

INHIBITORY EFFECT OF SOME α -AMINOCARBOXYLIC ACIDS ON CORROSION OF ALUMINIUM IN HYDROCHLORIC ACID SOLUTION

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التأثير التثبيطي لبعض الأحماض الكربوكسيلية الأمينية على تآكل الألومنيوم في محلول حمض الهيدروكلوريك

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تمت دراسة التأثير التثبيطي لكل من الألانين والتيروسين والهستيدين والتربتوفان على تآكل فلز الألومنيوم في محلول 2ع من حمض الهيدروكلوريك باستخدام طريقة تصاعد الهيدروجين والطريقة الثرمومترية. وقد أعطت الطريقتان نتائج متشابهة. وقد وجد أن التأثير التثبيطي لهذه المواد يعتمد على كل من تركيز المادة المثبطة وبنيتها الكيميائية. وقد وجد أن إدمصاص هذه المواد على سطح الفلز يتبع أيزوثرم فرومكين.

Key Words: Acid corrosion, Aluminium, μ - Aminocarboxylic acids, Hydrogen evolution, Thermometric method, Inhibition.

ABSTRACT

The corrosion of metallic aluminium in 2N hydrochloric acid solution in the presence of L-alanine, L-tyrosine, L-histidine and L-tryptophan as corrosion inhibitors has been studied using hydrogen evolution and thermometric methods. The two methods gave similar results. The inhibitory character of these compounds depends upon the concentration of the inhibitor, and their chemical structures. The adsorption of these additives on aluminium was found to obey the Frumkin adsorption isotherm.

INTRODUCTION

Much work has been reported on the inhibition of aluminium metal corrosion in hydrochloric acid solution. Various organic compounds have been studied with regard to their usefulness as inhibitors. Of these, amino compounds (Subramanyan *et al*, 1970), hydrazone compounds (Ahmed *et al*, 1985), and p-substituted benzoates (Mourad *et al*, 1990) have been found to be effective. The object of the present investigation is to investigate the use of some α -aminocarboxylic acids as corrosion inhibitors for aluminium in acid solution.

EXPERIMENTAL

The chemical composition of aluminium metal used (Riedel-de Haen - West Germany) is given in (Table 1).

Table 1
Chemical composition of al metal

Element	Al	Fe	Cu	Si	Ti	Zn
Weight percent (%)	99	0.2	0.2	0.2	0.03	0.08

A stock solution of HCl (2N) was prepared. The inhibitive effect of the following additives was investigated:

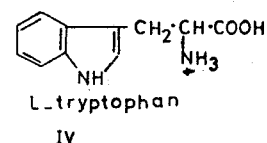
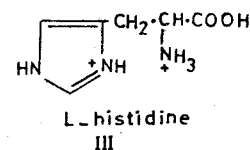
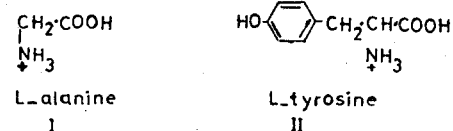


Fig. a: *

Since aluminium is readily soluble in aqueous acids with liberation of hydrogen, the hydrogen evolution method was used to measure the rate of dissolution of aluminium in HCl solutions (Quartaroli *et al*, 1939; Bukowiecki, 1959; Mourad *et al*, 1989). The reaction vessel and the procedure for determining the dissolution of Al in corroding media were described elsewhere (Deren *et al*, 1963).

The efficiency of a given inhibitor can be evaluated as the percentage reduction in reaction rate R, % inhibitor efficiency (% IE).

$$= \frac{R_{\text{uninhibited}} - R_{\text{inhibited}}}{R_{\text{uninhibited}}} \times 100 \quad \dots(1)$$

A simple and rapid method, based on the thermometric corrosion test of Mylius (Mylius, 1922), has been developed (Aziz *et al*, 1965) and used successfully for comparing the inhibition efficiency of different organic additives in reducing the rate of dissolution of Al (Fouda *et al*, 1986; Mourad *et al*, 1990).

