INHIBITION OF ALUMINIUM CORROSION IN HYDROCHLORIC ACID

By

A. S. FOUDA*, Y. A. ELAWADY**, H. A. MOSTAFA** and M. N. MOUSSA**

*Department of Chemistry, Faculty of Science, University of Qatar, Doha, Qatar.
**Department of Chemistry, Faculty of Science, Mansoura University, Mansoura, Egypt.

منع تآكل الألومنيوم في حمض الهيدروكلوريك

عبدالعزيز السيد فوده و يحـــــــــى العواضـي
هــانم مـــــصطـــفى و محمود نور الدين موسى

تم دراسة تأثير بعض مشتقات الاكزيم ، بيتا ثنائي الكيتون والهيدرازيد كموانع لتآكل الألومنيوم في محلول ٢ عياري من حمض الهيدروكلوريك وذلك بالطريقة الجلفانوستاتيكية ومن الواضح أن هذه المواد تعمل خلال الادمصاص الكيميائي الضعيف تابعة أيزوثرم تمكن . كما تم التوصل إلى كفاءة استخدام هذه المواد كمثبطات للتآكل تزداد في الاتجاه : مشتقات الاكزيم > بيتا ثنائي الكيتون > الهيدرازيد .

ومن نتائج هذه الطريقة يتبين أن هذه المواد تؤثر على التفاعل المصعدي وذلك تحت تأثير التيار الخارجي . وقد حسبت ونوقشت الطاقة الحرة القياسية للادمصاص .

Key Words: Aluminium, oximes, β-diketones, hydrazides, inhibitors.

ABSTRACT

The inhibitive effect of oximes, β-diketones and hydrazides, on the corrosion of aluminium in 2M HCl has been investigated galvanostatically. The results suggest that, in presence of inhibitors, the anode is preferentially polarized under the influence of an external current. The order of decreasing inhibition efficiency among the three groups of compounds is: oximes > β-diketones > hydrazides. The inhibitors appear to function through a Temkin adsorption isotherm. The free energy of adsorption ΔG^o_a is also computed and discussed.

INTRODUCTION

Aluminium is an industrially important metal and is corroded by several corrosive agents of which the aqueous acids are the more dangerous. The corrosion of aluminium and its alloys and their inhibition by organic inhibitors in acid solutions has been studied by several authors (Desai *et al.*, 1969, Natarajan *et al.*, 1974, Talati *et al.*, 1976, Desai *et al.*, 1981, Fouda *et al.* 1988, 1989, 1991). Recent studies (Moussa *et al.*, 1976, Hassan *et al.*, 1981 and Fouda *et al.* 1987) have been shown that β-diketones, hydrazides, and oximes inhibit the corrosion of aluminium, iron and zinc in presence of HCl and NaOH solutions. The inhibition was attributed (Moussa *et al* 1976) to adsorption of the organic compounds on the metal surface via the oxygen atom of the carbonyl group (C = O).

The aim of the present work is to through some light on the mechanism of inhibition of corrosion of these compounds.

EXPERIMENTAL

Aluminium wire used as an electrode in the polarization method, has the following composition:

%	Si	Fe	Mn	Mg	Cu	Al
	0.15	0.19	0.005	0.10	0.02	rest

The 1 cm long cylindrical aluminium electrode having a thickness of 0.53 mm was sealed to a glass tube with araldite and mechanically polished with a fine grade G 400 emery paper, then degreased by degreasing mixture (15 g Na_2CO_3+15g Na_3PO_4 per liter), washed and dried as before (Abd El-Kader *et al.*, 1970). All experiments were carried out at $25 \pm 1°C$.

The anodic polarization of aluminium was carried out galvanostatically in the presence and in absence of the inhibitors. All potentials were measured with respect to SCE. The same procedures for the potential measurements were adopted as those described by Gatos (Gatos 1956).

The protection efficiency was calculated from the formula:

$$\% \text{ Protection efficiency (P}_{i\,corr.}) = (1 - \frac{I'}{I}) \times 100 \qquad (1)$$

where I and I' are the corrosion current without and with inhibitor, respectively.

