

MECHANISM OF THE INHIBITION AFFORDED BY SOME HYDRAZONE OXIME DERIVATIVES TOWARDS ALUMINIUM IN 2M NaOH SOLUTION

By

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Key Words: Aluminium, Mechanism, Inhibition, Hydrazone oxime derivatives.

ABSTRACT

The effect of some hydrazone oxime derivatives on the corrosion of aluminium in 2M NaOH solution was studied by polarization and weight-loss techniques. Polarization data indicated that all inhibitors tested were of a mixed type, and appeared to function through adsorption following the Temkin adsorption isotherm.

The results showed that addition of Ba²⁺ ions enhanced inhibition action by being chemisorbed on aluminium surface.

The effect of temperature on the rate of corrosion with and without inhibitors was studied using weight-loss measurements. Some thermodynamic functions were also computed.

INTRODUCTION

One of the most important consideration in any industry today is the reduction of overall cost in their protection and maintenance. Aluminium and its alloys may be applicable to organic chemical industries. The corrosion of aluminium in sodium hydroxide has been studied by many workers (Muller *et al.*, 1939, Straumanis *et al.*, 1939, Dionis'ev *et al.* 1987). Fouda (1982) has been reported that Ba²⁺ ions could be used to improve the efficiency of some β -diketo compounds in inhibiting the corrosion of zinc in 2M NaOH solution. In the present investigation, an attempt has been made to improve the inhibition of corrosion of aluminium in 2M NaOH solution and to throw some light on the mechanism of inhibition afforded by some hydrazone oxime derivatives.

method. Coupons were polished with emery paper (G 400), degreased in alkaline solution (15g Na_2CO_3 + 15g Na_3PO_4 pre liter) weighed and then immersed in 100 ml of 2M NaOH solution with and without inhibitors for 15 min. at $25 \pm 0.2^\circ\text{C}$. The weight-losses were determined after thoroughly washing the samples several times with distilled water and drying.

For the galvanostatic measurements, samples of total area 0.37 cm^2 were used as a working electrode. A saturated calomel electrode (SCE) with a Luggen capillary bridge and a platinum wire counter electrode were used. The procedures for the potential measurements were adopted as those described before (Gatos, 1956). The potential at any given current under similar experimental conditions was reproducible within $\pm 4\%$.

RESULTS AND DISCUSSION

Anodic and cathodic polarization curves and Tafel lines in 2M sodium hydroxide solution in presence and in absence of different concentrations of compound (I) are shown in Figs. 1 and 2, respectively. Similar results were obtained for the other inhibitor compounds. In general, the addition of inhibitors induce an increase in

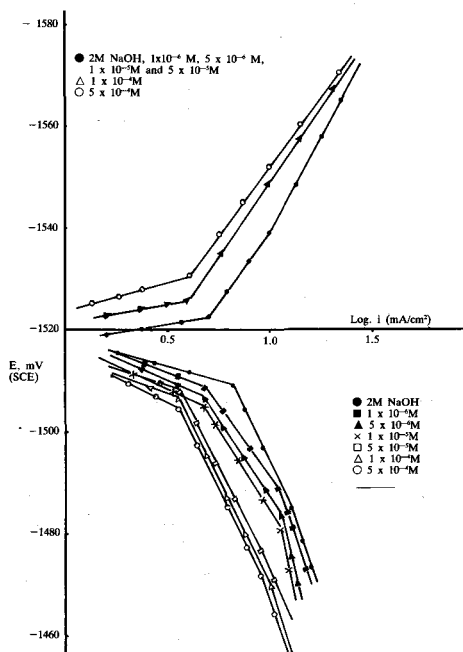


Fig. 1: Galvanostatic polarization curves for Al in 2M NaOH solution without and with different concentrations of compound I.

both anodic and cathodic overvoltages, indicating that these compounds influence both anodic and cathodic processes.