The procedure for the determination of the metal dissolution rate by the thermometric method has been described previously (Aziz *et al*, 1965). The reaction number (RN) is defined (Mylius, 1924) as:

$$RN = (T_m - T_i) / t \quad \dots(2)$$

where T_m and T_i are the maximum and initial temperature, respectively, and t is the time (in minutes) required to reach the maximum temperature. The percent reduction in reaction number (% RR) is given (Mourad *et al*, 1989), as:

$$\frac{RN_{\text{uninhibited}} - RN_{\text{inhibited}}}{RN_{\text{uninhibited}}} \times 100 \quad \dots(3)$$

Aluminium test pieces measuring 0.1 x 10 x 30 mm were used for hydrogen evolution, while 0.1 x 10 x 10 mm test pieces were used for thermometric measurements. These were degreased and etched as has been described previously (Radon, 1930).

The experimental data were analyzed using a BEAM professional computer and the curve fitting was carried out with a standard linear regression package.

RESULTS AND DISCUSSION

Hydrogen evolution measurements:

Figs. 1 and 2 show the volume of hydrogen evolved as a function of time for dissolution of Al in 2N HCl at 35°C in the absence and presence of L-alanine (I) and L-tyrosine (II) over the concentration range 0.01 — 0.30 M. It was found that the hydrogen evolution increases linearly with time after a certain time interval and that the latter increases with an increase of the additive concentration Figs. 3, 4. The initial time interval was attributed to an incubation period (Muller *et al*, 1936) representing the breakdown of the oxide film on the metal surface and the start of the attack (Aronson *et al*, 1940). Accordingly, it can be stated that the dissolution of Al itself is linearly related to the reaction time. The behavior is characteristic of a zero-order reaction (Smrcek *et al*, 1958), generally given by:

$$V = k t \quad \dots(4)$$

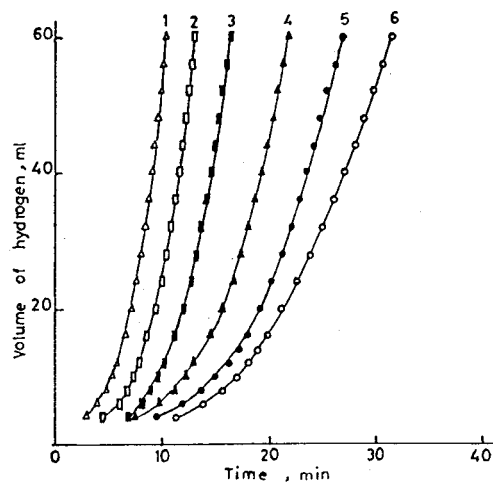


Fig. 1: Effect of L-alanine (I) concentration (M) on volume-time curves of Al in 2N HCl at 35°C.
(1) 0.0 (2) 0.01 (3) 0.03 (4) 0.20 (5) 0.25

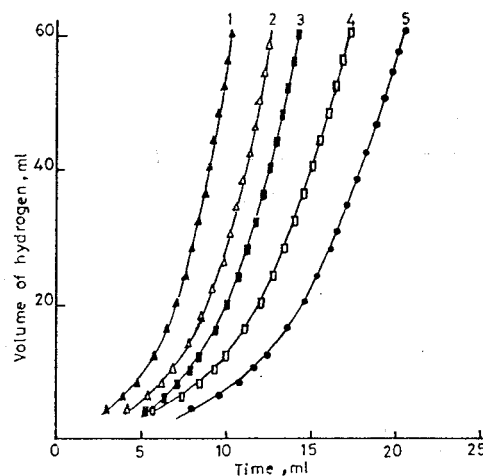


Fig. 2: Effect of L-tyrosine (II) concentration (M) on volume-time curves of Al in 2N HCl at 35°C.
(1) 0.0 (2) 0.01 (3) 0.03 (4) 0.20 (5) 0.25 (6) 0.30

