8], Guar gum [9] *Albizia* gum [10], *Raphia hookeri* exudate gum [11], *Dacryodes edulis* gum [12], *Ficus glumosa* gum [13], *Commiphora kerstingii* gum [14], *Ficus benjamina* gum [15], *Anogeissus leiocarpus* gum [16], *Commiphora pedunculata* gum [17], *Ficus platyphylla* gum [18], *Ficus trichopoda* gum [19], *Gloriosa superba* gum [20], *Khaya ivorensis* gum [21], *Ficus thonningii* gum [22], and *Daniella oliveri* gum [23] as corrosion inhibitors. In our attempt to explore environmentally safe green inhibitors,

gum exudates of *Azadirachta indica* were used to investigate the corrosion behavior of mild steel in 1 M HCl solution. We have already reported the corrosion inhibition performance of *Azadirachta indica* gum on mild steel in the acidic medium [24] and its synergistic effect between GAI and substituted piperidones [25]. Compounds present in *Azadirachta indica* gum were reported using GCMS analysis along with physicochemical properties in our previous work [26].

In our continuous quest for exploring stable corrosion inhibitors for longer immersion time, the present work reports on the influence of time on corrosion inhibition of mild steel in 1 M HCl medium using *Azadirachta indica* gum.

2. Materials and Methods

2.1. Material Preparation. The mild steel specimens containing the compositions 0.2 wt.% C, 1.0 wt.% Mn, 0.25 wt.% P, and 0.025 wt.% S and the rest of the iron were mechanically press-cut into 2.5 cm × 1 cm × 0.1 cm dimensions and used as working specimens. The metal specimens with the hole drilled at the upper edge in order to hook them in the glass rod in the acid medium were used for weight loss measurements. A substantial layer formed in the specimen was removed by using different grades of abrasive papers, cleaned using acetone, dried at room temperature, and stored in desiccators. Laboratory grade hydrochloric acid solution was used as an aggressive medium. 1 M HCl was prepared in deionized water and the gum was found to be completely soluble in water as well as HCl.

Collection and Purification of Gum. The gum exudates of *Azadirachta indica* A. Juss. (Meliaceae) were collected locally, identified taxonomically, and authenticated by the Botanical Survey of India (BSI), Coimbatore, Tamil Nadu, India. GAI was dispersed in double distilled water for 5 hours and filtered through muslin cloth to remove the dust and impurities. The resulting mucilage was dried in a desiccator to obtain a glassy mass (GAI was found to be completely soluble in 1 M HCl).

2.2. Weight Loss Measurements. Gravimetric experiments were carried out on the basis of the ASTM practice standard G-31 [27]. Before initiating the experiments, the pre-cleaned specimens were weighed using a balance with 0.1 mg precision. The weighed specimens were immersed in the corrosive medium with and without inhibitors for a stipulated immersion period. After the experiment, the specimens were removed from the acid solution and immersed in Clark's solution for 30 seconds, washed with water, cleaned with acetone, dried in hot air, and finally weighed. The mean of weight loss values of three identical specimens was used to calculate the corrosion rate, surface coverage, and inhibition efficiency using the following known equations:

$$\text{corrosion rate (mmpy)} = \frac{(87.6 \times W)}{\rho A t}, \quad (1)$$

where W is the weight loss in g, " ρ " is the density of the mild steel specimen in gcm^{-3} , " A " is the area of specimen in cm^2 , and t is the time of exposure in h.

$$\text{inhibition Efficiency (IE)} = \frac{(W_0 - W_i)}{W_0} \times 100, \quad (2)$$

$$\text{surface Coverage } (\theta) = \frac{(W_0 - W_i)}{W_0}, \quad (3)$$

where W_i and W_0 are the weight losses of mild steel in the presence and absence of the inhibitor, respectively.

2.3. Electrochemical Measurements. Electrochemical measurements were carried out by using an electrochemical workstation, Ivium instrument. A three-electrode cell assembly consisting of a platinum counter electrode, a saturated calomel electrode, and the working electrode immersed in the acid solution was used to perform electrochemical experiments. To attain constant steady state, the electrode was immersed in the test solution for a minimum of half an hour before taking electrochemical measurements. The polarization studies were carried out in the potential range of +200 to -200 mV with 1 mV s^{-1} scan rate. The corrosion potential and corrosion current density were obtained from cathodic curves and the calculated anodic Tafel lines, respectively. The inhibition efficiency was evaluated employing

$$\text{inhibition efficiency} = \left(\frac{i_{\text{corr}}^{\circ} - i_{\text{corr}}}{i_{\text{corr}}} \right) \times 100, \quad (4)$$

where i_{corr}° is the corrosion current density in the absence and presence of inhibitor.

10 mV amplitude AC signals in the frequency range from 10 KHz to 0.01 Hz were employed to carry out electrochemical impedance spectroscopic measurements. The charge transfer resistance (R_{ct}) values were derived from Nyquist plots which were obtained using the impedance data, automatically controlled by Z_{view} software. From the charge transfer resistance values, the inhibition efficiency of the inhibitor was obtained using

$$\text{inhibition efficiency (\%)} = \left(\frac{R_{\text{ct}} - R_{\text{ct}}^{\circ}}{R_{\text{ct}}} \right) \times 100, \quad (5)$$

where R_{ct} and R_{ct}° are the charge transfer resistance with and without inhibitors, respectively.

Surface Analysis. Inhibitor-metal specimen interaction was determined using a Shimadzu FT-IR 8000 spectrophotometer in the $4000\text{--}400 \text{ cm}^{-1}$ region with KBr disc technique.

