Studies on the Kinetics of Aluminium Metal Dissolution in Aggressive Acid Media Containing Inorganic Anions

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ABSTRACT. The kinetics of chloride ion pitting and inorganic anions inhibition of aluminium metal corrosion in 1.0M solutions of perchloric acid were studied at 30°C in the ranges $0 \leq Cl^- \leq 0.8$ mol L^{-1}; $0 \leq NO_3^- \leq 0.18$ mol L^{-1} and $0 \leq S_T \leq 1.0$ mol L^{-1}, where S_T represents the sum of SO_4^{2-} and HSO_4^- species all at an ionic strength I = 2.0, $NaClO_4$. The reactions were found to be governed by multistep equilibria in which Cl^-, NO_3^-, HSO_4^-, SO_4^{2-} and dissolved oxygen O_2 (g) compete for the metal surface. The rate of corrosion was found to be zero-order overall with an observed rate constant dependence on Cl^- of the form:

$$(k_{obs} - k_o) = \frac{kK_2K_3[Cl^-]^2}{K_1[O_2] + K_2[Cl^-] + K_2K_3[Cl^-]^2}$$

where K_1 is the equilibria constant for $O_2(g)$ adsorption and K_2 & K_3 are successive adsorption constants for Cl^- ions. The addition of nitrate or sulfate ions resulted in the inhibition of aluminium corrosion. The results are discussed in terms of multistep competitive equilibria in which the nitrate or the sulfur containing species (SO_4^{2-}, HSO_4^-) screen the metal surface from chloride attack. In all cases a mechanism involving three competitive equilibria viz. molecular oxygen adsorption, Cl^- adsorption and inhibitor adsorption followed by a rate determining dissolution step is proposed for the reactions.

Introduction

The breakdown of the passivity of aluminium by aggressive anions such as Cl^- is the subject of considerable interest and discussion[1-5]. The excellent resistance of Al to corrosion in acid, neutral and basic media is attributed to the rapid formation of a coherent inert oxide layer[6,7]. Thus it has been estimated[8] that a layer of the oxide 10-12μm thick, would render the metal inactive in the pH range 4-9. The thicknes of the oxide layer, however, ranges from 0.005 to 0.01μm in polished aluminium that has not been

exposed to air for considerable length of time. The layer has a large number of pores and weak points[9] where it is possible for the metal to go into solution. The corrosion products, however, usually block the small points of attack and the process is halted. The complete formation of an oxide layer, however, is not necessary for the protection of the metal. Several authors[10-12] attributed the passivity of the metal to the formation of a chemisorbed layer of $O_2(g)$ on the surface of the metal.

The presence of an aggressive anion[13-16] such as Cl^-, accelerates the process of corrosion and causes severe pitting of the underlying metal[17]. This process has been attributed to the tendencies of the halides to form soluble aluminium complexes[18,19]. It is generally accepted that the following steps are involved in localized corrosion. These steps involve:

a) The adsorption of the reactive anions on the oxide-covered aluminium or competitive adsorption of the anion with O_2 or OH^- for the sites on the metal surface[20,21]. Here it is assumed that the transport of the reactive species from the bulk solutions to the metal surface is fast.

b) The chemical reactions of the adsorbed anion with the aluminium ion in the oxide lattice or the precipitated aluminium hydroxide possibly by an anion exchange process with the lattice.

c) Penetration of the oxide film by the aggressive anions[22], resulting in its thinning by dissolution.

d) Direct attack of the exposed metal by the anion possibly assisted by an anodic potential. This last step is called pitting propagation and could very well take place simultaneously with step (c) above.

In a recent publication[23] we looked into some thermodynamic and kinetic factors governing chloride ion pitting and nitrogen donor ligands inhibition of aluminium metal corrosion in a number of mineral acids. These studies pointed to the competitive nature of the corrosion process between the aggressive anion and dissolved O_2 and that the actions of the inhibitor is to block available surface sites from Cl^- ions attack. In the present work we give a detailed kinetic study of the chloride ion catalysis of aluminium metal dissolution in perchloric acid solutions and the effects of added inorganic anions such as NO_3^- and SO_4^{2-} on the process.

Experimental

All the chemicals used were analytical reagent grade. Freshly doubly distilled water was used in all preparations. Sodium perchlorate was prepared by the neutralization of reagent grade sodium carbonate with reagent grade 70% perchloric acid and crystallized three times from hot distilled water.

