Thermometric Study of Inhibition of Aluminium Corrosion in Hydrochloric Acid Solution

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دراسة ثرمومترية لتثبيط تآكل الألمونيوم في محلول حمض الهيدروكلوريك

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تمت دراسة تأثير المركب العضوي

(6-amino - 4 - (4 - phenyl) - 1,4 - dihydro - 3 - methylpyrano [2,3 - c] pyrazole 5 - carbonitrile)

وبعض مشتقاته كمواد مثبطه لتآكل الالمونيوم في محلول ٢ مولر من حمض الهيدروكلوريك باستخدام الطريقة الثرمومترية .

وقد بينت النتائج أن هذه المواد تقلل من معدل التآكل عن طريق الادمصاص الضعيف من خلال الاكسيجين الكاتيوني في حلقة البيران كما أنها تؤثر كمثبطات مختلطة وأن إدمصاصها يتبع أيزوثرم فرومكين .

وقد تم ايجاد الارتباط بين كفاءة تثبيط هذه المواد والقيم المطلقة لثوابت هامت .

Key-words : Aluminium Corrosion, Hydrochloric Acid

ABSTRACT

The use of 6- amino - 4- (4-phenyl)-1,4- dihydro -3- methylpyrano [2,3- c] pyrazole -5- carbonitrile and some related compounds as corrosion inhibitors for aluminium in 2 M HCl solution was studied by the thermometric method. The results indicate that the additives reduce the corrosion rate via weak adsorption through the cationic oxygen of the pyran ring. They act as mixed inhibitors and their adsorption was found to obey Frumkin's isotherm. The inhibition efficiency of the additives is related to the absolute value of the Hamment constant.

Introduction

Since aqueous solutions of acids are among the most corrosive media for metals and alloys, especially when soluble corrosion products are formed, the study of inhibition of acidic corrosion is of great importance. The selection of appropriate inhibitors depends mainly on the type of the acid, its concentration and temperature, the presence of dissolved organic and/or inorganic substances and the type of metallic material exposed to the action of the acidic solution.

Most of the known commercial acid inhibitors are organic compounds containing nitrogen, sulphur or oxygen [1-15] . Azoles and fused azoles have been widely used as both potential CNS regulants and antimetabolites in purine biochemical reactions [16-18]. In this work, the thermometric method [19], which is based on the thermometric corrosion test of mylius [20], was employed

to investigate the role played by 6- amino - 4 - (4-phenyl) -1,4-dihydro-3-methylpyrano[2,3-c] pyrazole-5-carbonitrile and related compounds (Scheme 1) in retarding the dissolution of aluminium specimens in 2M HCl solution, and to elucidate the influence of the structural changes of these compounds on their inhibition efficiency. The used additives were synthesized following the literature method [21,22]. They were crystallized twice from ethanol.

Scheme 1

Experimental

The experiments were performed with aluminium test pieces measured 0.1 x 10 x 100 mm and have chemical composition given in Table 1.

Table 1 - Chemical composition of aluminium (Riedel- de - Haen - Germany).

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

Before measurement the test pieces were chemically degreased as previously described [19].

The thermometric measurements were run in the reaction vessel described elsewhere [19]. The variation of temperature of the system is monitored with time and the reaction number (RN) defined as [23]:

$$RN = \frac{T_m - T_i}{t_m} \ ^oC/min \qquad ...(1)$$

where T_m and T_i are the maximun and initial temperatures, respectively. t_m is time in minutes from the start of the experiment till the attainment of the maximum temperature. The extent of corrosion inhibition can expressed in terms of the percentage reduction in reaction number (%RR) given as [24] :

$$\%RR = \frac{RN_{uninhibited} - RN_{inhibited}}{RN_{uninhibited}} \ x100 \qquad ...(2)$$

The initial temperature T_i was 25°C.