The inhibitors and their structures used in the investigations are shown below, G. P., G. T. and diacetylmonoxime are BDH products, while other inhibitors were prepared and purified as before (Fouda 1979). The purity of these substances was checked by IR and NMR analyses.
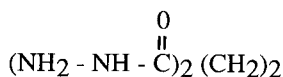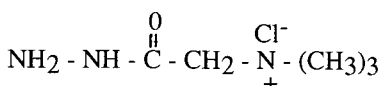
A) Hydrazides group:

I) Girard's reagent P (G.P.):

$$NH_2 - NH - \underset{\underset{O}{\parallel}}{C} - CH_2 - \overset{+}{N}\diagup\bigcirc\diagdown Cl^-$$
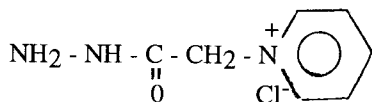
II) Succinic acid hydrazide:

$$(NH_2 - NH - \underset{\underset{\parallel}{O}}{C})_2 (CH_2)_2$$

III) Girard's reagent T (G.T.):

$$NH_2 - NH - \underset{\underset{O}{\parallel}}{C} - CH_2 - \underset{+}{N} - (CH_3)_3 \quad Cl^-$$

B) β-diketones group:

IV) 6-acetyl-5-H-1-pyridine-5, 7 (6H)-dione:

a structure with COCH$_3$
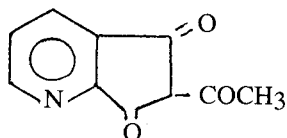
V) Sodio-derivatives of 2-ethoxy carbonyl-1, 3-indandione:

a structure with Na, COOC$_2$H$_5$
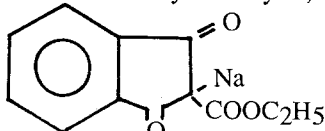
VI) Sodio-derivatives of 2-ethoxy carbonyl-5-nitro-1, 3-indandione:

a structure with O$_2$N, Na, COOC$_2$H$_5$
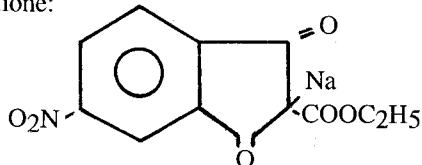
C) Oximes group:

VII) Diacetyl monoxime benzoyl hydrazone:

$$\bigcirc - \underset{\underset{I}{\underset{HON=C-CH_3}{}}}{\underset{\parallel}{C}} - NH - N = C - CH_3$$
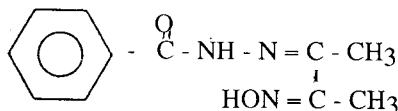
X) Diacetyl monoxime acetyl hydrazone:

$$CH_3 - \underset{\underset{O}{\parallel}}{C} - NH - N = \underset{\underset{I}{\underset{HON=C-CH_3}{}}}{C} - CH_3$$

IX) Diacetyl monoxime:

$$O = \underset{\underset{I}{\underset{HON=C-CH_3}{}}}{C} - CH_3$$
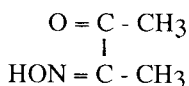
RESULTS AND DISCUSSION
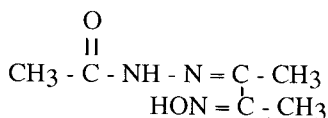
Fig. (1) shows the anodic dissolution of aluminium in 2M HCl in the presence and in the absence of different concentrations of inhibitor I. The measured free corrosion potential in the absence of inhibitors was found to be -810 mV. This value is in good agreement with the published results (Desai et al. 1976). The concentration of the additives has a clear effect on the current potential relations. Results of Table (1) show that the examined compounds give rise to the following effects as their concentration increases:

a) The straight line semi-logarithmic portions of Tafel lines are shifted in the positive direction in the range of 10-75 mV depending on the magnitude of the inhibitor concentration.

b) The free corrosion potential $E_{corr.}$ is shifted in the anodic direction by 5 to 10 mV.

c) The Tafel slope is a constant (change by 5 to 8 mV), independent of concentration of the inhibitor. This indicates that the mechanism of corrosion inhibition does not change.