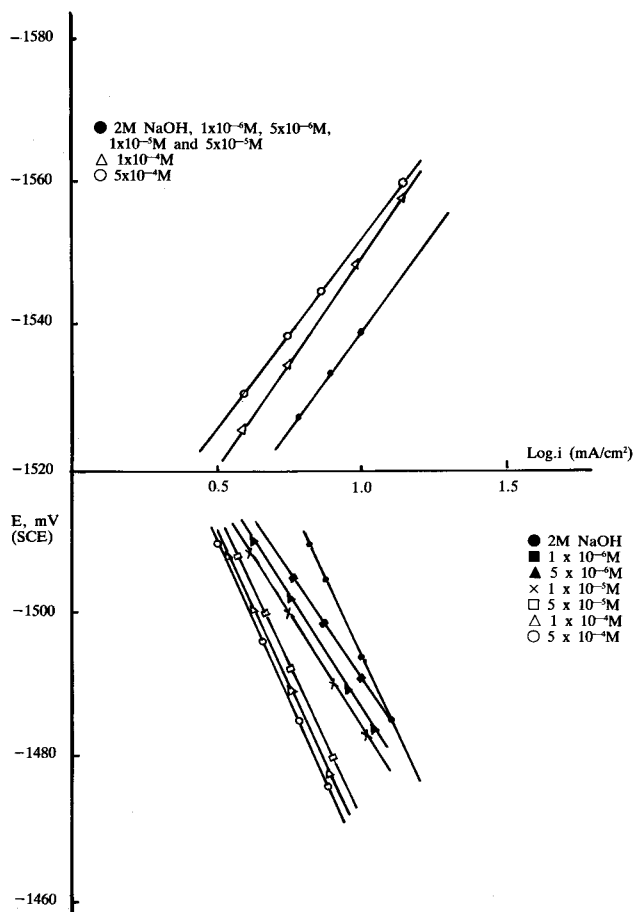


Fig. 2: Tafel lines for both anodic and cathodic processes.

Tables (1) and (2) show the effect of compound (I) concentration on: the free corrosion potential, Tafel slopes (b_a & b_c), corrosion current (I_{corr}), degree of surface coverage (θ) and percentage inhibition (I_e). The decrease in I_{corr} with increase in additive concentration demonstrates the efficiency of the tested material as a corrosion inhibitor. The measured free corrosion potential in 2M NaOH solution is -1520 mV vs. SCE in satisfactory agreement with published result (Kamel *et al.*, 1979). The approximately constant value of E_{corr} suggests that inhibition takes place by simple blocking of the electrode surface.

Table 1

The effect of compound I concentration on the free corrosion potential, Tafel slope, corrosion current density, its percentage decrease and degree of surface coverage for cathodic polarization of aluminium in 2M NaOH at 25°C.

Concentration M/L	E_{corr} mV	b_c mV/current decade	I_{corr} mA/cm ²	Pi_{corr}	θ
0	-1524	0.039	4.46	—	—
1.0×10^{-4}	-1526	0.039	3.02	32.4	0.3506
5.0×10^{-4}	-1526	0.034	2.39	46.3	0.4377

Table 2

The effect of compound I concentration on the free corrosion potential, Tafel slope, corrosion current density, its percentage decrease and degree of surface coverage for anodic dissolution of aluminium in 2M NaOH at 25°C.

Concentration M/L	E_{corr} mV	b_a mV/current decade	I_{corr} mA/cm ²	Pi_{corr}	θ
0	-1517	0.037	5.01	—	—
1.0×10^{-6}	-1520	0.032	3.16	36.9	0.1586
5.0×10^{-6}	-1520	0.037	3.02	43.7	0.2714
1.0×10^{-5}	-1520	0.034	2.88	42.5	0.3317
5.0×10^{-5}	-1520	0.046	2.75	45.1	0.4377
1.0×10^{-4}	-1520	0.046	2.57	48.7	0.4988
5.0×10^{-4}	-1520	0.046	2.45	51.0	0.5368

The corrosion current was determined by extrapolating anodic and cathodic Tafel lines to free corrosion potential values. The inhibitive efficiency was calculated employing the formula:

$$\%I_c = \frac{I - I'}{I} \times 100 \quad (1)$$

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

The results of Tables (1) and (2) indicate that the following order in the inhibitive power for the studied compounds is:

$$I > III > IV > VI > II$$

The degree of surface coverage (θ) was calculated from the polarization method from the equation:

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

where i_1 and i_2 are the currents of the blank and inhibited solutions. The above equation was used here by reading the values of $\log i_{\text{corr}}$, corresponding to a constant potential (-1500 mV for anodic and -1540 mV for cathodic processes) in Tafel line for blank and inhibited solutions. A correlation between θ and $\log C$ of adsorbate is given by Temkin adsorption isotherm. The experimental results (Fig. 3) are in good agreement with the following equation (Conway, 1965):

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

$$f = \frac{1}{RT} \cdot \frac{d(\Delta G_o^\circ)}{d\theta} \quad (4)$$

showing that the adsorption of the hydrazone oxime derivatives following the Temkin adsorption isotherm.