3. Results and Discussion

3.1. Effect of Inhibitor Concentration. The corrosion inhibition behavior of various concentrations of GAI (10, 20, 40, and 60 ppm) on mild steel in 1 mol L^{-1} HCl has been studied in the temperature range of 303–323 K for various immersion periods (1, 2, 4, 6, and 12 h) using the gravimetric

TABLE 1: Corrosion parameters for different concentrations of GAI on mild steel in 1 mol L⁻¹ HCl for various immersion periods at 303, 313, and 323 K.

Time (hours)	C (ppm)	303 K		313 K		323 K	
		IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)
1	Blank	—	0.0136	—	0.0197	—	0.0552
	10	30.56	0.0095	32.69	0.0132	64.38	0.0197
	20	38.89	0.0083	40.38	0.0117	69.86	0.0166
	40	55.56	0.0060	50.00	0.0098	79.45	0.0113
	60	63.89	0.0049	57.69	0.0083	79.45	0.0113
2	Blank	—	0.0085	—	0.0163	—	0.0590
	10	44.44	0.0047	46.51	0.0087	67.63	0.0191
	20	48.89	0.0043	53.49	0.0076	76.60	0.0138
	40	53.33	0.0040	69.77	0.0049	82.05	0.0106
	60	68.88	0.0026	72.09	0.0045	83.33	0.0098
4	Blank	—	0.0071	—	0.0208	—	0.0662
	10	30.67	0.0049	62.27	0.0078	79.71	0.0134
	20	34.66	0.0046	69.09	0.0064	88.71	0.0075
	40	49.33	0.0036	71.82	0.0059	89.71	0.0068
	60	56.00	0.0034	74.55	0.0053	90.29	0.0064
6	Blank	—	0.0066	—	0.0179	—	0.0179
	10	49.04	0.0033	68.66	0.0051	86.14	0.0051
	20	51.92	0.0032	73.94	0.0047	89.86	0.0047
	40	48.07	0.0034	75.35	0.0044	90.56	0.0044
	60	59.62	0.0026	77.82	0.0040	90.36	0.0040
12	Blank	—	0.0044	—	0.0209	—	0.0691
	10	51.77	0.0021	70.18	0.0061	86.37	0.0094
	20	54.61	0.0020	79.97	0.0042	87.05	0.0089
	40	58.87	0.0018	84.19	0.0033	91.29	0.0060
	60	57.45	0.0019	87.05	0.0027	92.11	0.0055

method. The corrosion rate, surface coverage, and inhibition efficiency were calculated by means of (1), (2), and (3) and the data obtained are given in Table 1. Analysis of data in the table reveals that the rise in the concentration of the inhibitor from 10 ppm to 60 ppm increased the inhibition efficiency and the highest inhibition efficiency was achieved at 60 ppm for various immersion periods at the studied temperature range (303–323 K). A significant increase in inhibition efficiency was also observed with the increase in temperature. The corrosion inhibition action primarily owes to GAI accumulating on the surface of mild steel which reduces the interaction between mild steel surface and aggressive medium. The interaction of GAI with mild steel may be due to the presence of polysaccharides and protein molecules in its structure. These molecules form a linkage with the metal surface by donating a lone pair of electrons. The high inhibition efficiency at relatively longer immersion time may be due to the formation of insoluble film/corrosion product on the mild steel surface [28] which prevents the penetration of Cl⁻ ions of aggressive medium and inward

diffusion of oxygen, thereby decreasing the corrosion rate [29]. Analysis of Table 1 also reveals that the increase in temperature increases the inhibition efficiency. The corrosion rate in the inhibited solution is less than in the free acid solution.

3.2. Potentiodynamic Polarization Studies. Polarization curve makes it possible to realize the characteristic aspects of corrosion inhibition process. Inhibitors are capable of altering the anodic process, the cathodic process, or both, resulting in the decreased rate of the corrosion process. Polarization curves for mild steel carried out in 1 mol L⁻¹ HCl solutions at room temperature in the absence and presence of different concentrations of GAI are shown in Figure 1. The corrosion current density (i_{corr}) and corrosion potential (E_{corr}) are obtained from the intersection point of anodic and cathodic current curves. It is evident from the figure that the gum exudate is found to block the electrochemical processes on mild steel undergoing corrosion. It reduces both the cathodic and the anodic reaction rates by reducing the corrosion

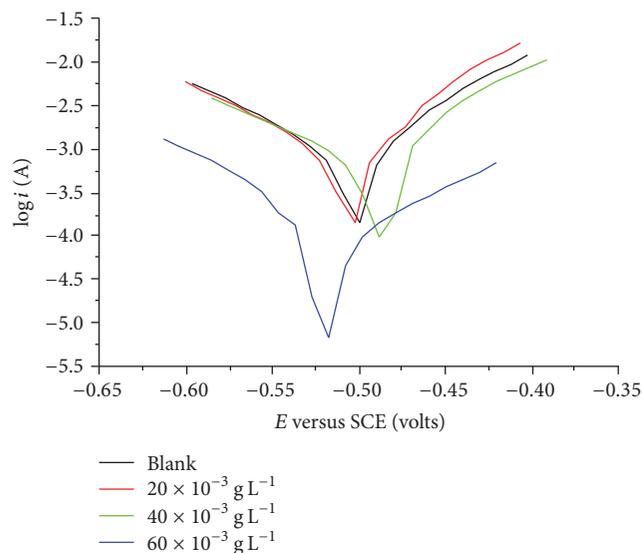


FIGURE 1: Potentiodynamic polarization curves for mild steel in 1 mol L^{-1} HCl in the absence and presence of various concentrations of GAI.

current densities on both sides of the polarization curves in the potential region studied and hence reduces the corrosion rate. The electrochemical parameters i_{corr} and E_{corr} and Tafel constants b_a and b_c are listed in Table 2.