The above results indicate that the compounds have a clear inhibition effect on the anodic dissolution reaction of aluminium in 2M HCl.
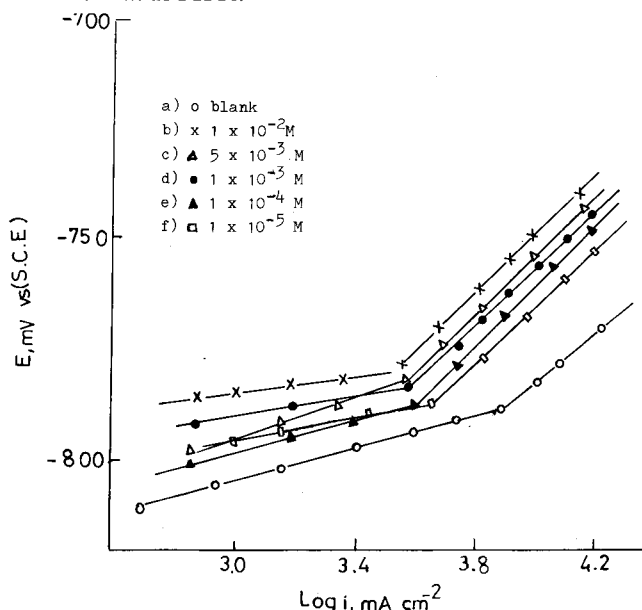

Fig. 1: Effect of the concentration of G. P. on the current-potential relations of the acodic aluminium dissolution reaction in 2M HCl at 25°C.

Table (1), reveals also that for all the inhibitors, the protection $(P_{i\ corr.})$ and the degree of surface coverage(θ) increases with the increase in the concentration.

Fig. (2) shows the variation of the surface coverage (θ) with the logarithm of concentration of all inhibitors. And because the Tafel slope is the same in inhibited and uninhibited solutions, so the degree of surface coverage (θ) can be calculated from the equation:

$$\theta = (1 - \frac{i_2}{i_1}) \qquad (2)$$

Table 1
Effect of inhibtors on the behaviour of aluminium in 2M HCl at 25°C.

Conc. of inhibitor (M)	$E_{corr.}$ mV.	b. mV.	$i_{corr.}$ A cm^{-2}	$Pi_{corr.}$	θ	$-\Delta G^o_a$ Kcal mol^{-1}
			Inhibitor (I)			
0	-810	6.25	3.31	-	-	-
1 x 10^{-5}	-815	5.80	1.70	49	0.50	9.3
1 x 10^{-4}	-815	6.30	1.56	50	0.53	8.0
1 x 10^{-3}	-815	5.90	1.32	61	0.63	6.8
5 x 10^{-3}	-815	6.00	1.17	65	0.65	5.9
1 x 10^{-2}	-815	6.20	0.98	71	0.72	5.7
			Inhibitor (II)			
1 x 10^{-5}	-810	5.70	2.19	34	0.37	8.9
1 x 10^{-4}	-810	5.70	2.04	38	0.41	7.7
1 x 10^{-3}	-815	5.60	1.45	56	0.51	6.5
5 x 10^{-3}	-820	6.50	1.17	65	0.60	5.8
1 x 10^{-2}	-810	0.30	1.05	68	0.71	5.7
			Inhibitor (III)			
1 x 10^{-5}	-805	6.13	1.95	41	0.43	9.1
1 x 10^{-4}	-805	6.13	1.41	49	0.53	8.0
1 x 10^{-3}	-805	5.70	1.51	54	0.58	6.7
5 x 10^{-3}	-810	6.00	1.20	64	0.67	6.0
1 x 10^{-2}	-810	6.30	1.12	66	0.69	5.6
			Inhibitor (IV)			
1 x 10^{-5}	-805	6.50	2.14	35	0.34	8.9
5 x 10^{-5}	-810	6.66	1.41	57	0.59	8.5
1 x 10^{-4}	-810	7.30	1.18	65	0.65	8.2
5 x 10^{-4}	-815	6.66	1.12	66	0.78	7.3
1 x 10^{-3}	-810	7.10	0.68	80	0.84	7.5
			Inhibitor (V)			
1 x 10^{-5}	-810	6.90	1.66	50	0.52	9.3
5 x 10^{-5}	-812	6.00	1.41	57	0.57	8.5
1 x 10^{-4}	-810	5.90	1.32	60	0.64	8.2
5 x 10^{-4}	-810	6.80	0.91	72	0.74	7.5
1 x 10^{-3}	-810	6.70	0.85	74	0.77	7.2
			Inhibitor (VI)			
1 x 10^{-5}	-810	7.30	2.82	15	0.16	8.3
5 x 10^{-5}	-815	6.90	2.24	33	0.34	7.9
1 x 10^{-4}	-810	6.90	2.19	34	0.37	7.6
5 x 10^{-4}	-815	7.70	1.55	52	0.55	7.0
1 x 10^{-3}	-815	7.10	1.26	62	0.61	6.8
			Inhibitor (VII)			
1 x 10^{-5}	-805	7.4	1.07	68	0.70	10.1
1 x 10^{-4}	-805	7.4	0.89	73	0.83	8.8
1 x 10^{-4}	-805	7.4	0.79	76	0.85	8.0
5 x 10^{-3}	-800	8.1	0.50	85	0.94	8.1
			Inhibitor (X)			
1 x 10^{-5}	-820	6.00	1.55	53	0.50	9.3
5 x 10^{-5}	-820	7.30	1.22	66	0.70	8.8
1 x 10^{-4}	-820	6.20	0.85	74	0.77	8.6
5 x 10^{-4}	-820	6.20	0.76	77	0.78	7.7
1 x 10^{-3}	-820	6.90	0.65	81	0.83	7.5
			Inhibitor (IX)			
1 x 10^{-5}	-815	6.75	1.91	43.00	0.40	9.0
5 x 10^{-5}	-815	7.10	1.74	48.00	0.46	8.2
1 x 10^{-4}	-815	7.10	1.66	50.00	0.50	7.9
5 x 10^{-4}	-815	7.10	1.38	58.00	0.57	7.1
1 x 10^{-3}	-820	7.00	1.22	66.00	0.62	6.8