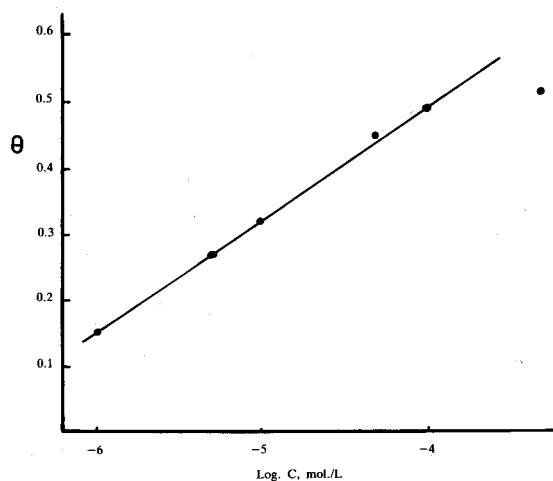


Fig. 3: θ -log. C of compound I for anodic reaction of Al in 2M NaOH solution at 25°C.

Fig. (4a) represents the data of weight loss-time curves for the system involving inhibitor (I). The curves of Fig. 4a are straight lines passing from the origin and are characterized by an increase in weight-loss from the beginning. Saleh *et al.* (1972) interpreted the linearity of the weight-loss with time from the beginning to the breakdown of the oxide film and the start of the attack. The weight-loss of aluminium depends upon both the type and concentration of the additive in the same way as the polarization does.

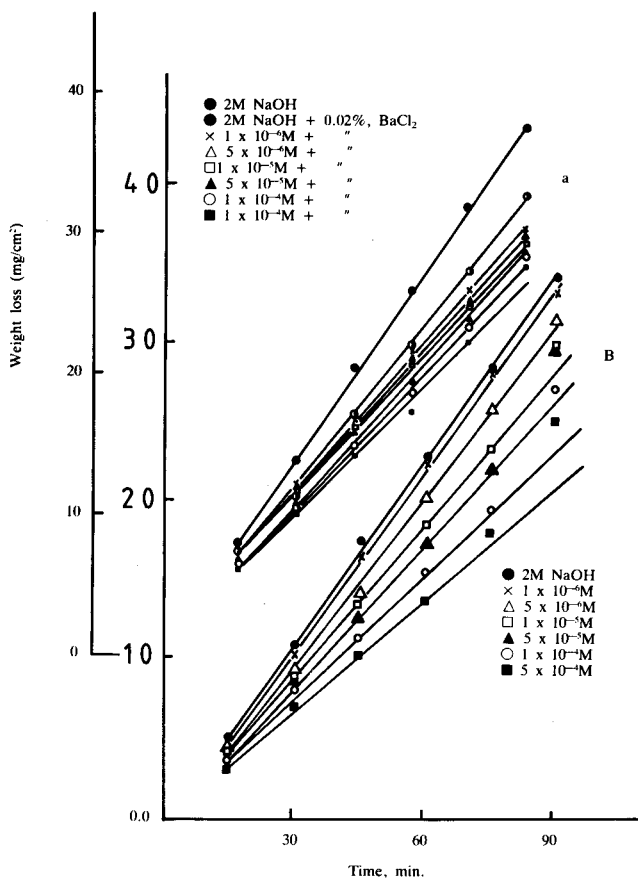


Fig. 4: Weight-loss — time curves for aluminium dissolution in alkaline solution in presence of: a) compound (I) and b) compound (I) and BaCl₂.

The inhibition efficiency was calculated from the weight-loss values using the following equation:

$$\%I_c = \frac{W_B - W_I}{W_I} \times 100 \quad (5)$$

where W_B = weight-loss in 2M NaOH solution, W_I = weight-loss in inhibited solutions.

The results of table 5 show that the order of increased inhibition of hydrazone oxime derivatives is:

I > III > IV > VI > II.

