

Inhibition of corrosion of aluminum in hydrochloric acid solution by 2-amino benzoic acid

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Abstract: The effect of 2-amino benzoic acid on the corrosion of aluminum in 1.0 M HCl solution was studied using weight loss technique. The inhibition efficiency was found to increase with increasing concentration of the inhibitors and decrease with raising temperature. The adsorption of inhibitor on the aluminum surface obeys the Langmuir adsorption isotherm. The thermodynamic functions of adsorption processes were calculated from weight loss at different temperatures data and were used to analyse the inhibitor mechanism.

Keywords: Corrosion, weight loss, aluminum

I. INTRODUCTION

Aluminum has an economic and industrial importance due to lightweight, high thermal and electrical conductivity. The resistance of aluminum against corrosion in aqueous media can be attributed to a rapidly formed compact, strongly adherent and continuous oxide film [1,2]. Therefore, aluminum and its alloys are widely used in many industries such as reaction vessels, pipes, machinery and chemical batteries. Hydrochloric acid solutions are used for pickling, chemical and electrochemical etching of aluminum [3]. Moreover, the presence of aggressive ions like chloride creates extensive localized attack [4]. Because of the general aggressive acid solutions, inhibitors are commonly used to reduce the

corrosive attack on metallic materials. Most of the corrosion inhibitors are synthetic chemicals which are toxic, expensive and non biodegradable. Therefore, it is desirable to source for environmentally safe inhibitors [4–10].

It has been observed that adsorption depends mainly on certain physico-chemical properties of the inhibitor group, like functional groups, electron density at the donor atom, π -orbital character, and the electronic structure of the molecule [11-16]. In general, organic compounds with oxygen, sulfur, and/or nitrogen as polar groups and conjugated double bonds in their structures have been reported to be good corrosion inhibitors for many metals and alloys in corrosive media [17-33]. The

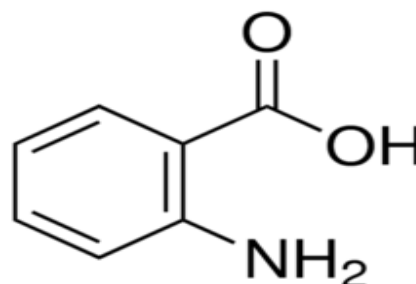
inhibiting action of these organic compounds is usually attributed to their interactions with the metallic surfaces via their adsorption. Polar functional groups are regarded as the reaction centre that stabilizes the adsorption process [29]. However, the adsorption of an inhibitor on a metal surface depends on a few factors, such as the nature and surface charge of the metal, the adsorption mode, the inhibitor's chemical structure, and the type of the electrolyte solution [34].

The objective of this study is to investigate the corrosion behavior of Aluminum in 1.0 M HCl at different temperatures in the presence of 2-aminobenzoic acid using chemical techniques.

II. EXPERIMENTAL:

Aluminum strips (BDH grade) containing 99% Al used in this investigation. All chemicals used were of AR grade. Specimens of aluminum strips were abraded successively by emery papers of different grades, i.e. 320, 400, 600, 800 and 1000 finally polished with a 4/0 emery paper to obtain mirror like finish, then degreased ultrasonically with ethyl alcohol and rinsed with bidistilled water several times and dried between two filter papers. AR grade hydrochloric acid (37 %) was used for preparing the corrosive solutions. Appropriate concentration of aggressive solutions used (1 M HCl) was prepared by dilution using bidistilled water. The structures of the investigated compounds are shown below:

2-aminobenzoic acid



2.1. Weight loss measurements

For weight loss measurements, rectangular C-steel specimens of size 20 x 20 x 2 mm were immersed in 100 ml inhibited and uninhibited solutions and allowed to stand for several intervals at $25 \pm 1^\circ\text{C}$ in a water thermostat. Therefore, the weight losses (W) given by:

$$W = (m_1 - m_2) \quad (1)$$

where m_1 and m_2 are the weights of metal before and after exposure to the corrosive solution, respectively. The percentage inhibition efficiency (% IE) and the degree of surface coverage (θ) of the investigated compounds were calculated from the following equations:

$$\%IE = \theta \times 100 = \left(1 - \frac{W_{(inh)}}{W_{(free)}}\right) \times 100 \quad (2)$$

where, W_{free} and W_{inh} are the weight loss in the absence and presence of inhibitor, respectively.