Results and Discussion

Temperature changes of the system involing Al in 2 M HCl were followed in the absence and the presence of varying concentrations of the additives. Figure 1 shows the temperature - time curves obtained in the absence and in the presence of several concentrations of additive I. All curves are characterized by an initial slow rise in the temperature (due to the oxide film originally present on the metal surface [25]) followed by sharp rise and finally a slight decrease after attaining a maximum value.

The maximum temperature measured in the additive - free acid solution is 63°C, and is obtained after 49 min. This corresponds to a reaction number (RN) of 0.775 °C/min. On increasing the concentration of the additive the time required to T_m increases. This indicates that the additive retards the dissolution of aluminium, presumably by its adsorption on the surface of the metal.
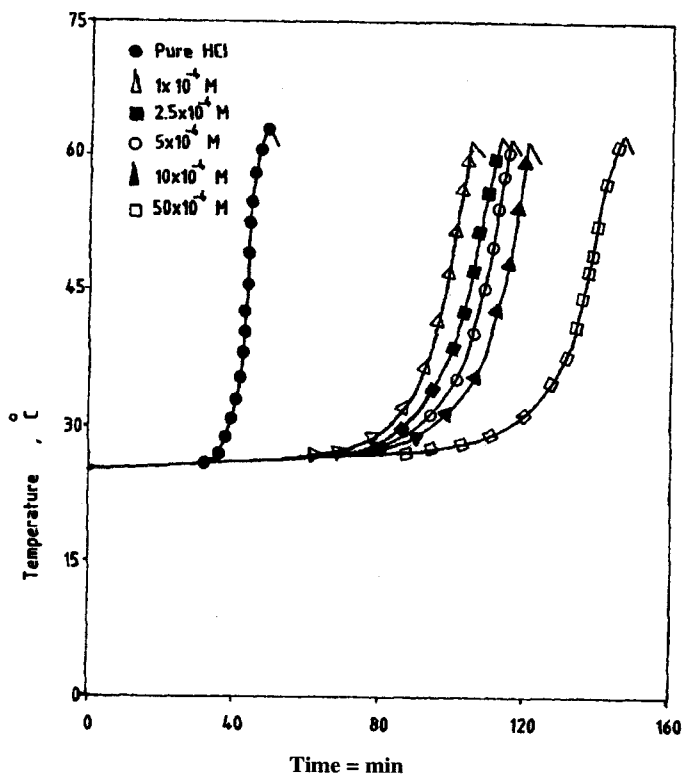

Fig.1: Effect of additive I on thermometric curves of Al in 2M HCl.

The extent of corrosion inhibition depends on the degree of coverage of the metal with the adsorbate. The temperature

Table 2 - Effect of concentration of additive I on the parameters of the thermometric curves of Al in 2 M HCl.

Concentration x 10^4 M/L		0.0	1.0	2.5	5.0	10	50
Additive 1	T_m , °C	63	60.5	61.6	61.7	60.2	61.6
	t_m , min	49	104.5	114.5	117.5	121.5	146.5
	RN , °C/min	0.775	0.340	0.320	0.312	0.290	0.250
	θ	0.0	0.561	0.587	0.597	0.625	0.677
	Δt_m	0.0	55.5	65.5	68.5	72.5	97.5

- time curves provide a means of differentiating between the weak and strong adsorption [19]. The obtained thermometric curves reveal that a weak adsorption is observed in acid medium since t_m increases, while the T_m remains practically identical to that measured in additive - free solutions.

The RN values are known as a relative measure of retardation of the dissolution process. The RN - log concentration of additive I plot (Fig. 2) has a sigmoid nature. substantaiting the idea that the additive reduces the corrosion rate by the way of adsorption . The turn in the curve is rather sharp, suggesting that it is associated with the formation of a monolayer of the inhibitor on the surface of the corroding meatal [25].