It is obvious from the table that the addition of $20 \times 10^{-3} \text{ g L}^{-1}$ GAI gum shows a higher value of E_{corr} (-503.29 mV) than the free acid solution (-499.38 mV). For the addition of $20 \times 10^{-3} \text{ g L}^{-1}$ of GAI gum, the corrosion potential shifted towards lower side of -486.34 mV . Such E_{corr} values indicate that the GAI gum inhibited mild steel corrosion. Conversely, with further increase in concentration, the corrosion potential (E_{corr}) is not varying much. In general, the changes in the polarization curves on inhibitor addition are used as a criterion to classify inhibitors as cathodic, anodic, or mixed type [30]. The figure shows a slight and considerable shift of corrosion potential in negative direction for $20 \times 10^{-3} \text{ g L}^{-1}$ and $60 \times 10^{-3} \text{ g L}^{-1}$ concentration of GAI gum, whereas a slight positive direction shift is found in the case of $40 \times 10^{-3} \text{ g L}^{-1}$ concentration of GAI gum. These results indicate that GAI gum acts as a mixed-type corrosion inhibitor, predominantly controlled by anodic reaction [31]. This means that the GAI have imperative effects on slowing down the anodic dissolution of mild steel and inhibiting the cathodic hydrogen evolution. Examination of the values obtained for both anodic and cathodic Tafel constants b_a and b_c showed remarkable changes in the presence of the exudates. This implies that GAI has a significant influence on both the anodic and the cathodic Tafel slopes, which in turn indicates that the inhibitor may change both the mechanism of cathodic reaction and that of anodic dissolution. The percentages of inhibition efficiency obtained are analogous with those calculated from weight loss measurement. Nevertheless, some difference could be attributed to the fact that, in the electrochemical process, the instant corrosion current is measured. However, IE in weight loss method is anticipated

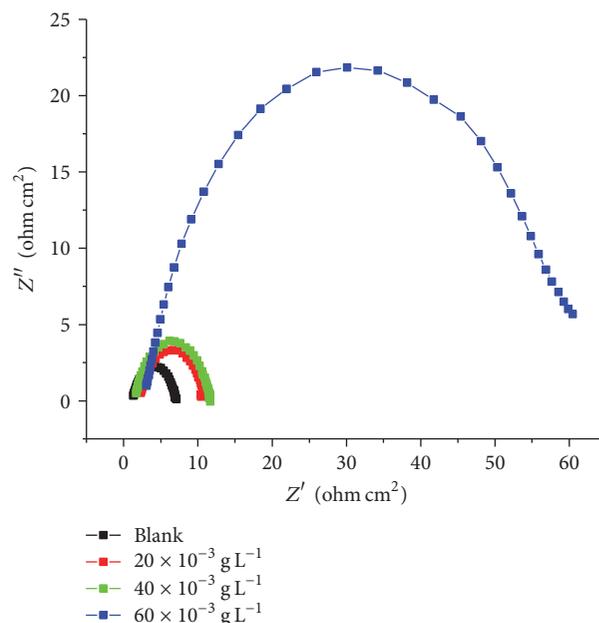


FIGURE 2: Nyquist plots for the corrosion inhibition of mild steel in 1 mol L^{-1} HCl in the absence and presence of various concentrations of GAI gum.

after a long time. The protective film formed is strengthened as the duration of immersion increases [32].

3.3. Electrochemical Impedance Spectroscopy Studies. The inhibition processes of the gum exudates were also studied by electrochemical impedance spectroscopy technique. AC impedance spectra have been used to detect the formation of a film on the metal surface. If a protective layer is formed, the charge transfer resistance will be boosted and the double layer capacitance value diminishes [33]. Impedance measurements provide information about resistance and capacitance at the interface, feasibility of a substance as a corrosion inhibitor, and the nature of the inhibition process. In Table 3, impedance measurements for mild steel in 1 mol L^{-1} HCl in the absence and presence of various concentrations of gum exudates at 303 K are listed.

The Nyquist plots obtained without and with inhibitor are not perfect semicircles. Deviations from the ideal circular shape are attributed to the frequency dispersion of interfacial impedance which is attributed to nonhomogeneity of the surface and roughness of the metal [34]. From the plots (Figure 2), it could be seen that impedance response of mild steel is increased by the addition of the inhibitor. The characteristic parameters associated with the impedance diagrams, namely, charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}), are listed in Table 3. R_{ct} is a measure of electron transfer across the interface and is inversely proportional to corrosion rate. Equation (6) is used to obtain double layer capacitance (C_{dl}):

$$C_{\text{dl}} = \frac{1}{2} \pi f_{\text{max}} R_{\text{ct}}, \quad (6)$$

TABLE 2: Potentiodynamic polarization parameters for the corrosion inhibition of mild steel in 1 mol L⁻¹ HCl in the presence and absence of GAI.

S. number	Concentration (ppm)	i_{corr} (mA cm ⁻²)	E_{corr} (mV/SCE)	b_a (mV dec ⁻¹)	b_c (mV dec ⁻¹)	IE (%)
1	Blank	1.21	-499.38	94.4	137.2	—
2	20	1.08	-503.2	79	124	10.5
3	40	0.595	-486.9	72	110	71.4
4	60	0.10	-514.7	68	119	81.7

TABLE 3: AC impedance parameters for mild steel in 1 mol L⁻¹ HCl in the presence and absence of GAI.