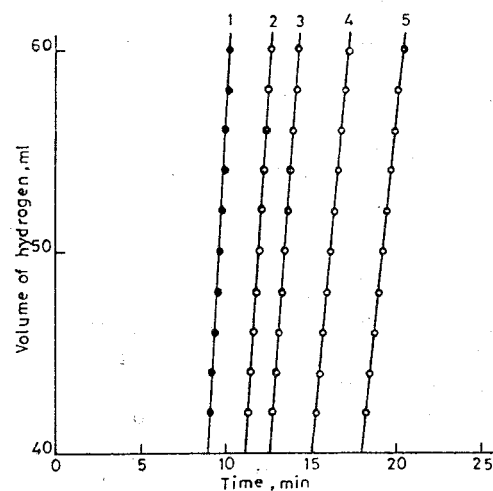


Fig. 3: Effect of L-alanine (I) concentration (M) on volume-time curves of Al in 2N HCl at 35°C.
(1) 0.0 (2) 0.01 (3) 0.03 (4) 0.20 (5) 0.25

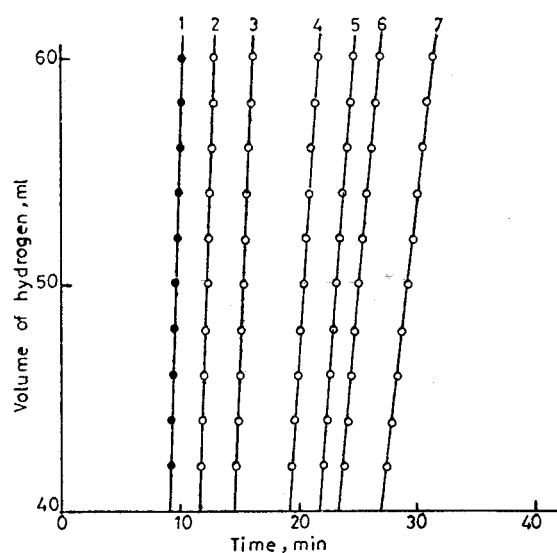


Fig. 4: Effect of L-tyrosin (II) concentration (M) on volume-time curves of Al in 2N HCl at 35°C.
 (1) 0.0 (2) 0.03 (3) 0.05 (4) 0.15 (5) 0.20 (6) 0.25 (7) 0.30

Table 2
 Effect of additive concentration on corrosion behavior of Al in 2N HCl at 35°C.

Additive Concentration mole/l	I		II		III		IV	
	R ml/min	% IE	R ml/min	% IE	R ml/min	% IE	R ml/min	% IE
0.0	15	0.0	15	0.0	15	0.0	15	0.0
0.01	13	15	---	---	9.7	36	11.3	26
0.03	11.4	25	13.6	11	8.9	42	---	---
0.05	10.8	29	11.5	24	8.7	43	7.1	53
0.07	10	34	10.3	32	6.9	55	7	54
0.10	9.7	36	8.2	46	6.3	59	---	---
0.15	9.7	37	7.9	48	5.9	61	6.2	59
0.20	8.9	41	6.9	54	---	---	5.1	66
0.25	8.0	47	5.8	62	4.6	70	4.7	69
0.30	7.5	51	4.3	72	4	74	3.8	76

Thermometric method

In this method, the temperature change of the system involving Al in 2N HCl was followed in absence and presence of different concentrations of the additives I-IV (Figs. 6-9). The maximum temperature measured in acid solution containing no inhibitor is 55.4°C, and is attained after 31.75 min. This corresponds to an RN of 1.1°C/min. The added compounds were found to influence the RN in one of two ways. Small additions of the additives I-IV brought about an increase in RN caused through rise in T_m and decrease in t . As the concentration of the additives is increased, dissolution is inhibited and lower RN

where V is the volume of hydrogen evolved, which is proportional to the fraction of the reactant converted into reaction product at time t , where k is the zero-order rate constant.

Similar curves were obtained when L-histidine (III) and L-tryptophan (IV) were used as inhibitors.

The data in Table 2 show the effect of increasing the concentration of the additives I-IV on the corrosion behavior of Al in 2N HCl.