The aluminium specimens used were in the form of strips 1cm × 10cm × 0.07cm. The samples were prepared from aluminium strips (99.99% from B.D.H.). The samples were mechanically polished with a series of emery papers of variable grade, starting with a course one and proceeding in steps to the finest (1000) grade available and then etched in an alkaline solution of $(15g \ Na_2CO_3 + 15g \ Na_3PO_4) \ L^{-1}$ before use[24]. Etching was conducted at 80-85°C for 30s. This was followed by rinsing with distilled water and drying.

The aluminium specimens were bent in a U- form and placed in a sample vessel containing the test solution thermostated at the desired temperature. The vessel has the same form described by Mylius[25]. Detailed description of the cell has been given in previous publication from the laboratory[23].

Rates were determined by gasometry, in which the volume of $H_2(g)$ evolved was measured as a function of time. The experiments were performed at $30 \pm 0.1°C$ under pseudo-zero order conditions, in which the change in the concentration of the mineral acid during the kinetic run was small compared to its total concentration. In addition the reaction was followed for a maximum of two hours to avoid any drastic changes in the surface characteristics of aluminium strip. All experiments were done at constant ionic strength of 2.0M adjusted with $NaClO_4$.

In a typical kinetic experiment, 100ml of 1.0M $HClO_4$ containing given concentration of NaCl, $NaNO_3$ and/or Na_2SO_4 was placed in the reaction vessel and thermostated for at least 15min (or until it reached temperature equilibrium) in the temperature bath, prior to the introduction of the aluminium strip. Measurements of evolved $H_2(g)$ as a function of time were then recorded under static conditions. The data were then graphically recorded. In all cases good straight lines were obtained after the lapse of a short induction period (varying between 0 and 10 min) indicative of the zero- order nature of the reaction. The slope of the obtained graph is the corrosion rate, which is equal to the observed rate constant for the reaction under the specified conditions of concentration and temperature. The final values were obtained from linear least squares fit of the data.

The reactions were studied in the ranges $0 \leq NaCl \leq 0.75M$; $0 \leq NaNO_3 \leq 0.18M$; $0 \leq Na_2SO_4 \leq 1.0M$ all in 1.0M $HClO_4$ and ionic strength I = 2.0M, $NaClO_4$.

Results and Discussions

It has been known to us from our previous studies[23] on the corrosion characteristics of aluminium in corrosive acid media, that the element behaves differently in different mineral acids. The dissolution of the metal, as evidenced from $H_2(g)$ evolution is significant (after the lapse of a short induction period) in 1.0M HCl solutions, and is very slight in 1.0M $HClO_4$ solutions. In presence of H_2SO_4 or HNO_3 practically no hydrogen evolution is observed for over 2.5hr. Table (1) gives the rate of hydrogen evolution (mL $H_2(g)$ · cm^{-2} (Al). min^{-1}) in the presence of the four mineral acids. The behavior evidently points to an anion effect. One could conclude that relative to perchlorate, the sulfate and nitrate anions show inhibition effects whereas the chloride ion catalyses aluminium dissolution.

TABLE 1. Rate of aluminium dissolution in 1.0M mineral acids.

Acid	Rate of $H_2(g)$ evolution (mL/cm^2· min)
HNO_3	$< 5.0 \times 10^{-5}$
H_2SO_4	6.8×10^{-4}
$HClO_4$	1.2×10^{-3}
HCl	8.2×10^{-2}

The perchlorate ion[26-28] unlike the chloride, sulfate and nitrate anions, has a low tendency to coordinate to metal atoms or ions. On the basis of hard and soft acids and bases

(HSAB)[29,30], all four anions are classified as hard bases and hence will have a tendency to adsorb on the surface of metals classified as hard acids. According to the concept of HSAB[31] the polar atoms or ions of the "hard" acids and bases hold valency electrons tightly, whereas those of "soft" acids and bases hold them loosely. Donor atoms or ions of high electronegativity and low polarizability are called hard bases, the acceptor atoms or ions of hard acids are small in size. The hard acids prefer to bind to hard bases forming a stable complex bond under the influence of electric interactions. The adsorption ability of anions is closely related to the HSAB principle[32]. The low coordination ability of the perchlorate ion, however, will tend to make it the least susceptible to adsorption and hence the least capable to modify or affect the corrosion characteristics of a given metal. The work of Aramaki *et al.*[33-38] on the adsorption of a variety of organic and inorganic molecules and ions supports this fact. The authors reported all of their studies in perchloric acid solutions in which they reported that the perchlorate ion is hardly adsorbed.