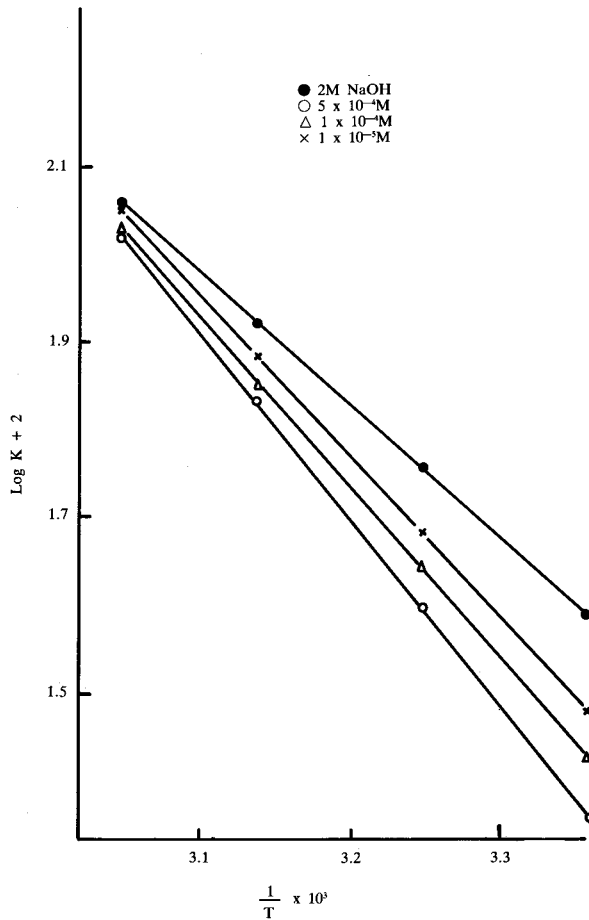


Fig. 5: Log. k vs. $\frac{1}{T}$ curves for aluminium dissolution in 2M NaOH in absence and presence of different concentration of compound I using weight-loss measurements.

Fig. 5 represents the relationship between log k (rate constant of corrosion) vs. $\frac{1}{T}$ (T = absolute temp.) for different concentrations of inhibitor (I) in 2M NaOH

solution using weight-loss measurements. The results obtained over the experiments in the inhibited and uninhibited acid, gave corrosion rates which were reproducible to within $\pm 5\%$. Fig. 6 shows the same above relation but for all inhibitors at 5×10^{-4} M. Both Figs. 5 & 6 gave straight lines. The results show that the rate of corrosion increases as the temperature increases, i.e. the inhibition efficiency of the additives decreases with rise in temperature. The values of the rate constants obtained at different temperatures permit the calculation of the Arrhenius, ΔE^* , enthalpy, ΔH^* , entropy, ΔS^* , and free energy of activation, ΔG^* , of aluminium in 2M NaOH (Table 3). These thermodynamic function were calculated from the following equations:

1) ΔE^* from:

$$\log k = \frac{\Delta E^*}{2.303RT} + \text{const.} \quad (6)$$

2) ΔH^* from:

$$\Delta H^* = \Delta E^* + RT \quad (7)$$

3) ΔG^* and ΔS^* using the transition state theory.

$$\Delta G^* = RT \left(\ln \frac{KT}{h} - \ln k \right) \quad (8)$$

$$\Delta S^* = \frac{\Delta H^* - \Delta G^*}{T} \quad (9)$$

where R = gas constant, k = the rate constant, K = the Boltzman constant, h = Planck's constant and T = absolute temperature.

These results reveal that the energy and free energy of activation increase with increase in the concentration of the additive which retards the corrosion reaction. Also the results show that the efficiency of different inhibitors at all temperature studied (25 – 55°C) was found to increase in the order:

I > III > IV > VI > II.

Effect of Ba²⁺ ions on the corrosion inhibition of aluminium in aqueous solutions:

The effect of Ba²⁺ ions on the corrosion inhibition of aluminium in 2M NaOH solution in presence and in absence of hydrazone oxime derivatives was studied by weight-loss method.