It is evident that the increase in the concentration of the additives used was accompanied by a decrease in hydrogen evolution rate and hence an increase in the % IE of the additive. The behavior suggests that inhibition is due to adsorption of the additives on the Al surface. Figure 5 shows the variation in the % IE with the logarithm of the concentration of the additives. The plots corresponding to the additives I, II and IV has the characteristic S-shape, indicating perhaps that they form a monolayer on the Al surface and that their adsorption takes place according to the Frumkin isotherm (Frumkin, 1925). Additive III is the only exception and gives a plot with two inflexion points, indicating that two-step adsorption takes place.

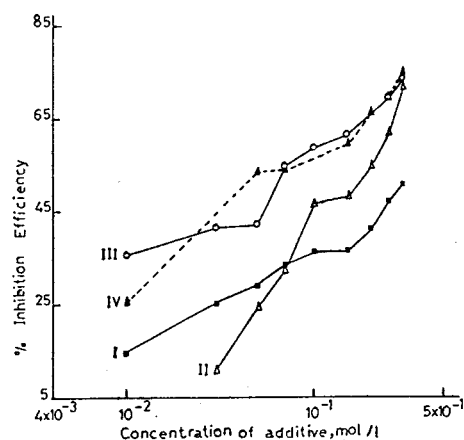


Fig. 5: Effect of concentration of the additives I-IV on % inhibition efficiency for Al in 2N HCl.
 (1) L-alanine (II) L-tyrosine (III) L-histidine (IV) L-tryptophan

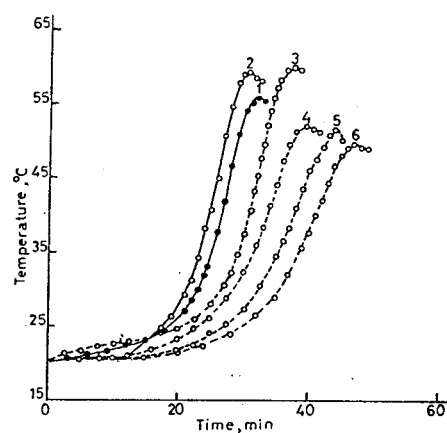


Fig. 6: Effect of L-alanine concentration (M) on thermometric curves for Al 2 N HCl.
 (1) 0.0 (2) 0.01 (3) 0.05 (4) 0.07 (5) 0.15 (6) 0.25

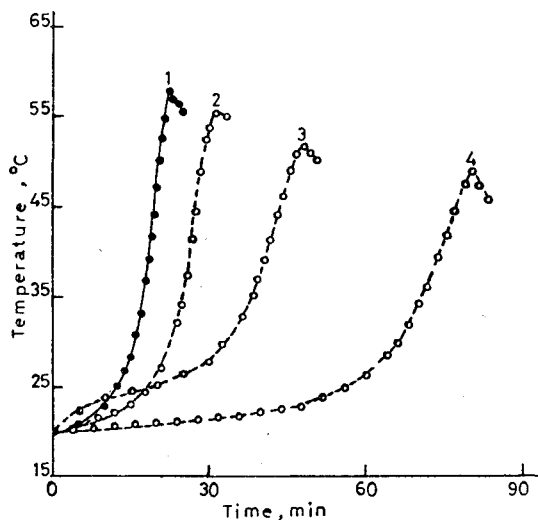


Fig. 7: Effect of L-tyrosine concentration (M) on thermometric curves for Al in 2N HCl.

(1) 0.0 (2) 0.01 (3) 0.25 (4) 0.30

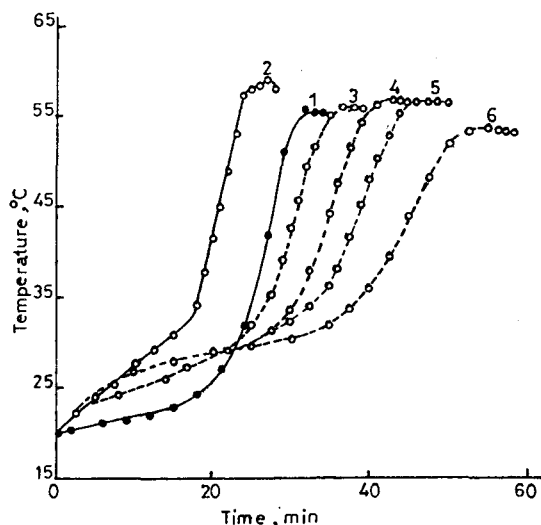


Fig. 9: Effect of L-tryptophan concentration (M) on thermometric curves for Al in 2N HCl.