The degree of coverage θ of aluminium surface by different concentrations of the additive was calculated using the following equation:

$$\theta = (1 - \frac{RN_{inhibited}}{RN_{uninhibited}}) \qquad ... (3)$$

The relationship between θ and log C (Fig. 3) is S-shaped. This obyes Frumikn's isotherm [26] which is represented by the formula:

$$BC = \frac{\theta}{1-\theta} \exp(-f\theta) \qquad .... (4)$$

where C is the concentration of the adsorbed substance in the bulk of the solution and B is the modefied equilibrium constant of the adsorption process.
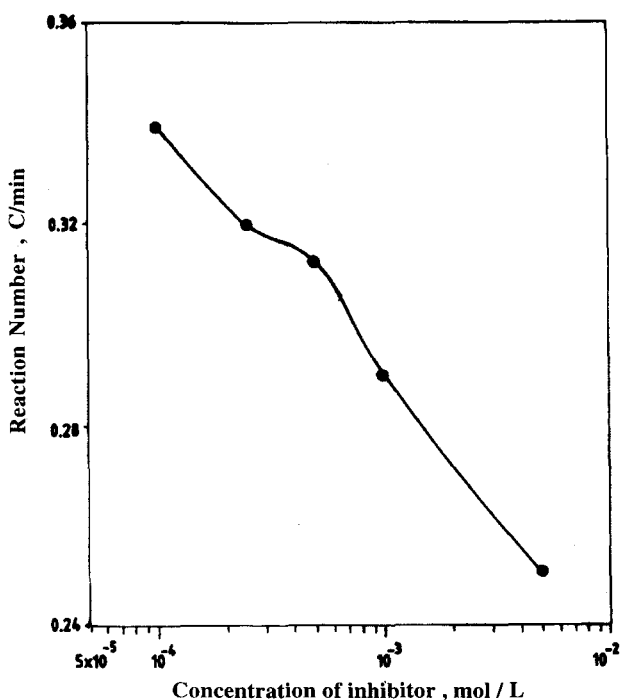

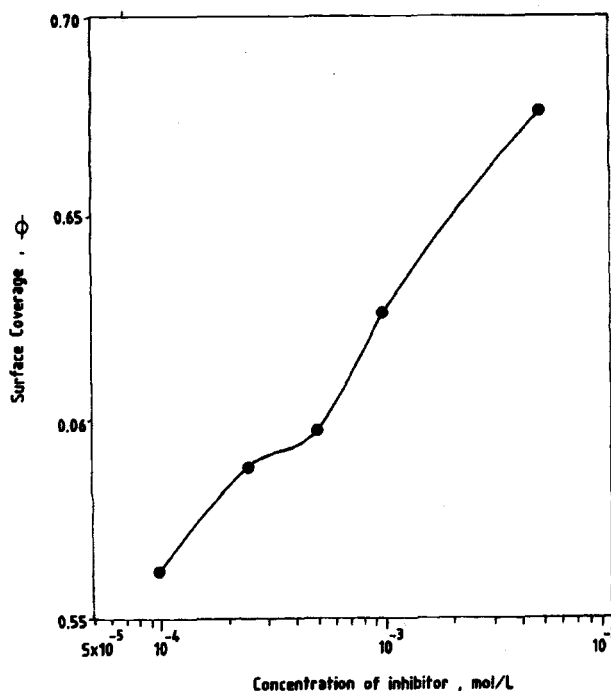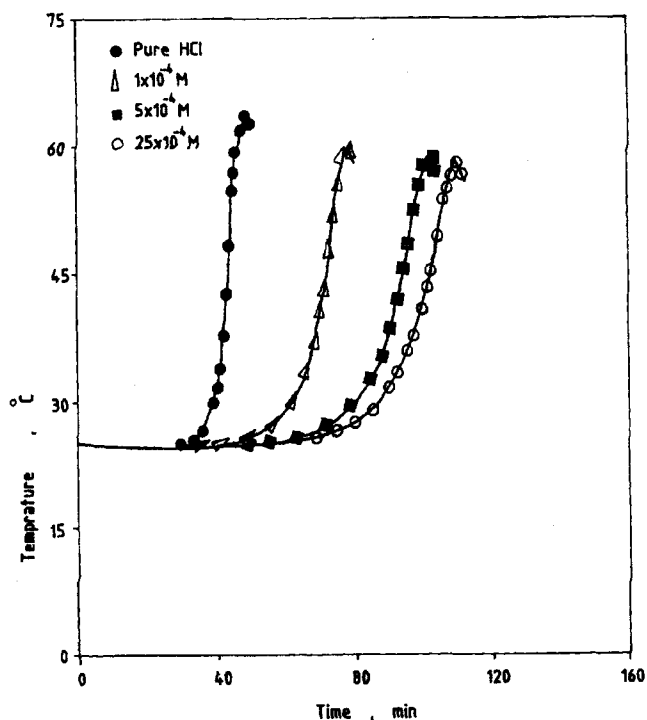Fig. 2 Effect of concentration of additive I on reaction number RN for Al in 2M HCl.