III. RESULTS AND DISCUSSION

3.1 Weight loss measurements

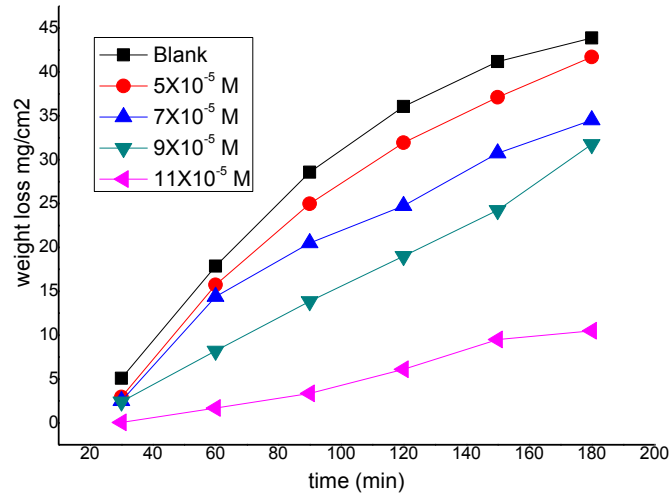


Fig. 1 Weight loss-time curves for the corrosion of aluminum in 1 M HCl in the absence and presence of different concentrations of inhibitor at 25°C

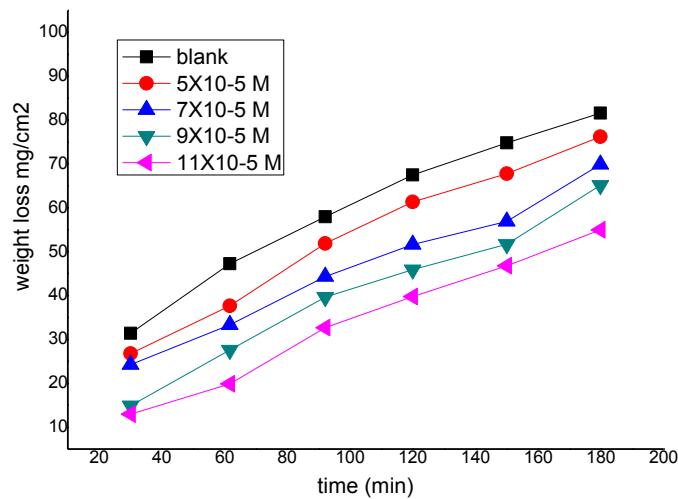


Fig. 2 Weight loss-time curves for the corrosion of aluminum in 1 M HCl in the absence and presence of different concentrations of inhibitor at 35°C

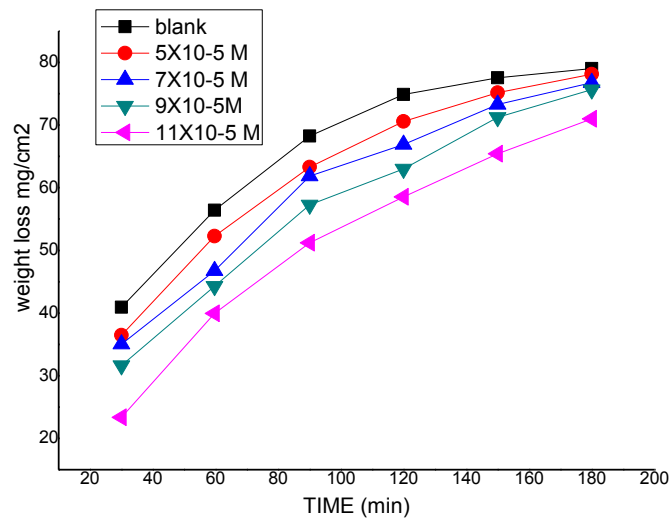


Fig. 3 Weight loss-time curves for the corrosion of aluminum in 1 M HCl in the absence and presence of different concentrations of inhibitor at 45°C