Kinetic of the Corrosion of Aluminium in 1.0M HClO$_4$ Solutions Containing Varied Cl⁻ Ion Concentrations

The foregoing discussion shows that the perchlorate ion is excellent for comparison purposes in media containing adsorptive anions such as chlorides, sulfates and nitrates. In the present study we used perchloric acid as the aggressive medium. Sodium perchlorate was then used to maintain a constant ionic strength. All reactions were done under pseudo-zero-order conditions in H$^+$, metal and the anions. The H$_2$(g) evolution curves were thus all straight lines, with slopes equal to the observed rate constants for the reactions under the specified conditions.

Table (2) gives the observed rate constants for the dissolution of aluminium in 1.0M HClO$_4$, containing various chloride ion concentrations at a fixed ionic strength I = 2.0, NaClO$_4$. In the table k$_{obs}$ referred to the observed rate constant for the reaction at a given chloride ion concentration and is given by the slope of the concentration (volume) of H$_2$(g), vs time graph, k$_0$ is the rate constant at zero chloride ions concentration and represents the uncatalyzed pathway for the acid dissolution of aluminium. The quantity (k$_{obs}$ - k$_0$) is thus the chloride ions catalyzed rate constants for the reaction. The variation of these rate constants with Cl⁻ concentrations takes the form of a curve frequently observed for systems governed by multiple step equilibria. Empirically speaking the data were well fitted by the use of a polynomial equation (1) of the form

$$[Cl^-]^2 /(k_{obs} - k_0) = a_0 + a_1[Cl^- + a_2[Cl^-]^2 \tag{1}$$

TABLE 2. Dependence of the Observed Rate Constants for the dissolution of Al in 1.0M HClO$_4$, I = 2.0, NaClO$_4$ on the chloride ion concentration.

[Cl⁻], mol/L	$10^2 \cdot$ k$_{obs}$, mL/cm$^2 \cdot$ min	$10^2 \cdot$ (k$_{obs}$ - k$_0$), mL/cm$^2 \cdot$ min
0.00	0.12	–
0.05	0.62	0.50
0.10	1.66	1.54

TABLE 2. Contd.

[Cl⁻], mol/L	$10^2 \cdot k_{obs}$, mL/cm² · min	$10^2 \cdot (k_{obs} - k_0)$, mL/cm² · min
0.15	2.91	2.79
0.20	4.14	4.02
0.25	4.89	4.77
0.30	5.75	5.63
0.35	6.70	6.58
0.40	7.86	7.74
0.45	8.67	8.55
0.50	8.45	8.33
0.55	9.24	9.12
0.60	11.35	11.23
0.65	10.34	10.22
0.70	11.73	11.61
0.75	11.67	11.55

where a_0, a_1 and a_2 are parameters to be evaluated by an appropriate fitting procedure. Non-linear least squares fit of the data to equation (1) gives the values $a_0 = 0.3 \pm 0.1$, $a_1 = 2.0 \pm 0.7$ and $a_2 = 4.1 \pm 0.9$. These parameters gave a very satisfactory fit of all experimental data. Figure (1) gives a plot of $[Cl^-]^2/(k_{obs} - k_0)$ calculated from the experimental data and from the use of eq (1) vs $[Cl^-]$ and illustrates the goodness of the fit.
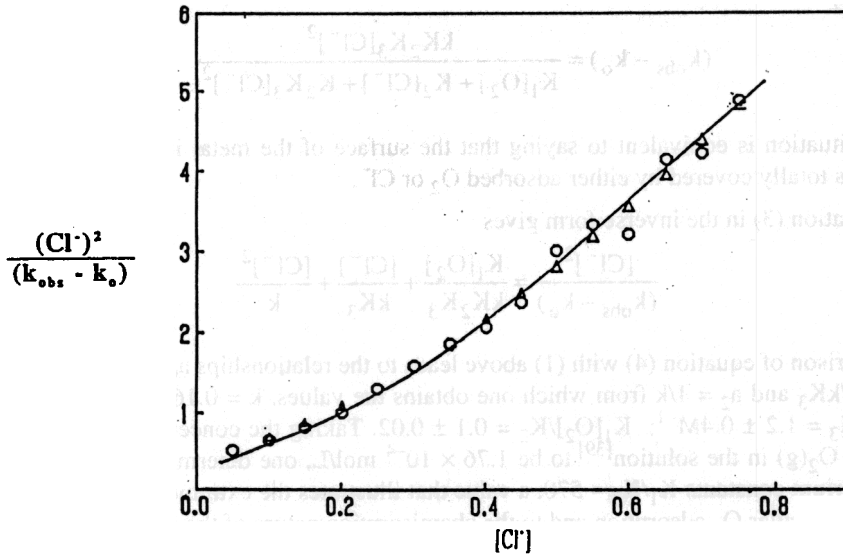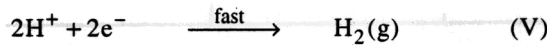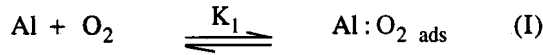

$$\frac{(Cl^-)^2}{(k_{obs} - k_0)}$$

[Cl⁻]

Fig. 1. Plot of $[Cl^-]^2/[k_{obs}-k_0]$ calculated from the experimental data (o) and from the use of equation (1) (Δ) vs (Cl^-) for the corrosion of aluminium in 1.0M HClO₄, I= 2.0M, NaClO₄.