S. number	Concentration * 10 ⁻³ g L ⁻¹	R_{ct} (Ω cm ⁻²)	C_{dl} (μF cm ⁻²)	IE (%)
1	Blank	9.2	0.00461	—
2	20	12.5	0.00253	25.9
3	40	14.8	0.00184	37.8
4	60	84.6	0.00006	67.1

where f_{max} is the frequency value at which the imaginary component of the impedance is maximum.

Table 3 clearly shows that the values of R_{ct} increase with the increase in GAI concentration which recommends that the charge transfer process is principally controlling the corrosion reaction. Decrease in C_{dl} values with the increase in concentration is due to the increase in the surface coverage by GAI, which resulted in an increase in the inhibition efficiency. The decrease in C_{dl} value may be attributed to the decrease in local dielectric constant and/or an increase in the thickness of the electric double layer implied that the GAI gets adsorbed onto the mild steel surface. Steady replacement of water molecules by the adsorption of inhibitor molecules on the mild steel surface decreases the amount of metal dissolution and consequently it causes the decrease in C_{dl} values. Further, the inhibition efficiency obtained by this method was found to be in good concurrence with those obtained from the weight loss measurements.

3.4. Thermodynamic and Kinetic Analysis. The corrosion parameters such as activation energy (E_a), enthalpy of activation (ΔH^*), and entropy of activation (ΔS^*) for mild steel in 1 mol L⁻¹ HCl solution in the absence and presence of GAI with different concentrations (10–60 ppm) at various immersion periods in the temperature range of 303–323 K were calculated and tabulated (Table 4).

Activation energy is calculated using Arrhenius equation:

$$\text{CR} = A \exp\left(\frac{-E_a}{RT}\right), \quad (7)$$

where CR is the corrosion rate, A is the frequency factor which depends on the nature of the metal and electrolyte, E_a is the activation energy, R is the universal gas constant, and T is the absolute temperature.

Activation parameters of the corrosion reaction, ΔH^* and ΔS^* , are calculated using the transition state equation:

$$K = RT/Nh \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right), \quad (8)$$

where N is Avogadro's number, h is Planck's constant, ΔS^* is the entropy of activation, and ΔH^* is the enthalpy of activation.

The activation energies (E_a) for various immersion times (1, 2, 4, 6, and 12 h) are determined by linear regression between $\log \text{CR}$ and $1000/T \text{ K}^{-1}$ (Figures 3(a)–3(e)). Plots of $\log \text{CR}$ versus $1000/T \text{ K}^{-1}$ give a straight line with slope ($-E_a/2.303R$) and intercept A . Similarly, the enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) are determined by plotting $\log(\text{CR}/T)$ versus $1000/T \text{ K}^{-1}$ (Figures 4(a)–4(e)), giving a straight line with slope ($-\Delta H^*/2.303R$) and intercept ($\log R/Nh + \Delta S^*/2.303R$) from which the values of E_a , ΔH^* , and ΔS^* are calculated for various immersion periods (Table 4).

In general, the higher value of E_a in the presence of inhibitor as compared to blank solution indicates physical adsorption whereas unchanged or lower value of E_a for inhibitor compared to blank indicates chemisorption mechanism [35]. The present studies reveal that the activation energy value (E_a) for inhibited solutions at various immersion periods (1, 2, 4, 6, and 12 h) and for different concentrations of GAI (10–60 ppm) decreased with increasing temperature while an increase in activation energy with temperature is noted for uninhibited solution. This is indicative of less energy barrier of corrosion reaction occurring at the steel surface representing the chemical nature of adsorption. The enthalpy of activation (ΔH^*) steadily decreases with increasing concentration of GAI from 10 to 60 ppm at various immersion periods and is found to be higher in the uninhibited solution, again suggesting that there is a decrease in energy barrier between the reactant and activated complex on the specimen surface. The positive values of enthalpy of activation show the endothermic nature of the corrosion process on mild steel. The negative and positive values of entropy of activation (ΔS^*) from Table 4 suggest that disorderness is increased on going from reactant to activated complex and also the decrease in entropy of activation with

TABLE 4: Corrosion kinetic parameters for mild steel in 1 mol L^{-1} HCl in the absence and presence of different concentrations of GAI at various immersion periods in the temperature range of 303 K–323 K.

Immersion period (hours)	Concentration (ppm)	E_a (kJmol^{-1})	ΔH^* (kJmol^{-1})	ΔS ($\text{Jmol}^{-1} \text{ k}^{-1}$)
1	Blank	56.66	54.05	-103.34
	10	29.76	27.16	-194.30
	20	28.19	25.58	-200.49
	40	25.71	23.11	-210.83
	60	34.11	31.50	-185.04
2	Blank	78.48	75.88	-35.21
	10	56.71	54.11	-111.30
	20	46.96	44.35	-144.01
	40	39.65	37.05	-169.54
	60	53.27	50.67	-127.56
4	Blank	90.82	88.22	04.71
	10	40.83	38.23	-163.24
	20	19.50	16.90	-233.771
	40	26.14	23.54	-213.76
	60	25.97	23.37	-214.88
6	Blank	94.94	92.34	17.32
	10	38.87	36.27	-172.95
	20	28.63	26.03	-206.98
	40	22.53	19.93	-226.63
	60	33.62	31.01	-192.11
12	Blank	111.78	109.18	70.57
	10	60.50	57.90	-104.31
	20	60.60	58.00	-105.37
	40	48.47	45.87	-146.15
	60	42.92	40.32	-164.63

increasing the concentration of GAI denotes the association of the inhibitor molecules instead of dissociation [36, 37] indicating the difficulty in the dissolution of mild steel, supporting the chemisorption mechanism. The values of ΔH^* and E_a are almost similar and are higher in the presence of the inhibitor which indicates an increase in energy barrier of the corrosion reaction without changing the mechanism of dissolution. The value of E_a is found to be larger than the corresponding ΔH^* value signifying that the deterioration process must employ a gaseous reaction, simply the hydrogen evolution reaction, associated with a decrease in the total reaction volume [38, 39]. In addition, the difference between E_a and ΔH^* is found to be 2.6 kJ/mol, which is equivalent to the typical value of RT (2.63 kJ/mol). This signifies that the corrosion process is a unimolecular reaction characterized as $E_a - \Delta H^* = RT$.