Fig. 3 Effect of concentration of additive I on the degree of coverage θ

Table 3 - Thermometric data for additives II-IV, at concentration 50×10^{-4} M/L.

Thermometric Parameter	Additive I	Additive II	Additive III	Additive IV
T_m , °C	61.6	60.2	57.7	62.7
t_m , min	146.5	120	103.5	158
RN , °C/min	0.250	0.293	0.316	0.239
% RR	67.7	62.2	59.2	69.1
Δt_m	97.5	71	54.5	109

In equation (4), f is a constant depending on intermolecular interactions in the adsorption layer and on the heterogeneity of the surface. This parameter can either be positive or negative.

The plot of time delay, Δt_m , versus log concentration of additive I confirms the above explaination (Fig. 4).

Fig. 4 Effect of concentration of additives I and III on the time delay for Al in 2M HCl.

Figures (5-7) show the obtained thermometric curves for the additives II - IV. They reveal that these additives behave similarly as weakly adsorbed inhibitors for aluminium corrosion in acid media. The curves representing θ -log C and Δt_m - log C for these additives have also the sigmoid nature (Fig. 4) indicating that inhibiting action is due to the formation of a monolayer of the additive on the metal surface in accordance with Frumkin's isotherm [26]. Taking

in consideration the slopes of the rising parts of the thermometric curves (Fig. 1, 5-7), it is evident that the used additive acts as mixed inhibitor for corrosion of aluminium in 2 M HCl solution [27].

The thermometric data summarized in Table 3 show that the efficiency of corrosion inhibition, as determined from the percentage reduction in reaction number (%RR), at concentration 50×10^{-4} M/L, varies with the type of the additive used.

The inhibition efficiency of the additive decrease in the following order :

IV > I > II > III

This behavior can be explained by taking into consideration the values of the Hammett constant [28] σ_p of the p- substituents in the phenyl ring attached to the pyran ring .σ_p is a measure of the resonance ($\pm$R) and the inductive power ($\pm$I) of the p- substitutent (see Table 4).

Table 4 - Values of the Hammett substituent constant [28] σ_p,($\sigma_p = \sigma_I + \sigma_R$).

Group	σ_I	σ_R	σ_p
CH_3O	+ 0.28	- 0.55	- 0.27
CH_3	- 0.01	- 0.16	- 0.17
H	0.00	0.00	0.00
Cl	0.45	- 0.22	+ 0.23