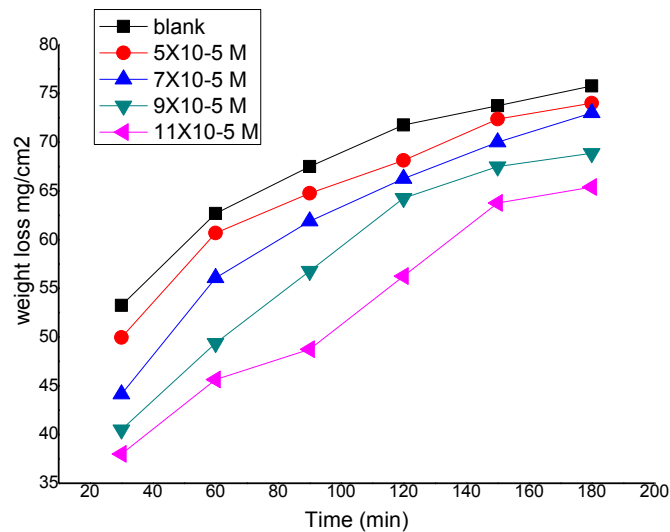


Fig. 4 Weight loss-time curves for the corrosion of aluminum in 1 M HCl in the absence and presence of different concentrations of inhibitor at 55°C.

Weight loss Figure 1- 4 shows the effect of concentration of inhibitor on the weight loss vs. time of aluminum at 25°C-55°C.

It is obvious that the weight loss of aluminum in presence of inhibitors varies linearly with time, and is much lower than that obtained in blank solution.

The linearity obtained indicated the absence of insoluble surface film during corrosion and that the inhibitor was first adsorbed onto the metal surface and, therefore, impede the corrosion process [35].

The calculated values of the percentage inhibition efficiency (% IE) at different concentrations of inhibitor in 1 M HCl at different temperatures (25-55°C) are given in Tables 1, 2. From these Tables, the inhibition efficiency increases by increasing the concentrations of inhibitor and decreases by raising the temperature. This behavior could be attributed to the increase of the number of adsorbed molecules at the metal surface and by raising the

temperature there is a desorption of inhibitor molecules from the metal surface.

Table. 1 Corrosion rate (C.R.) in (mg cm⁻² min⁻¹) and inhibition efficiency data obtained from weight loss measurements for aluminum in 1 M HCl solution in the absence and presence of different concentrations of investigated inhibitor at 25°C

Compound	Conc. X 10 ⁻⁵ M	Corrosion Rate(CR), mg cm ⁻² min ⁻¹	θ	IE %
1M HCl		.0500	----	----
2-aminobenzoic acid	5 X 10 ⁻⁵	0.0201	0.598	59.8
	7 X 10 ⁻⁵	0.0177	0.646	64.6
	9 X 10 ⁻⁵	0.0077	0.846	84.6
	11 X 10 ⁻⁵	0.0062	0.876	87.6

Table. 2 Data of weight loss measurements for Aluminum in 1 M HCl solution in the absence and presence of different concentrations of investigated inhibitor at 35–55°C.

Conc. X 10 ⁵ M	35°C		45°C		55°C	
	θ	IE%	θ	IE%	θ	IE%
5 X 10 ⁻⁵	0.574	57.4	0.527	52.7	0.471	47.1
7 X 10 ⁻⁵	0.638	63.8	0.609	60.9	0.588	58.8

9×10^{-5}	0.807	80.7	0.771	77.1	0.724	72.4
11×10^{-5}	0.844	84.4	0.805	80.5	0.781	78.1

3.2 Adsorption isotherm

Basic information on the interaction between the inhibitors and the Aluminum can be provided by the adsorption isotherm. Two main types of interaction can describe the adsorption of the organic compound: physical adsorption and chemical adsorption. These are influenced by the chemical structure of the inhibitor, the type of the electrolyte, the charge and nature of the metal. The surface coverage, θ , of the metal surface by the adsorbed inhibitor was evaluated from weight loss measurements using equation (2).