3.5. Adsorption Isotherm. Adsorption isotherms are very much imperative in determining the mechanism of electrochemical reactions involving organic compounds as they rely upon a number of factors such as the nature of the

metal surface and the inhibitor, conformation of inhibitors in aqueous solution, composition of the medium, temperature, and electrochemical potential at the metal solution interface. Thus, the construction of adsorption isotherms for corrosion inhibitor can help in understanding the nature of the metal-inhibitor interactions. The corrosion inhibition of mild steel in 1 mol L^{-1} HCl medium with the addition of various concentrations of GAI can be attributed to the adsorption of the molecules on the steel surface. Inhibition efficiency (%) is directly proportional to the portion covered on the surface by the adsorbed inhibitor molecules (θ). Consequently, the adsorption isotherm illustrates the relation between the surface coverage and the inhibitor concentration in solution. Various adsorption isotherms were tried and Langmuir isotherm was found to fit best with high correlation coefficient value. The same results were obtained at high temperature also. The Langmuir adsorption equation is

$$\frac{C}{\theta} = \frac{1}{K} + C, \quad (9)$$

where C is the concentration of inhibitor, K is the adsorption equilibrium constant, and θ is the degree of surface coverage

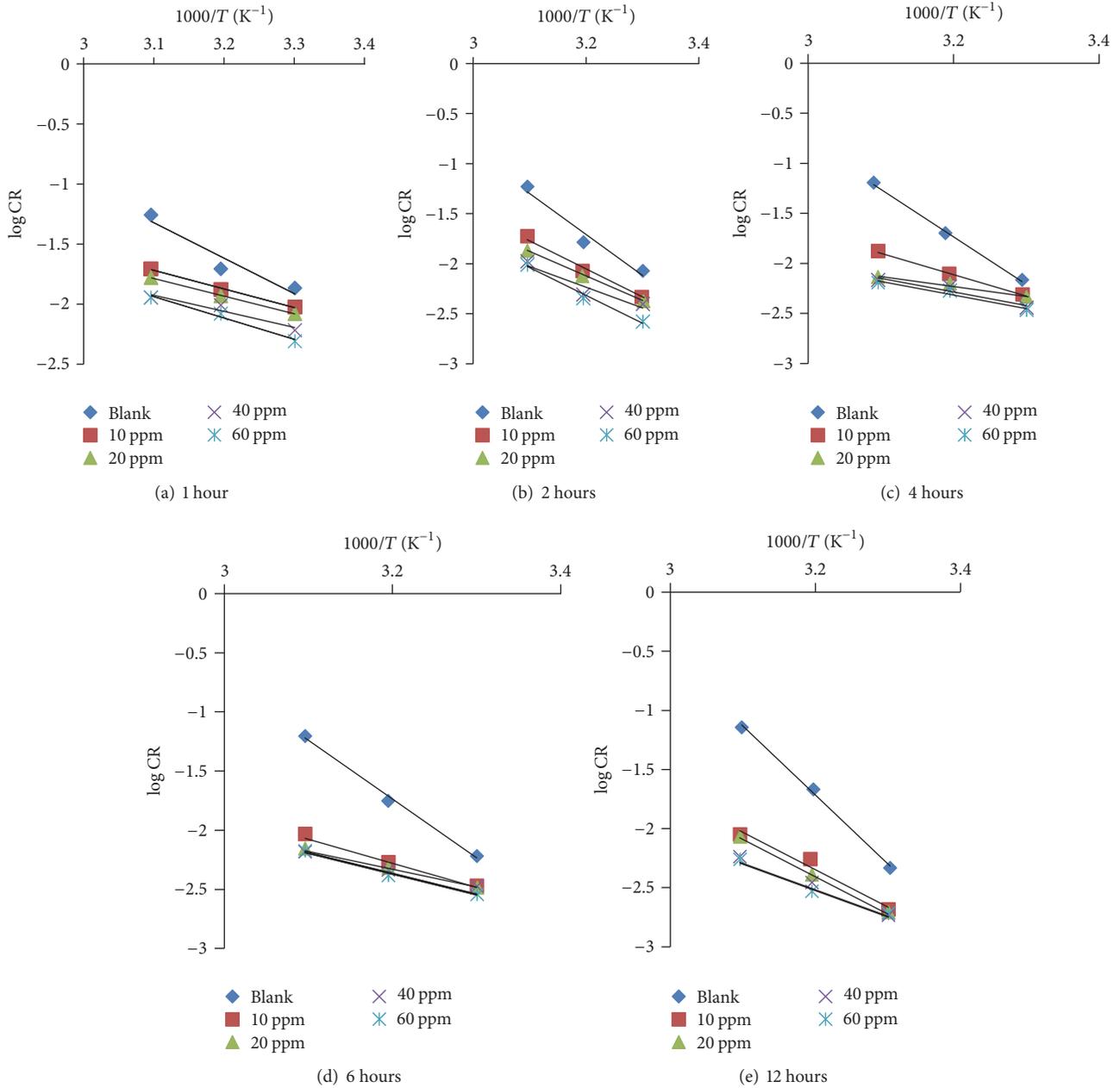


FIGURE 3: (a–e) Arrhenius plots for different concentrations of GAI on mild steel in 1 mol L⁻¹ HCl at various immersion periods in the temperature range of 303–323 K.

of the inhibitor. The plot (Figures 5(a)–5(e)) of C/θ versus C gives a straight line with slope values greater than 1 and the intercept is equal to $1/K$. Deviation of slope (Table 5) from unity is indicative of heterogeneous adsorbing species occupying more or less a typical adsorption site at the metal/solution interface [40]. Also, it could be attributed to the molecular interactions among the adsorbed inhibitor species, a factor which was not taken into consideration during the derivation of the Langmuir equation.