The weight loss - time curves for aluminium dissolution in 2M NaOH solution in presence of 0.02% Ba²⁺ ions and inhibitor (I) give straight lines passing through the

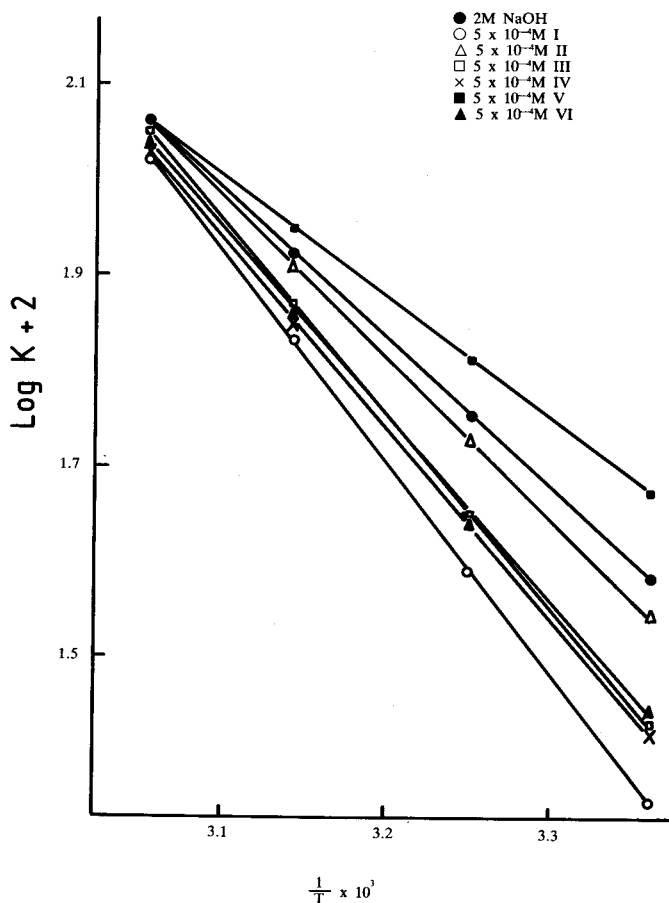


Fig. 6: Log k vs. $\frac{1}{T}$ curves for aluminium dissolution in 2M NaOH solution in presence and in absence of different inhibitors, using weight-loss measurements.

origin (Fig. 4b). The slope of the lines increases with increase in the concentration of the inhibitor. All the curves in presence of the additives and Ba^{2+} ions fall below that of the free alkali.

Table 4 shows the comparative performance of hydrazone oxime derivatives in inhibiting the corrosion of aluminium in 2M NaOH solution in presence and in absence of Ba^{2+} ions after 60 min. immersion and at $5 \times 10^{-4}M$ concentration of inhibitors.

Table 3

Energy (E_A^*), enthalpy (ΔH^*), entropy (ΔS^*), and free energy (ΔG^*) of activation for Al dissolution in 2M NaOH in presence of 5×10^{-4} M of different inhibitors at different temperature.

Temperature in °C	25	35	45	55
2M NaOH				
E_A^* in Kcal mol ⁻¹		7.109		
ΔH^* in Kcal mol ⁻¹	6.513	6.493	6.473	6.453
$-\Delta S^*$ in cal K ⁻¹	70.3	71.1	71.7	72.4
ΔG^* in Kcal mol ⁻¹	27.48	28.39	29.28	30.22
Inhibitor I				
E_A^* in Kcal mol ⁻¹		10.04		
ΔH^* in Kcal mol ⁻¹	9.44	9.42	9.40	9.38
$-\Delta S^*$ in cal K ⁻¹	61.6	62.3	62.9	63.7
ΔG^* in Kcal mol ⁻¹	27.80	28.61	29.41	30.28
Inhibitor II				
E_A^* in Kcal mol ⁻¹		7.736		
ΔH^* in Kcal mol ⁻¹	7.140	7.120	7.100	7.080
ΔS^* in cal K ⁻¹	68.4	69.1	69.8	70.5
ΔG^* in Kcal mol ⁻¹	27.54	28.41	29.30	30.22
Inhibitor III				
E_A^* in Kcal mol ⁻¹		9.200		
ΔH^* in Kcal mol ⁻¹	8.604	8.584	8.564	8.544
$-\Delta S^*$ in cal K ⁻¹	64.4	64.7	65.3	66.1
ΔG^* in Kcal mol ⁻¹	27.69	28.53	29.35	30.23
Inhibitor IV				
E_A^* in Kcal mol ⁻¹		8.990		
ΔH^* in Kcal mol ⁻¹	8.394	8.374	8.354	8.334
$-\Delta S^*$ in cal K ⁻¹	64.7	65.40	66.10	66.80
ΔG^* in Kcal mol ⁻¹	27.70	28.54	29.39	30.26
Inhibitor V				
E_A^* in Kcal mol ⁻¹		5.855		
ΔH^* in Kcal mol ⁻¹	5.259	5.239	5.219	5.199
ΔS^* in cal K ⁻¹	74.2	74.8	75.5	76.3
ΔG^* in Kcal mol ⁻¹	27.36	28.30	29.24	30.22
Inhibitor VI				
E_A^* in Kcal mol ⁻¹		8.782		
ΔH^* in Kcal mol ⁻¹	8.186	8.166	8.146	8.126
$-\Delta S^*$ in cal K ⁻¹	65.40	66.10	66.70	67.40
ΔG^* in Kcal mol ⁻¹	27.67	28.53	29.36	30.25