The θ values of different inhibitor concentrations at 25 °C were tested by fitting to various isotherms including, Frumkin, Langmuir, Temkin and Flory-Huggins. By far the best fit was obtained with the Langmuir isotherm is given as [36]:

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

where C is the inhibitor concentration and K_{ads} is the equilibrium constant of adsorption process.

A plot of (C / θ) against C, for all concentrations of inhibitor (Figure 5) a straight line relationship was obtained in all cases with correlation coefficients (R^2) in more than 0.994. The standard free energy of adsorption ΔG°_{ads} can be calculated from Eq. (4):

$$K_{ads} = \frac{1}{55.5} e^{\frac{-\Delta G^{\circ}_{ads}}{RT}} \quad (4)$$

The value of 55.5 is the concentration of water in solution expressed in mole per liter, R is the

universal gas constant and T is the absolute temperature.

The deviation of the slope from unity as observed from this study could be interpreted that there are interactions between adsorbed species on the metal surface as well as changes in adsorption heat with increasing surface coverage [37, 38], factors that were ignored in the derivation of Langmuir isotherm. The negative ΔG°_{ads} values (Table 3) are consistent with the spontaneity of the adsorption process and the stability of the adsorbed layer on the Aluminum [39].

It is generally accepted that the values of ΔG°_{ads} up to -20 kJ mol^{-1} the types of adsorption were regarded as physisorption, the inhibition acts due to the electrostatic interaction between the charged molecules and the charged metal, while the values around -40 kJ mol^{-1} or larger, were seen as chemisorption, which is due to the charge sharing or a transfer from the inhibitor molecules to the metal surface to form covalent bond [40, 41]. The ΔG°_{ads} values obtained in this study range from -36.2 to $-36.7 \text{ kJ mol}^{-1}$. It suggested that the adsorption mechanism of investigated inhibitor on Aluminum in 1 M HCl solution was typical of physisorption and chemisorption (mixed one).

Moreover, the adsorption heat can be calculated according to the Van't Hoff equation (5) [42]:

$$\ln K = -\frac{\Delta H^{\circ}_{ads}}{RT} + const \quad (5)$$

Figure 3 show the plot of log K vs. 1/T for Aluminum dissolution in 1 M HCl in the presence of 2-aminobenzoic acid. The ΔH_{ads}° values (Table 3) are negative, which show that the adsorption is an exothermic process [43].

Finally, the standard adsorption entropy ΔS_{ads}° can be calculated by the equation (6):

follows: the adsorption of organic inhibitor molecules from the aqueous solution.

Table 3 lists all the above calculated thermodynamic parameters [44-45].

$$\Delta S_{ads}^{\circ} = \frac{\Delta H_{ads}^{\circ} - \Delta G_{ads}^{\circ}}{T} \quad (6)$$

The ΔS_{ads}° values (Table 3) are negative, which show that the adsorption is an exothermic process and always accompanied by a decrease of entropy.