The observations and results given above point to mechanism in which the Cl^- is adsorbed on the metal surface in competition with dissolved $O_2(g)$ followed by a rate determining dissolution step. This type of mechanism is given by the following series of steps:

$$Al + O_2 \xrightleftharpoons{K_1} Al:O_{2\ ads} \qquad (I)$$

$$Al + Cl^- \xrightleftharpoons{K_2} AlCl^-_{ads} \qquad (II)$$

$$AlCl^-_{ads} + Cl^- \xrightleftharpoons{K_3} AlCl^{2-}_{2\ ads} \qquad (III)$$

$$AlCl^{2-}_{2\ ads} \xrightarrow{k} AlCl_2^+ + 3e^- \qquad (IV)$$

$$2H^+ + 2e^- \xrightarrow{\text{fast}} H_2(g) \qquad (V)$$

This mechanism leads to an observed rate constant dependence on Cl^- of the form

$$(k_{obs} - k_0) = \frac{kK_2K_3[Cl^-]^2}{1 + K_1[O_2] + K_2[Cl^-] + K_2K_3[Cl^-]^2} \qquad (2)$$

under the conditions $K_1[O_2]$; $K_2[Cl^-]$; $K_2K_3[Cl^-]^2 >> 1$ equation (2) reduces to equation (3)

$$(k_{obs} - k_0) = \frac{kK_2K_3[Cl^-]^2}{K_1[O_2] + K_2[Cl^-] + K_2K_3[Cl^-]^2} \qquad (3)$$

This situation is equivalent to saying that the surface of the metal in the reaction medium is totally covered by either adsorbed O_2 or Cl^-.

Equation (3) in the inverse form gives

$$\frac{[Cl^-]^2}{(k_{obs} - k_0)} = \frac{K_1[O_2]}{kK_2K_3} + \frac{[Cl^-]}{kK_3} + \frac{[Cl^-]^2}{k} \qquad (4)$$

comparison of equation (4) with (1) above leads to the relationships $a_0 = K_1[O_2]/kK_2K_3$; $a_1 = 1/kK_3$ and $a_2 = 1/k$ from which one obtains the values. $k = 0.16 \pm 0.05$ mL/cm^2 · min; $K_3 = 1.2 \pm 0.4M^{-1}$; $K_1[O_2]/K_2 = 0.1 \pm 0.02$. Taking the concentration of the dissolved $O_2(g)$ in the solution[39] to be 1.76×10^{-4} mol/L, one determines a ratio of the equilibrium constants $K_1/K_2 \approx 570$, a value that illustrates the extremely high affinity of Al to molecular O_2 adsorption and to the chemisorption nature of the process.

The mechanism given by the reaction steps equations I to V, shows that the corrosion of aluminium is a multistep process. Such a situation is now well recognized as evidenced from the review article by Foley[1]. The process of pit initiation is highly de-

pendent on surface properties such as crystallographic orientation[39,40]. The amorphous oxide protective film on aluminium contains flaws that serve as pit nucleation sites[41,42]. Such a flaw defect model of pitting implies that the process is determined by local kinetic considerations rather than a predictable criterion of thermodynamic, stability or instability[43].

In aerated aqueous solutions the main passivating (film forming) species are dissolved $O_2(g)$ molecules that form a chemisorbed layer of $O_2(g)$, on the surface of the metal[10-12]. Recently Lauderback *et al.*[44,45] examined the interaction of O_2 with Al using angle resolved secondary ion mass spectrometry (ARSIMS), auger electron spectroscopy (AES) and low energy electron diffraction. These studies showed that for oxygen exposures of up to 250L (corresponding to a coverage of roughly 0.15ML at 300K) only chemisorbed oxygen phase forms, which does not disorder or reconstruct the Al surface. In addition surface defects were shown to dramatically increase the rate of oxygen adsorption[46].