where i_1 and i_2 are the currents of the blank and inhibited solutions. A correlation between θ and log of adsorbate is given by Temkin adsorption isotherm. The experimental results (Fig. 2) are in good agreement with the following equation (Conway 1965):

$$\theta = \text{const.} + \frac{2.303}{f} \log C \qquad (3)$$

$$f = \frac{1}{RT} \cdot \frac{d(\Delta G^{o}_{o})}{d\theta} \qquad (4)$$

showing that the adsorption of oximes, β-diketones and hydrazides derivatives following the Temkin adsorption isotherm.
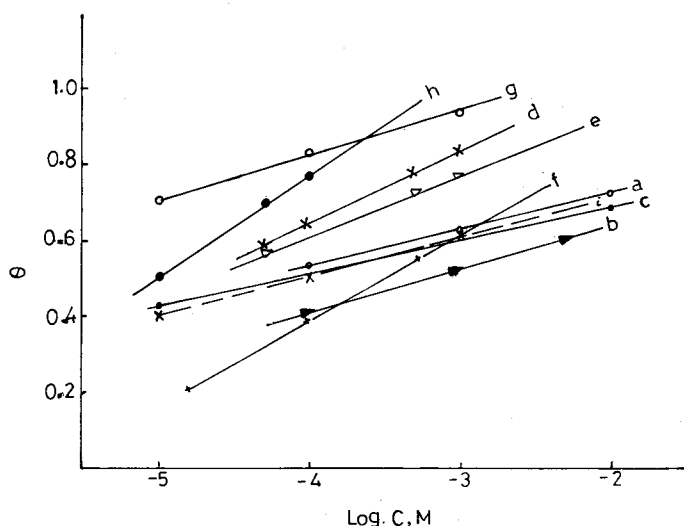

Fig. 2: 2-θ vs. log C curves for all the additives used.
a) I, b) II, c) III, d) IV, e) V, f) VI, g) VII, h) X,
and i) IX.

The experimental data are collected in Table (1). These data indicated that compounds, which are less effective corrosion inhibitors have low values of standard free energy of adsorption, whereas the compounds that are more effective corrosion inhibitors have higher values of standard free energy of adsorption. This relationship is only qualitative and cannot be expressed by a general equation. Fig. (3), shows the relation between the protective effectiveness, (P_i corr.) and the standard free energy of adsorption.