The reason can be explained as

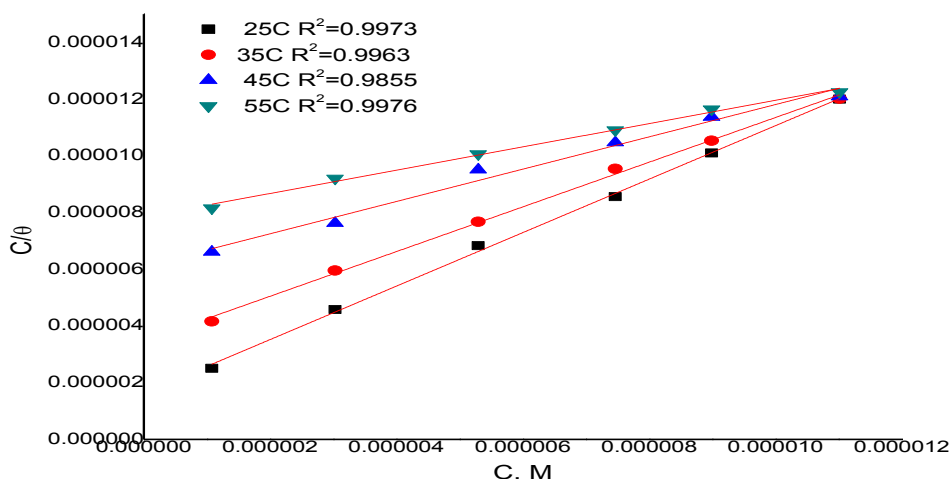


Fig. 5 Langmuir adsorption isotherm of inhibitor on Aluminum surface in 1 M HCl at different temperatures

Table. 3 Data of weight loss measurements for Aluminum in 1 M HCl solution in the absence and presence of different concentrations of investigated inhibitor at 35–55°C.

Temp.K	$K_{ads} \times 10^4 \cdot M^{-1}$	ΔG_{ads}° kJ mol	ΔH_{ads}° kJ mol	$-\Delta S_{ads}^{\circ}$ J mol ⁻¹ k

298	77.25	42.99	76.23	108.59
308	52.87	42.90		106.77
318	38.96	42.36		105.34
328	17.26	42.02		111.853

3.3 Kinetic-thermodynamic corrosion parameters

The adsorption process was well elucidating by using a thermodynamic model, in addition a kinetic-thermodynamic model was another tool to explain the mechanism of corrosion inhibition for an inhibitor. The apparent effective activation energies (E_a^*) for the corrosion reaction of Aluminum in HCl in the absence and presence of different concentrations of investigated inhibitor were calculated from Arrhenius-type equation (7) [46]:

$$Rate(k) = A e^{\frac{-E_a^*}{RT}} \quad (7)$$

where A is the Arrhenius pre-exponential factor. A plot of $\log k$ (corrosion rate) vs. $1/T$ gave straight lines as shown in Figure 4. The entropy of activation (ΔS^*) and the enthalpy of activation (ΔH^*) for the intermediate complex in the transition state for the corrosion of Aluminum in HCl in the absence and presence of different concentrations of investigated inhibitor were obtained by applying the transition-state equation (8) [47-49]:

$$Rate(k) = \frac{RT}{Nh} e^{\frac{\Delta S^*}{R}} e^{\frac{-\Delta H^*}{RT}} \quad (8)$$

where h is the Planck's constant and N is the Avogadro's number.

A plot of $\log k$ (corrosion rate) / T vs. $1/T$ should give a straight lines (Figure 5), with a slope of $(-\Delta H^* / 2.303R)$, and an intercept of $[(\log(RT / Nh) + (\Delta S^* / 2.303R)]$ [47,48], from which the values of ΔH^* and ΔS^* were calculated, respectively. (Table 4) exhibited values of apparent activation energy, apparent enthalpies ΔH^* and entropies ΔS^* for Aluminum dissolution in 1 M HCl solution in the absence and presence of compound. The presence of inhibitor increased the activation energies of Aluminum indicating strong adsorption of the inhibitor molecules on the metal surface and the presence of this compound the adsorption of these additives on the surface of Aluminum. Values of the entropy of activation ΔS^* in the absence and in presence of the studied compound are negative. This implies that the activated complex in the rate determining step represents an association rather than a dissociation step [49]. This means that the activated molecules were in higher order state than that at the initial stage [50, 51].