From the intercept value, the equilibrium constant of adsorption process was calculated (Table 6). The equilibrium

constant (K) and the standard free energy ($\Delta G^\circ_{\text{ads}}$) of the adsorption process are related as follows:

$$(\Delta G^\circ_{\text{ads}}) = 2.303 * RT \log (55.5 * K), \quad (10)$$

where $\Delta G^\circ_{\text{ads}}$ is the standard free energy of the adsorption process, K is the equilibrium constant of the adsorption process, R is the universal gas constant, T is the absolute temperature, and the value 55.5 indicates the molar concentration of water molecules at electrode and electrolyte interface during the adsorption process.

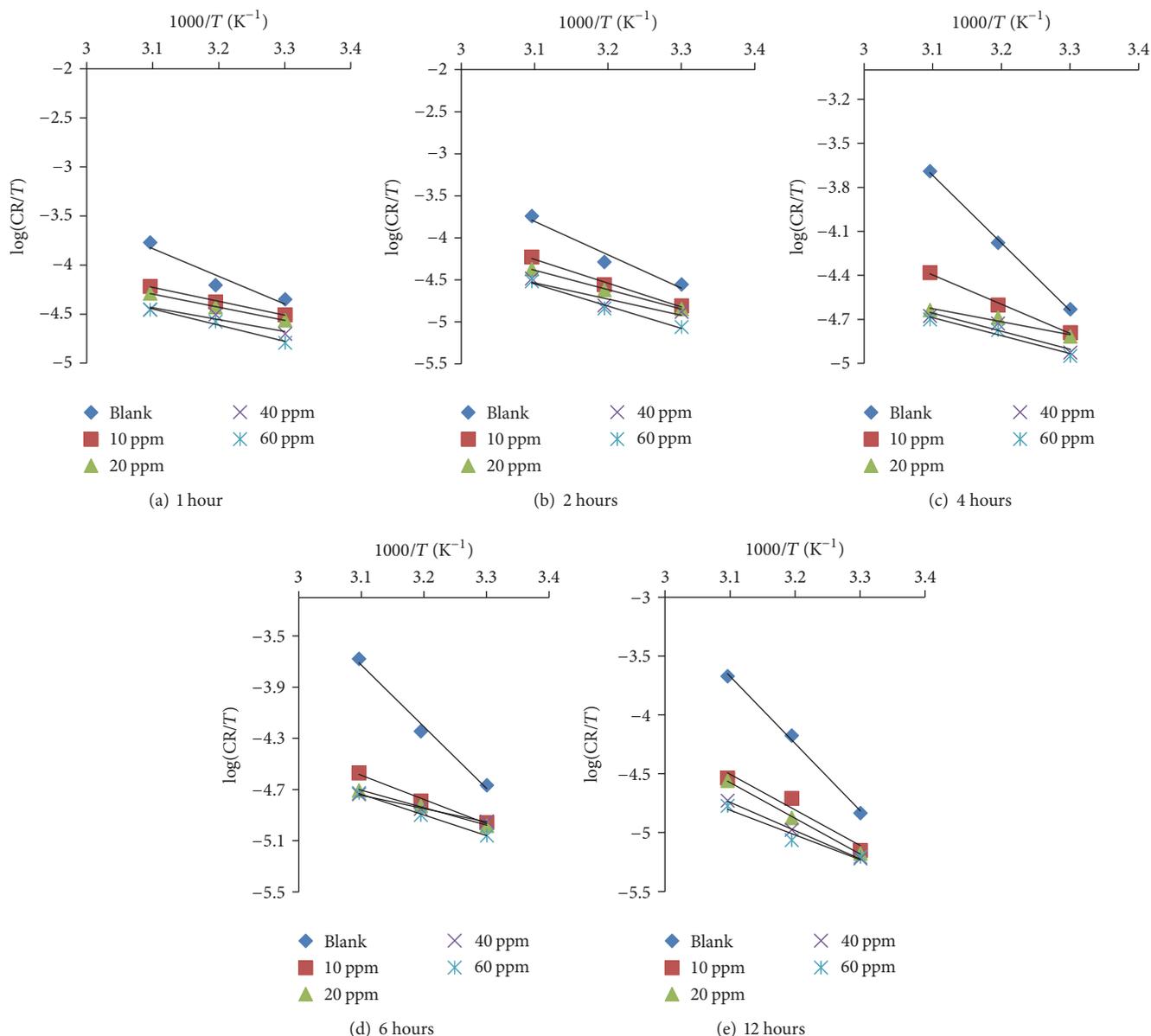


FIGURE 4: (a–e) Transition state plots for different concentrations of GAI on mild steel in 1 mol L^{-1} HCl at various immersion periods in the temperature range of 303–323 K.