Table 4

Inhibition of aluminium corrosion in 2M NaOH in the presence and in the absence of Ba²⁺ and the inhibitor compounds using weight-loss measurements at 25°C.

Nature of the system	Inhibition efficiency (In %)
1. Medium + 5.0 × 10 ⁻⁴ M I	40.37
2. Medium + 5.0 × 10 ⁻⁴ M I + 0.02% Ba ²⁺	59.50
3. Medium + 5.0 × 10 ⁻⁴ M II	9.48
4. Medium + 5.0 × 10 ⁻⁴ M II + 0.02% Ba ²⁺	34.71
5. Medium + 5.0 × 10 ⁻⁴ M III	29.88
6. Medium + 5.0 × 10 ⁻⁴ M III + 0.02% Ba ²⁺	54.98
7. Medium + 5.0 × 10 ⁻⁴ M IV	31.33
8. Medium + 5.0 × 10 ⁻⁴ M IV + 0.02% Ba ²⁺	52.08
9. Medium + 5.0 × 10 ⁻⁴ M V	—
10. Medium + 5.0 × 10 ⁻⁴ M V + 0.02% Ba ²⁺	15.53
11. Medium + 5.0 × 10 ⁻⁴ M VI	27.42
12. Medium + 5.0 × 10 ⁻⁴ M VI + 0.02% Ba ²⁺	36.99
13. Medium + 0.02% Ba ²⁺	14.62

It is known that high inhibition efficiencies are obtained in the acid medium, whereas the substances give only nominal inhibition in alkaline solutions (Murakawa *et al.*, 1968). This may be attributed to the high negative potential of aluminium in the alkaline solution which may not be favourable for the adsorption of the organic compounds. Also, aluminium may form soluble complexes with

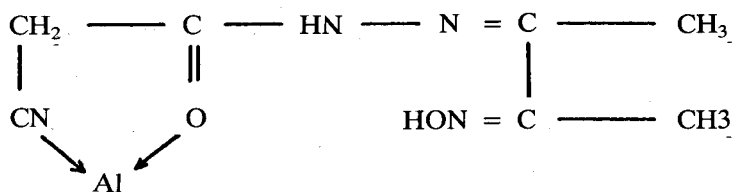
these substances. Addition of Ba^{2+} ions, in general, improves the inhibitive action of the organic substances in alkaline solutions. This may be due to the fact that Ba^{2+} ions are chemisorbed on aluminium in this medium, as has already been proved by radio-tracer study (Subramanyan *et al.*, 1971). This aids in bringing negatively charged species inclusive of the AlO_2^- ion closer to the metal surface, thus enhancing inhibition as has actually been observed. Also, from Table 4 we observe that the inhibition exceeds the inhibition efficiency of the medium + 0.02% Ba^{2+} . This could be explained on the basis that the inhibitor (I) at high concentration tends to withdraw the Ba^{2+} ions on the surface of the corroding metal into the solution (Murakawa *et al.*, 1968). Hence, coadsorption of Ba^{2+} ions and inhibitor ions is possible ($I^- Ba^{2+} Ba^{2+} I^-$,). The extent of desorption of Ba^{2+} ions from the surface depends on the extent of adsorption of inhibitor ion (I^-), which is a function of the concentration of the inhibitor.