Mechanism of inhibition:

The results recorded in Table (1) reveal that the efficiency of corrosion inhibition of aluminium varies with both concentration and the type of the additive used. The protection efficiency of the hydrazide derivatives decreases in the order : I > II > III. This arrangement agrees with that given before (Moussa et al. 1976). Adsorption on aluminium metal surface is assumed to take place through the C = 0 group and would depend on its charge density. The protonated amino group would not participate in the bonding process. The higher adsorption tendency of G. P. over that of succinic acid dihydrazide and G. T. could be attributed to a different mode

of adsorption (Saleh et al. 1972). In case of G. P. the aromatic nucleus might be expected to lie flat on the aluminium surface providing a large surface coverage area. The higher adsorption tendency of succinic acid dihydrazide over that of G. T. may be due to the presence of two C = O groups.
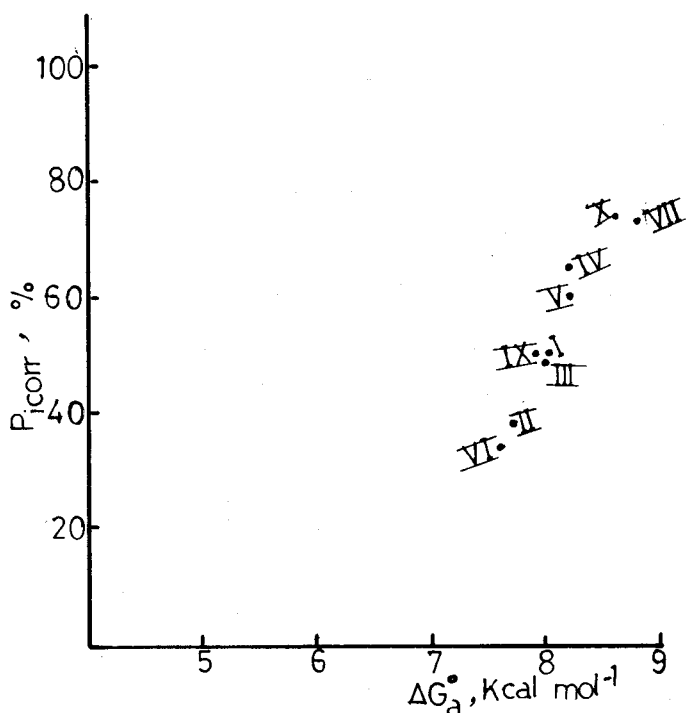

Fig. 3: The dependence of the protective effectiveness of the examined compounds on their standard free energy of adsorption (ΔG°). Inhibitor concentration 1 x 10^{-4}M. Symbols as in Table 1.

The inhibition efficiency of the β-diketo compounds (Table 1) decreases in the order IV > V > VI. This was also shown previously (Hassan et al 1981). The oxygen atom of the carbonyl group and the substituted N-atoms are the sites involved in the adsorption of the inhibitors over the metallic surface. The inhibition efficiency of the studied β-diketo compounds would depend on the number of adsorption sites and their basicity. Compound IV has four probable sites of adsorption. In compound V there are only three oxygen sites of adsorption, whereas compound VI has four adsorption sites, but their basically would still lower due to the electron attracting character of the nitro group.

The inhibition efficiency of the oxime compounds (Table 1) decrease in the order : VII > X > IX. The same order was found earlier by El-Sum (El-Sum 1980). This observed order could be explained on the basis of the number of active adsorption sites available in the molecule, their electronic charge density and other effects such as hydrogen bonding and molecular size. In diacetyl monoxime acetyl and benzoyl hydrazones there are four active sites. Despite the electron repelling character of the methyl group, monoacetyl hydrazone is less bulky than the benzoyl hydrazone which has the highest inhibition efficiency amongst the oxime compounds. Diacetyl monoxime has two active sites and a smaller size.

The order of inhibition efficiency of the additive compounds in acid media depends mainly upon the number of adsorption sites and their electronic charge density. The order of decreasing inhibition efficiency among the three groups

studied in the present work for aluminium system is: oximes > β-diketo compounds > hydrazides.

The standard free energy of adsorption ΔG^{o}_{a} values calculated from equations of the Temkin isotherm vary from 5.6 Kcal mol^{-1} for the weakest corrosion inhibitors, to 9.3 Kcal mol^{-1} for one of the strongest inhibitors used. Thus the standard free energy of adsorption values are within the limits of 5-10 Kcal mol^{-1} which have been observed for the majority of organic inhibitors of various types in aqueous media. Values of ΔG^{o}_{a} indicate that the adsorption of the inhibitors on an aluminium surface is a spontaneous process.

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