In the presence of Cl^-; there is competition between $O_2(g)$ and Cl^- ions for adsorption sites on the metal surface, consistent with Kruger's[47] adsorbed ion displacement model of passivity breakdown. Cl^- ions lead to localized dissolution as suggested by the idealized reactions of equations III, IV and V. Evidence for Cl^- ions adsorption as primary step in pitting was offered by Videm[48], who measured ^{36}Cl pick up on oxide covered Al surface using autoradiography. The conclusions drawn from the work is that Cl^- is adsorbed and that the primary adsorption occurs at sites that will subsequently be pits. Similar results were obtained from the work of Berzins *et al.*[49] by measuring adsorption isotherms on corroding Al with $^{36}Cl^-$. The chloride adsorption was primarily localized to corroding pit sites.

Kinetics of the Corrosion of Aluminium in 1.0M $HClO_4$ Solutions Containing Fixed Cl^- and Varied NO_3^- Ion Concentration

The inhibition of aluminium corrosion will involve as a primary step, chemical or physical adsorption of the passive species on the metal surface. In general two mechanisms of pitting inhibition can be distinguished[50].

1 – Prevention of the adsorption of the aggressive anions because of the competitive adsorption of the inhibitor and

2 – The formation of a protective film on the metal surface or modifications of the previous film[4].

In an attempt to gain further understanding of this phenomenon we have thus looked into the inhibition of aluminium corrosion by nitrate and sulfate ions. For this purpose, the hydrogen evolution studies were conducted using solutions containing a fixed Cl^- ion concentration (0.3M, NaCl) and varying concentrations of nitrate or sulfate ions all in 1.0M $HClO_4$ and ionic strength I = 2.0M, $NaClO_4$.

Table (3) gives the observed rate constants for the dissolution of aluminium as functions of added $NaNO_3$. Our previous discussions concerning the competitive nature of the corrosion process point to a series of reaction steps, in which three competitive equi-

libria, *viz* molecular oxygen adsorption, Cl^- adsorption and NO_3^- adsorption are established in the reaction mixture. This is followed by a rate determining dissolution step of $AlCl_{2\,ads}^{2-}$. Thus in addition to the reaction sequence I through V given for the dissolution of aluminium in Cl^- ion media, we suggest the equilibrium adsorption reaction VI in which "y" is the number of nitrate ions that occupy one reactive site on the metal surface.

TABLE 3. Dependence of the observed rate constants for the dissolution of Al in 1.0M $HClO_4$; 0.3M NaCl solutions on nitrate concentrations at I = 2.0M, $NaClO_4$.

[NO$_3^-$], mol·L^{-1}	$10^2 \cdot k_{obs}$ mL·cm^{-2}·min^{-1}
0.000	5.577
0.010	4.918
0.030	4.546
0.040	3.912
0.050	3.748
0.060	2.680
0.075	2.409
0.100	1.414
0.125	0.978
0.150	0.436
0.175	0.292

$$Al + y\ NO_3^- \xrightleftharpoons{K_4} Al(NO_3)_y^{y-} \qquad (VI)$$

This number "y" has been previously[51] termed the active site occupancy parameter meaning that a given inhibitor molecule occupies a number l/y of surface active sites. This number has been estimated[52] for Cl^- ion adsorption using the Engell-Stolica method[53] to be in the range of 2.

The suggested mechanism using reactions I through VI leads to an observed rate constant dependence of the form (5)

$$k_{obs} = \frac{kK_2K_3[Cl^-]^2}{1 + K_1[O_2] + K_2[Cl^-] + K_2K_3[Cl^-]^2 + K_4[NO_3^-]^y} \qquad (5)$$

Equation (5) reduces to

$$k_{obs} = \frac{kK_2K_3[Cl^-]^2}{K_1[O_2] + K_2[Cl^-] + K_2K_3[Cl^-]^2 + K_4[NO_3^-]^y} \qquad (6)$$

Since the Cl^- is kept constant one could write:

$$k_0' = \frac{kK_2K_3[Cl^-]^2}{1 + K_1[O_2]_{ads} + K_2[Cl^-] + K_2K_3[Cl^-]^2} \qquad (7)$$

Where k_0' is the observed rate constant in absence of added nitrate ions. Dividing equation (7) by (6) one gets

$$\frac{k'_o}{k_{obs}} - 1 = \frac{K_4[NO_3^-]^y}{K_1[O_2] + K_2(Cl^-] + K_2K_3[Cl^-]^2} \qquad (8)$$

$$\log\left(\frac{k'_o}{k_{obs}} - 1\right) = \log\left(\frac{K_4}{K_1[O_2] + K_2[Cl^-] + K_2K_3[Cl^-]^2}\right) + y\log[NO_3^-] \qquad (9)$$