Effect of chemical constitution on inhibition efficiency:

The order of increased inhibition efficiency of hydrazone oxime derivatives is: I > III > IV > VI > II as indicated by the results in Table (5). Compound (V) is excluded as it accelerates corrosion in this medium. Differences in the inhibition efficiency for aluminium corrosion in 2M NaOH solution as indicated by the above order probably do not originate from the diacetylmonoxime side chain, but arise from the substituents in the hydrazone group which include the carbonyl group, the adsorption active center. The electron charge density of the C = O group would depend on substituents in the phenyl ring conjugated with it. It is evident that the nucleophilic character of these substituents plays a determining role in imparting inhibition efficiency.

The nucleophilic character of the substituents used is increased in the order: $p-CH_3 > p-Cl > o-OH > H > p-NO_2$. This order runs parallel to the above mentioned observed sequence of increased inhibition efficiency of the hydrazone oxime derivatives. Compound (I) is the most efficient one due to the presence of CH_3 -group in the p-position to the carbonyl which increase the charge density and consequently enhances its adsorption on aluminium electrode surface. In compound (III) the p-chloro derivative has two opposite effects one is to increase the molecular size and the other is the mesomeric effect (+M) involving electron pairs on Cl. The overall mechanism constitute electron release which maintains sufficient electron charge density on the C = O. A similar effect was noted before (Abd El-Naby *et al.*, 1986). Compound (II) has the lowest inhibition efficiency due to the presence of p- NO_2 group. There are two reasons for this: a) coplanarity of the p- NO_2 group with phenyl ring brings about maximum electron withdrawal and b) the NO_2 -group with the highest -I effect among the substituents imparts the lowest inhibition efficiency. The presence of o-OH group to the carbonyl in inhibitor (IV) allows for hydrogen bonding to operate leading to a decrease in the availability of

electrons on the oxygen adsorption site (Hassan *et al.*, 1981). Therefore, compound (IV) comes after I and III in the succession of decreased inhibition efficiency. Compound (VI) has two C = O adsorption centers also the pyridinium chloride ring may be expected to lie flat (Moussa *et al.*, 1976) on the surface but the presence of methylene group disrupts conjugation with the ring and reduces the electron charge density on the hydrazone C = O group. Moreover, enolization from adjacent NH group lower the basicity of the other C = O group in the molecule. Thus compound (VI) is somewhat less effective than (IV). Compound (V) is an accelerator for aluminium in 2M NaOH solution. This may be due to: a) decreased molecular size owing to absence of a phenyl group and b) the presence of the cyano group may lead to the formation of Al-complex of the type: (Fouda *et al.*, 1986).



It is obvious that this complex is soluble in alkaline medium rendering the compound an accelerator.

Table 5

Effect of inhibitor concentration on the percentage inhibition in alkaline solution at 90 min. using weight-loss measurements at 25°C.

Concentration of the additive, M	Inhibition					
	I	II	III	IV	V	VI
1.0 x 10 ⁻⁶	2.02	1.55	8.48	5.68	—	2.66
5.0 x 10 ⁻⁶	7.12	3.67	9.22	10.34	—	4.69
1.0 x 10 ⁻⁵	11.68	6.59	9.52	17.07	—	6.63
5.0 x 10 ⁻⁵	13.18	7.76	9.66	20.91	—	9.08
1.0 x 10 ⁻⁴	19.71	21.14	14.55	23.57	—	10.63
5.0 x 10 ⁻⁴	26.09	18.13	27.94	24.45	—	17.22

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ميكانيكية منع تآكل الألومنيوم في محلول هيدروكسيد الصوديوم باستخدام بعض مشتقات هيدرازون - اكزيم

عبد العزيز السيد فوده و عطا محمد الباز و محمود نور الدين موسى

استخدمت بعض مشتقات هيدرازون - اكزيم كموانع لتآكل الألومنيوم في محلول ٢ ع هيدروكسيد الصوديوم وذلك باستخدام طريقة فقد الوزن وطريقة الاستقطاب . وقد دلت النتائج أيضاً أن ميل هذه المركبات للادمصاص على الأسطح المعدنية تزداد في الاتجاه I < III < VI < IV < II .

وقد وجد أن اضافة ايونات الباريوم إلى الوسط تزيد من فعالية هذه المواد في منع التآكل وذلك بادمصاصها كيميائياً على سطح الألومنيوم . كما درس أيضاً تأثير درجة الحرارة على معدل التآكل في وجود وفي عدم وجود هذه الموانع ، كما عينت ونوقشت بعض الدول الثيرموديناميكية لعملية الادمصاص .