(1) 0.0 (2) 0.07 (3) 0.10 (4) 0.20 (5) 0.25 (6) 0.30

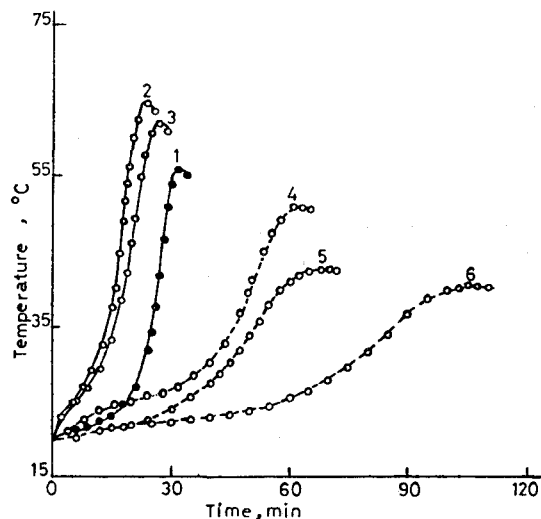


Fig. 8: Effect of L-histidine concentration (M) on thermometric curves for Al in 2N HCl.

(1) 0.0 (2) 0.01 (3) 0.03 (4) 0.15 (5) 0.25 (6) 0.30

values are obtained. The decrease in RN is brought about mainly through an increase in the time, t , necessary to reach T_m Table 3.

That the additives act either as accelerator or as inhibitor for the dissolution of Al in 2N HCl, depending upon their concentration in solution, can be readily accounted for by assuming the occurrence of two counteracting reactions. The acceleration effect observed at low additive concentration can be explained by assuming that adsorbed additive molecules are displaced by chloride ions which are corrosion accelerators and that this process is highly exothermic. Increased additive concentration, on the other hand, enhances its adsorption on the metal surface, and leads to retardation of the dissolution reaction. Also, since the energies of adsorption of the various additives on the surface of the metal vary from one additive to the other, the concentration at which the additive changes its character from corrosion accelerator to corrosion retardant will depend on its nature.

The thermometric curves allow distinction between weak and strong adsorption (Aziz *et al*, 1965). Weak adsorption is noted whenever the time necessary to reach T_m increases whilst this

Table 3

Effect of concentration of additives I-IV on the parameters of the thermometric curves of Al in 2N HCl solution.

Additive T ₁ Concentration mole/l	I					II				III				IV			
	T _m °C	t min	RN °C/min	% RR		T _m °C	t min	RN °C/min	% RR	T _m °C	t min	RN °C/min	% RR	T _m °C	t min	RN °C/min	% RR
0.0	20	56.1	31.8	1.1	—	55.4	31.8	1.1	—	55.4	31.8	1.1	—	55.4	31.8	1.1	—
0.01		58.9	30.3	1.3	-15	57.7	22.5	1.7	-50	64.5	23.5	1.9	-69	—	—	—	—
0.03		—	—	—	—	60.5	27.0	1.5	-34	61.7	26.8	1.6	-40	—	—	—	—
0.05		59.5	37.3	1.1	5	56.4	32.0	1.1	-2	—	—	—	—	—	—	—	—
0.07		51.9	39.5	0.8	28	52.7	31.0	1.1	6	53.0	35.8	0.9	17	59.0	27.0	1.4	-5
0.10		—	—	—	—	53.2	32.3	1.0	9	55.7	58.5	0.6	45	55.9	36.5	0.9	12
0.15		51.1	44.0	0.7	37	—	—	—	—	50.6	62.0	0.5	56	57.2	40.0	0.9	17
0.20		—	—	—	—	54.6	16.5	0.7	34	45.9	63.0	0.4	63	56.9	43.0	0.9	23
0.25		49.2	46.8	0.6	44	51.5	48.5	0.6	42	42.7	68.8	0.3	71	56.5	47.5	0.8	31
0.30		51.9	54.5	0.6	48	48.8	80.0	0.4	68	40.4	106	0.2	83	53.6	54.8	0.6	45