A plot (Fig. (2)) of the left hand side of equation (9) vs log [NO$_3^-$] gave a straight line of slope y and intercept of log $\{K_4/(K_1[O_2] + K_2[Cl^-] + K_2K_3[Cl^-]^2)\}$. Linear least squares fit of the data to equation (9) gave an intercept of 2.3 ± 0.3 and a slope of 1.8 ± 0.2. This gives a value of $(2.00 \pm 0.3)10^2$ for the ratios of the equilibrium constants $K_4/K_1[O_2] + K_2[Cl^-] + K_2K_3[Cl^-]^2)$.
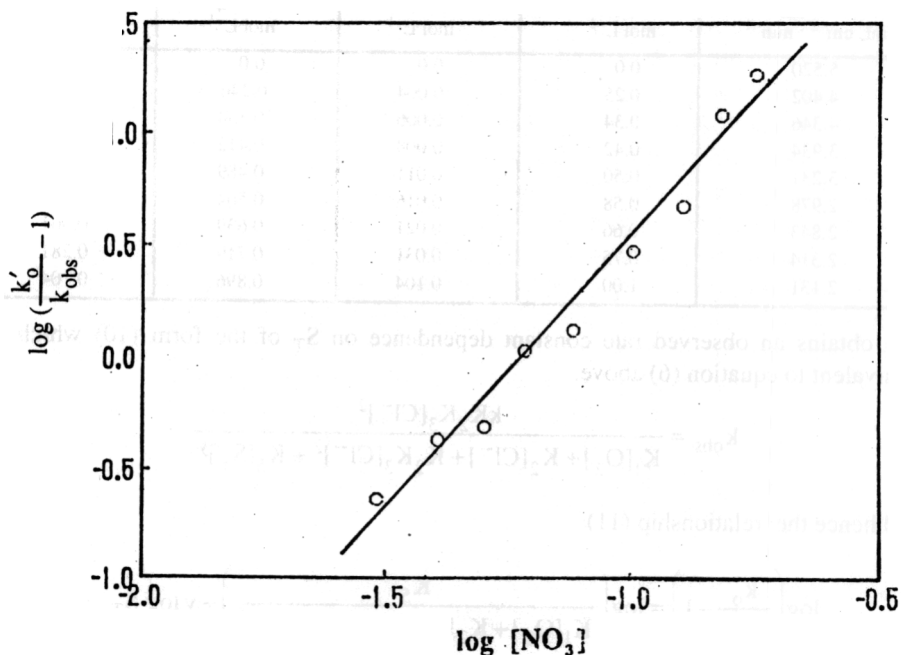

FIG. 2. Plot of $\log\left(\frac{k'_o}{k_{obs}} - 1\right)$ vs log [NO$_3^-$] for the corrosion of aluminium in 1.0M HClO$_4$, 0.3M NaCl, I = 2.0M, NaClO$_4$.

Kinetics of the Corrosion of Aluminium in 1.0M HClO$_4$ Solutions Containing Fixed Cl$^-$ and Varied SO$_4^{2-}$ Ion Concentrations

The study of the inhibition characteristics of the sulfate species on the corrosion of aluminium was done in the same fashion as that of the nitrate ions. The reaction was stud-

ied at 30°C in the range $0 \leq S_T \leq 1.0$, M in the presence of 1.0M $HClO_4$ and at an ionic strength of 2.0M, $NaClO_4$. In this case S_T represents total sulfur containing species, *i.e.* SO_4^{2-} and HSO_4^- because the weak acid properties of the hydrogen sulfate ion, with an acid dissociation constant $K_a = 0.012$.

Table (4) gives the observed rate constant values as functions of added S_T in the form of Na_2SO_4, together with the calculated concentrations of SO_4^{2-}, HSO_4^- and H_{aq}^+. These data point out to the decrease in the observed rate constants with added S_T. Realizing that both SO_4^{2-} and HSO_4^- are capable of adsorption on the surface of aluminium via equilibrium VII,

$$Al + y \ S_T \ \xrightarrow{K_5} \ Al(S_T)_{y(ads)} \qquad (VII)$$
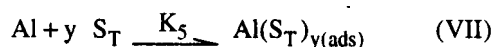
TABLE 4. Dependence of the observed rate constants for the corrosion of Al in 1.0M $HClO_4$; 0.3m NaCl solutions on sulfur containing species ($S_T = [SO_4^{2-}] + [HSO_4^-]$ at I = 2.0M, $NaClO_4$ at 30°C.