Retardation of aluminium dissolution by the additives I-IV can be assumed to be due to their adsorption on the metal surface in cationic form at the oxygen atom of the pyran ring (Scheme 2).
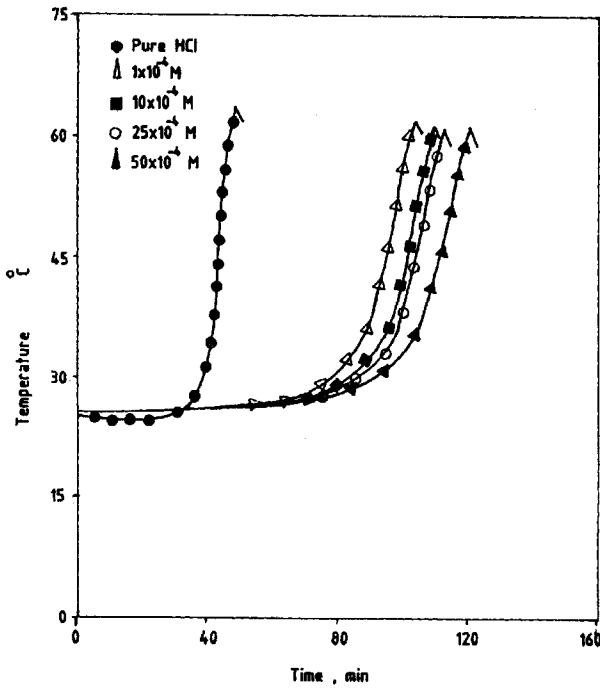
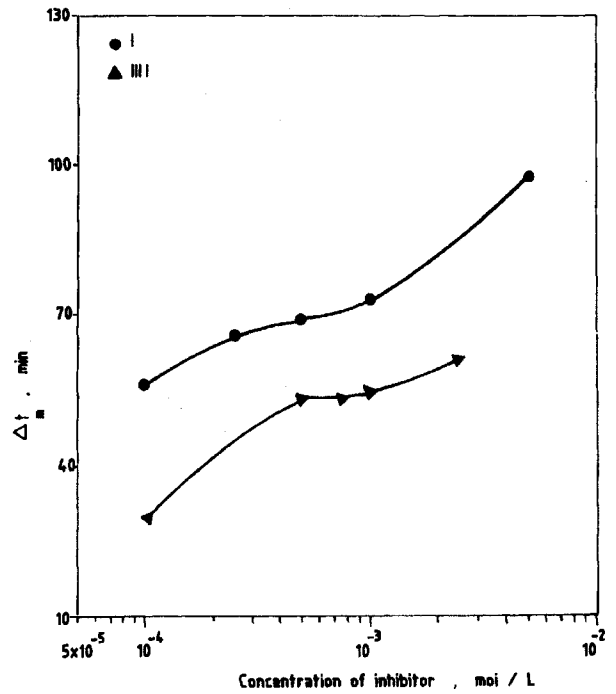**Fig. 5 Effect of additive II on thermometric curves of Al in 2M HCl.**

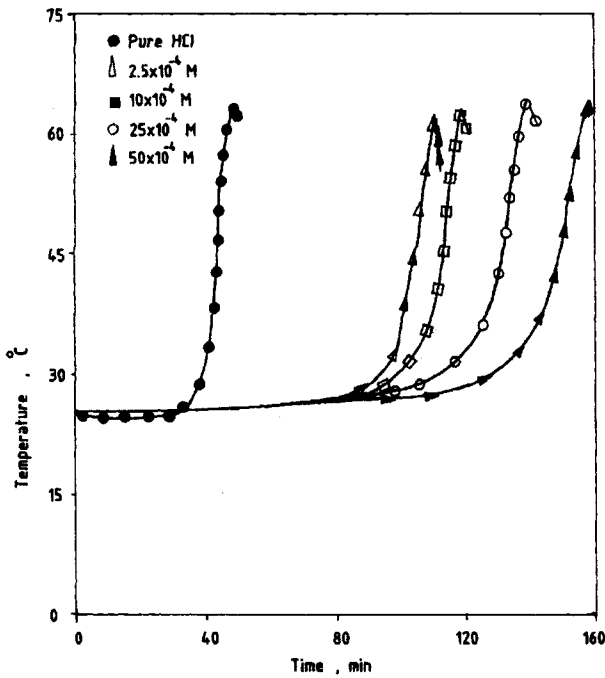**Fig. 7 Effect of additive IV on thermometric curves of Al in 2M HCl.**

Fig. 6 Effect of additive III on thermometric curves of Al in 2M HCl.

Scheme 2

Since the Hammett constant σ_p describes the relative ability of the substituent to decrease the electron density on the pyran ring and consequently enhances its conversion to the cationic form. the inhibition efficiency increases with the increase of σ_p (Tables 3 and 4).

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