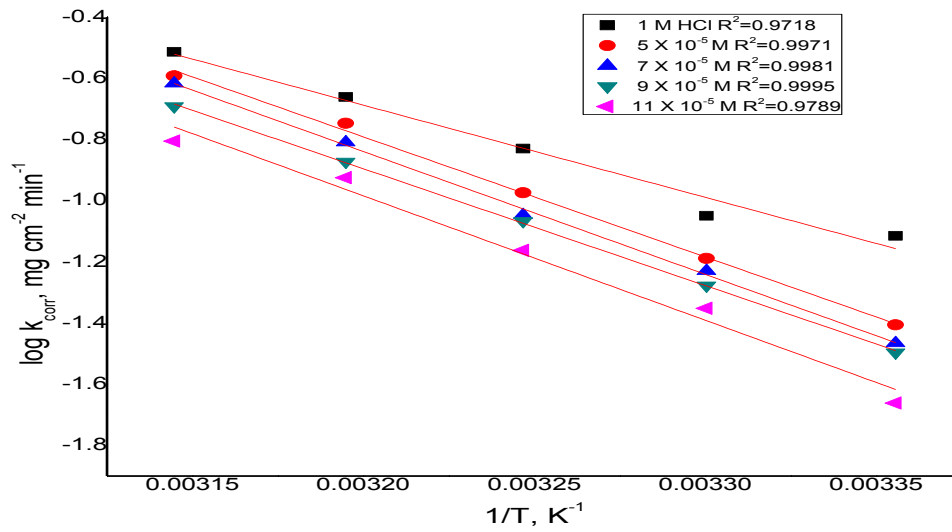


Fig. 6 Arrhenius plots for Aluminum corrosion rates ($k_{corr.}$) after 120 minutes of immersion in 1 M HCl in the absence and presence of different concentrations.

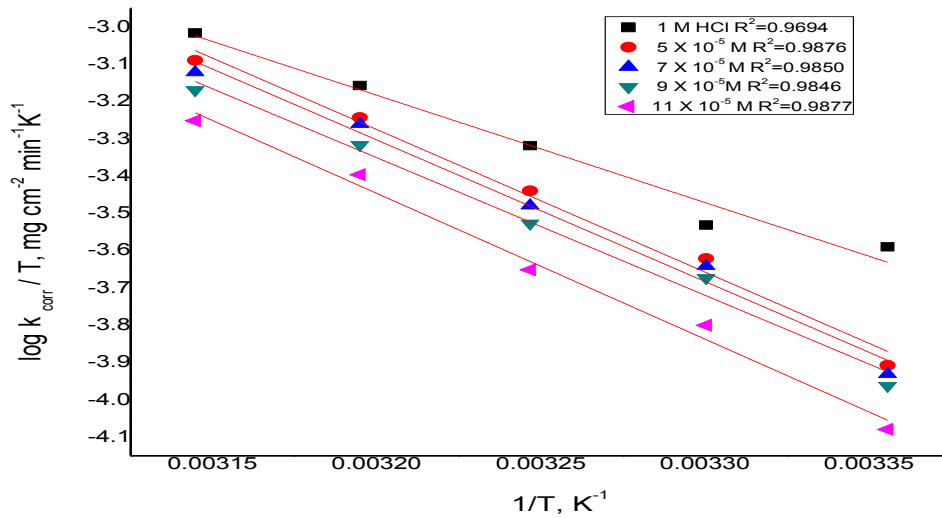


Fig. 7 Plots of ($\log k_{corr}$) vs. $1/T$ for corrosion of Aluminum in 1M HCl in the absence and presence of different concentrations.

Table. 4 Activation parameters for the dissolution of Aluminum in the presence and absence of different concentration of inhibitor in 1 M HCl.

Conc., x 10 ⁻⁵ M	Activation parameters		
	E _a * kJ mol ⁻¹	ΔH*kJ mol ⁻¹	-ΔS*J mol ⁻¹ k ⁻¹
blank	54.60	22.91	77.18
5	69.02	32.27	85.33
7	75.25	45.67	92.17
9	82.57	59.74	98.41
11	91.71	68.88	101.78

IV. CONCLUSION

From the study, the following conclusions are made:

- 1) 2-aminobenzoic acid acts as a good inhibitor for Aluminum corrosion.
- 2) Inhibition efficiency of 2-aminobenzoic acid depends on concentration and temperature.
- 3) Inhibition of Aluminum corrosion by 2-aminobenzoic acid is thermodynamically feasible.
- 4) The adsorption process is spontaneous and follows Langmuir adsorption isotherm.

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