The values of K and $\Delta G_{\text{ads}}^{\circ}$ are calculated by using the above relationship (see (9) and (10)) and the values are listed in Table 5. Similar calculation of $\Delta G_{\text{ads}}^{\circ}$ using (10) was cited in investigations of gums as corrosion inhibitors [11, 41, 42]. In general, two modes of adsorption are possible. Physical adsorption needs the presence of an electrically charged metal surface and charged species in the bulk solution and the chemisorption process involves charge sharing or charge transfer from the inhibitor molecule to the metal surface. This is possible in the case of positive charges as well as negative charges on the metal surface [43, 44]. The value of $\Delta G_{\text{ads}}^{\circ}$ up to -20 kJ mol^{-1} or lower indicates physical adsorption, while a value more than -40 kJ mol^{-1} involves sharing or transfer of electron from the inhibitor molecules to the metal

surface to form a coordinate type bond (chemisorption) [45]. From the table, the calculated values of $\Delta G_{\text{ads}}^{\circ}$ for different immersion periods in the temperature range of 303–323 K are $-19.5 \text{ kJ mol}^{-1}$ to 31.4 kJ mol^{-1} , which indicates that the adsorption of GAI on mild steel surface is due to the chemisorption process, and the negative value of $\Delta G_{\text{ads}}^{\circ}$ shows that the adsorption of AI gum on mild steel surface is a spontaneous process. Other isotherms models attempted suffer from profound variation from unity and thus Langmuir isotherm was considered the best fit for the adsorption of GAI onto mild steel.

FT-IR Spectra. The corrosion inhibition mechanism of mild steel in hydrochloric acid solution by the use of inhibitors

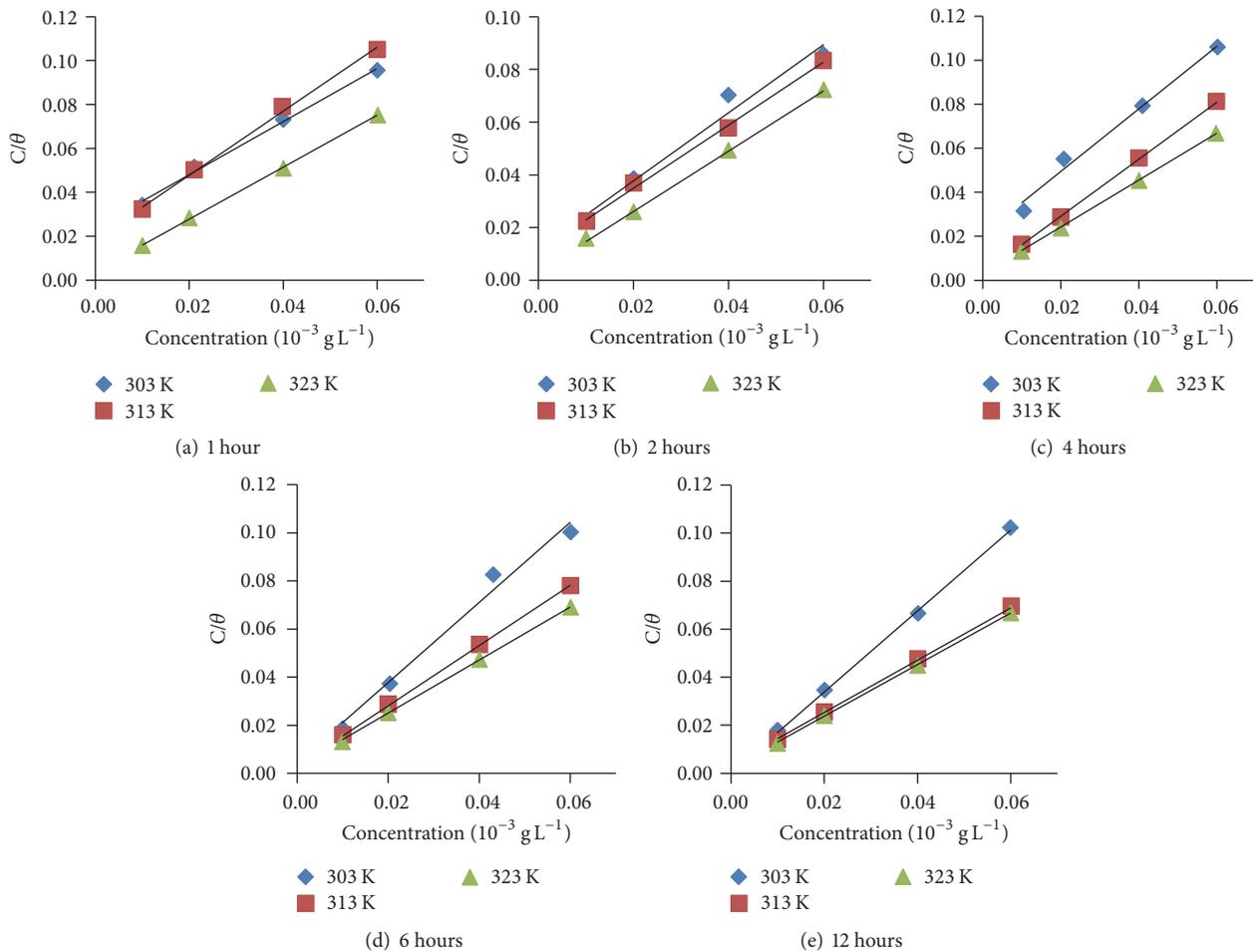


FIGURE 5: (a–e) Langmuir isotherms for different concentrations of GAI on mild steel in 1 mol L^{-1} HCl at various immersion periods in the temperature range of 303–323 K.