$10^2 \ k_{obs}$ mL cm$^{-2} \cdot$ min^{-1}	$[S_T]$ mol L^{-1}	$[SO_4^{2-}]$ mol L^{-1}	$[HSO_4^-]$ mol L^{-1}	$[H^+]$ mol L^{-1}
5.520	0.0	0.0	0.0	1.00
4.402	0.25	0.004	0.246	0.754
4.346	0.34	0.006	0.334	0.666
3.934	0.42	0.008	0.412	0.588
3.231	0.50	0.011	0.489	0.511
2.978	0.58	0.016	0.564	0.436
2.843	0.66	0.021	0.639	0.361
2.314	0.75	0.031	0.719	0.281
2.131	1.00	0.104	0.896	0.104

one obtains an observed rate constant dependence on S_T of the form (10) which is equivalent to equation (6) above.

$$k_{obs} = \frac{kK_2K_3[Cl^-]^2}{K_1[O_2] + K_2[Cl^-] + K_2K_3[Cl^-]^2 + K_5[S_T]^y} \qquad (10)$$

and hence the relationship (11)

$$\log\left(\frac{k_o'}{k_{obs}} - \right) = \log\left(\frac{K_5}{K_1[O_2] + K_2[Cl^-] + K_2K_3[Cl^-]^2}\right) + y \log S_T$$

linear least square fit of the data to equation (11) (Fig. (3)) gave the values $y = 1.5 \pm 0.13$ and $K_5/(K_1[O_2] + K_2[Cl^-] + K_2K_3[Cl^-]^2) = 1.8 \pm 0.3$. Dividing the later value with the corresponding value for nitrate inhibition gives the value of 9×10^{-3} for the ratio K_5/K_4 illustrating the superior inhibition characteristics of the nitrate over that of the combined SO_4^{2-} and HSO_4^- species. It now remains to see whether the observed reduction in the corrosion rate of Al is due to the adsorption of sulfate on the surface of the metal and hence the screening of the metal surface from the Cl^- ion pitting and proton attack or is

in fact due to the reduction in acid strength. As was previously indicated HSO_4^- is a weak acid, meaning that the addition of SO_4^{2-} in the form of Na_2SO_4 will result in the formation of HSO_4^- ion and hence the reduction of hydrogen ion activity. We have thus looked at the corrosion of aluminium in presence of a fixed $[Cl^-]$ concentration of 0.3M and varied the concentration of $HClO_4$ at a fixed ionic strength of 2.0M, $NaClO_4$ all at 30°C.
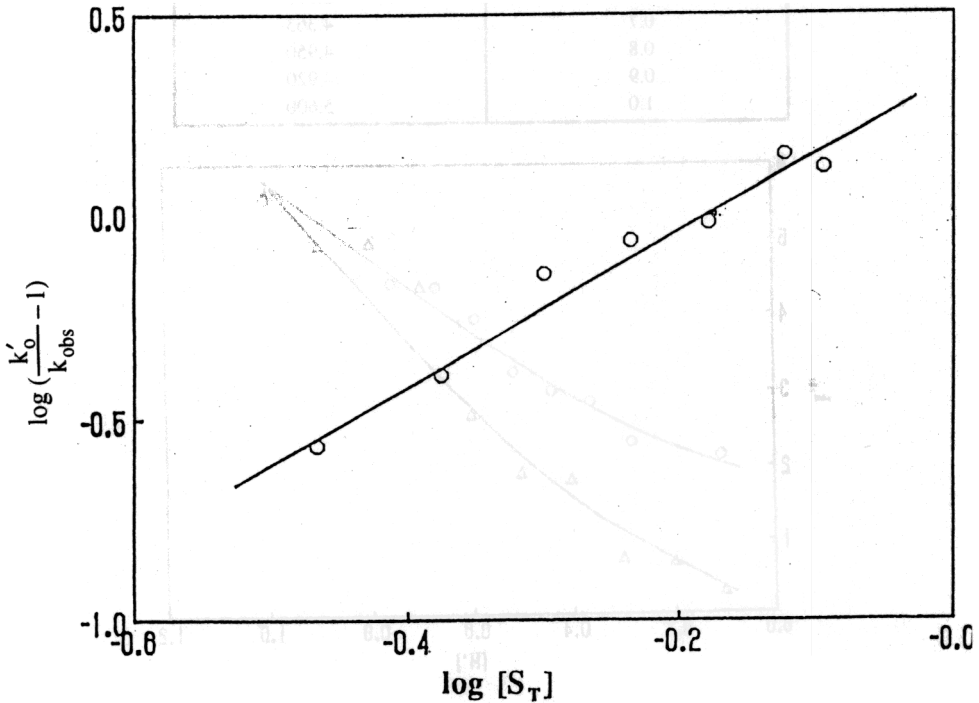

FIG. 3. Plot of log $(\frac{k_0'}{k_{obs}} - 1)$ vs (S_T) for the corrosion of aluminium in 1.0M $HClO_4$, 0.3M NaCl, I = 2.0M, $NaClO_4$.