latter remains practically the same as that measured in inhibitor-free solution. Strong adsorption on the other hand is characterized by simultaneous increase in the time and a diminution in T_m . Accordingly, additives I, II and IV seem to be weakly adsorbed while additive III seems to be strongly adsorbed.

Figure 10 shows the relation between the percentage reduction in reaction number (% RR) and the molar concentration of the different additives used. The curves obtained are invariably sigmoid in nature, substantiating the idea that they retard the corrosion rate by adsorption according to Frumkin isotherm (Frumkin, 1925), which has the formula:

$$B \cdot C = \frac{\theta}{1 - \theta} \cdot \exp(-f Q) \quad \dots(5)$$

where C is the concentration of the adsorbed substance in the bulk of solution and θ is the degree of coverage of the investigated surface by the adsorbed molecules calculated from the equation:

$$\theta = 1 - \frac{k}{k_0} \quad \dots(6)$$

where k and k_0 are the dissolution rates in absence and presence of the investigated inhibitor. B is the modified equilibrium constant of the adsorption process and f is a constant depending on intermolecular interaction in the adsorption layer and on the heterogeneity of the surface.

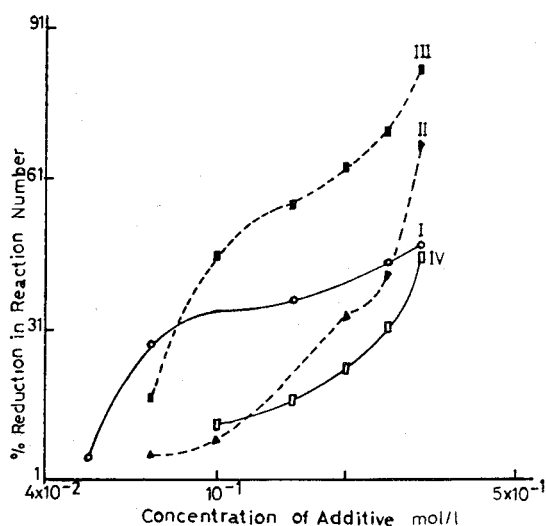


Fig. 10: Effect of concentration of the additives I/IV on % reduction in reaction number for Al in 2N HCl.
(I) L-alanine (II) L-tyrosine (III) L-histidine (IV) L-tryptophan

The order of inhibition efficiency of the additives as determined by the percentage reduction in reaction number in concentration range 0.1 — 0.3 M seems to be:

$$III > I > II > IV$$

The inhibition efficiency of additives depends on many factors which include the number of adsorption sites and their charge density, molecular size and mode of interaction with the metal surface. Retardation of aluminium dissolution by the additives of

this study is expected to be due to their adsorption on the metal surface via the carboxylate groups. Nevertheless, the adsorption of the carboxylate group on the metal surface would depend essentially on its charge density. Histidine (III) is found to be the most efficient inhibitor. This may be due to the presence of the highly donating imidazol group which increases considerably the charge density on the adsorbed sites of the molecule. Tyrosine (II) and Tryptophan (IV) come after alanine (I). This is due to the comparable decrease in the basicity of the carboxylate group. Since the benzamido group is more withdrawing than the p-hydroxyphenyl group, tryptophan (IV) is found to be the least efficient inhibitor.

Two different techniques demonstrate the agreement and conformity of the experimental results as to the type of inhibition of the corrosion of aluminium in hydrochloric acid solution. However, the differences are small under our experimental conditions.

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