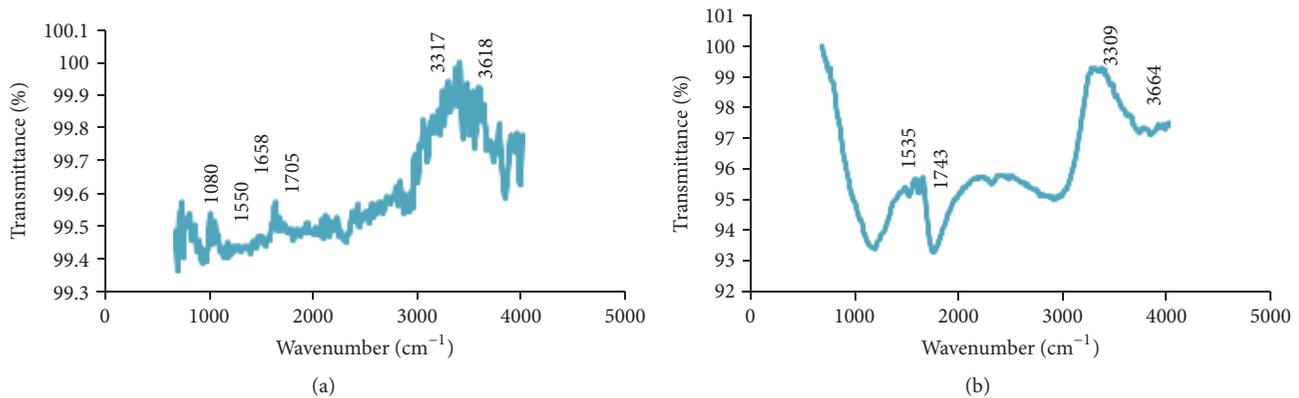


FIGURE 6: (a) FT-IR spectrum of pure GAI. (b) FT-IR spectrum of mild steel immersed in 1 mol L^{-1} HCl in the presence of GAI.

can be explained on the basis of molecular adsorption [46]. The adsorption process is affected by the chemical structures, distribution of charge in molecule, the nature and surface charge of metal, and the type of aggressive media [47]. The mechanism of inhibition of GAI on the mild steel surface is established using FT-IR spectroscopy.

In Figure 6(a), the FT-IR spectrum of pure GAI exhibits very obvious and strong features analogous to the constituent molecules in GAI. This FT-IR spectrum is exemplified with characteristic hydroxyl group and carboxylate group stretching frequency between 3317 cm^{-1} – 3618 cm^{-1} and 1550 cm^{-1} , respectively. The bending mode of adsorbed water is seen [48]

TABLE 5: Thermodynamic adsorption parameters for the different concentrations of GAI on mild steel in 1 mol L⁻¹ HCl at different immersion periods in the temperature range of 303–323 K.

Immersion periods (hr)	Temperature (K)	Intercept	Equilibrium constant (K_{ads}) (M ⁻¹)	$-\Delta G^{\circ}_{ads}$ (kJmol ⁻¹)
1	303	0.0241	41.487	19.506
	313	0.0186	53.763	20.824
	323	0.0040	249.198	25.609
2	303	0.0136	73.390	20.943
	313	0.0109	91.619	22.211
	323	0.0032	307.786	26.176
4	303	0.0234	42.784	19.583
	313	0.0033	306.790	25.357
	323	0.0013	753.081	28.579
6	303	0.0067	149.806	22.741
	313	0.0021	469.507	26.464
	323	0.0005	2170.37	31.422
12	303	0.0022	448.287	25.502
	313	0.0033	306.710	25.356
	323	0.0012	810.184	28.775

TABLE 6: Langmuir isotherm for the adsorption of GAI.

Langmuir isotherm					
Slope			R^2 values		
303 K	313 K	323 K	303 K	313 K	323 K
1.18	1.45	1.18	0.987	0.992	0.998
1.31	1.19	1.14	1	0.953	0.995
1.42	1.29	1.08	0.979	0.989	0.999
1.66	1.25	1.09	0.965	0.999	0.999
1.68	1.09	1.06	0.998	0.999	0.999

at 1658 cm⁻¹. Comparisons of relative intensities of the major vibrational modes of pure GAI spectrum with that of GAI (60 × 10⁻³ g L⁻¹) after immersing in 1 mol L⁻¹ HCl for 1 hour at 303 ± 1 K following remarkable information were disclosed.

The major bands pertaining to the O-H stretching vibrations at 3317–3618 cm⁻¹ departed to the absorption frequency of 1309 cm⁻¹ whereas the –C=O stretching vibrations of the carboxylate group coupled with the GAI at 1550 cm⁻¹ experience a decrease to 1535 cm⁻¹ which is observed in Figure 6(b). The peak for bending mode of water molecule is also shifted towards lower wavenumbers. This obviously specifies that insoluble hydroxides may be formed on the surface of the mild steel by the hydroxyl group of GAI which suppresses the cathodic hydrogen evolution. The above shifting in the characteristic peaks can be attributed to the completely adsorbed constituent molecules on the surface of mild steel in HCl [24]. The features of the FT-IR spectrum show that there is good adsorption of GAI onto the mild steel surface, because of electrostatic binding of the carboxylate groups of the GAI to oxides surfaces of the metal.

4. Conclusions

- (i) Gum exudate of *Azadirachta indica* acts as a good inhibitor for mild steel in 1 mol L⁻¹ HCl solution. Even very low concentration (60 ppm) of GAI gives the maximum inhibition efficiency.
- (ii) The inhibition efficiency increased with concentration as well as temperature.
- (iii) The calculated values of activation energy (E_a), enthalpy of activation (ΔH^*), and standard free energy of adsorption (ΔG°_{ads}) conclude a chemisorption mechanism.
- (iv) The adsorption behavior of GAI molecules on mild steel surface in 1 mol L⁻¹ HCl is confirmed by the Langmuir adsorption isotherm.
- (v) The polarization measurements show that the GAI gum acts as a mixed-type inhibitor.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

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