Table (5) gives the results of this study and Fig. (4) gives a plot of cobs from this study and that of cobs obtained in the sulfate experiments Vs. the calculated H^+ ion concentrations (Table 4). Inspection of the graph shows that the reduction in the observed rate constants for the SO_4^{2-} experiments can not be attributed to the reduction in acid strength and that both the specific acid, *a*. H_{aq}^+ ion as well as the general acid HSO_4^{2-} assist in the corrosion process. The relative magnitude for the contribution of each to the

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corrosion process can not be fully evaluated from the present data. A detailed study of this system is currently underway in our laboratory.

TABLE 5. Dependence of the observed rate constants for Al corrosion of H^+ ion concentration $(HClO_4)$ at $I = 2.0M$, $NaCl_4$, $0.3M$ $NaClO_4$ and $30°C$.

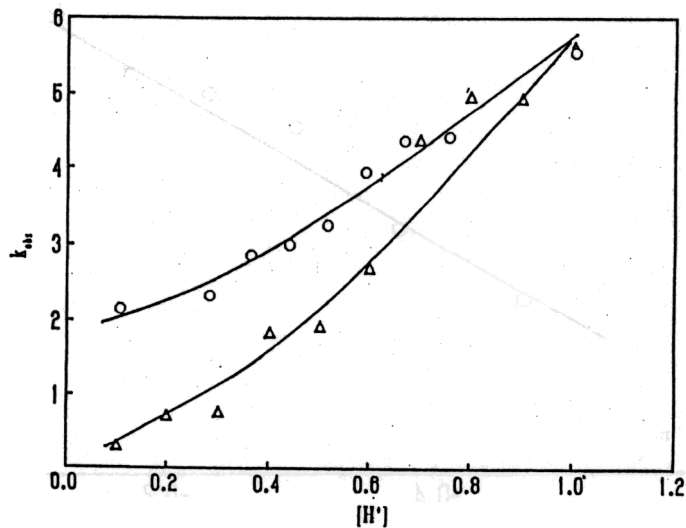| $[HClO_4]$, mol $\cdot$ L^{-1}	10^2, k_{obs} mL $\cdot$ $Cm^{-2} \cdot min^{-1}$
0.1	0.290
0.2	0.699
0.3	0.747
0.4	1.820
0.5	1.914
0.6	2.690
0.7	4.363
0.8	4.950
0.9	4.920
1.0	5.600

FIG. 4. Plot of k_{obs} for the corrosion of aluminium in presence of sulfate vs calculated $[H^+]$ ions (o) and that of k_{obs} vs $(HClO_4)$ in absence of sulfate (Δ) at 30°C.

Conclusion

The kinetics of the corrosion of aluminium metal in 1.0M perchloric acid solutions were investigated in the presence of varying concentrations of Cl^-, NO_3^- and SO_4^{2-}/ HSO_4^- ions and at the fixed ionic strength of 2.0M, $NaClO_4$. The chloride ions were found to have an accelerating effect on the rate of corrosion and resulted in pitting of the metal and its eventual dissolution. On the other hand the NO_3^- and SO_4^{2-}/HSO_4^- ions inhibit the corrosion process. In all cases the reactions were found to be controlled by

multistep competitive equilibria in which Cl^-, NO_3^-; SO_4^{2-} and or HSO_4^- adsorbed on the aluminium metal surface in competition with dissolved molecular oxygen.

The rate of corrosion was found to be zero-order overall with an observed rate constant dependence on Cl^- of the form

$$(k_{obs} - k_o) = \frac{kK_2K_3[Cl^-]^2}{K_1[O_2] + K_2[Cl^-] + K_2K_3[Cl^-]^2}$$

where k_o is the observed rate constant in absence of Cl^- ions, K_1 is the equilibrium constant for molecular oxygen adsorption and K_2 and K_3 are the successive adsorption constants for Cl^- ions. In the presence of the inhibitor (NO_3^- or SO_4^{2-}/HSO_4^- ions) and at a fixed Cl^- ion concentrations the observed rate constant follows a relationship of the form

$$\log\left(\frac{k_o'}{k_{obs}} - \right) = \log\left(\frac{K_I}{K_1[O_2] + K_2[Cl^-] + K_2K_3[Cl^-]^2}\right) + y\,\log I$$

where k_o' is the observed rate constant in absence of the inhibitor (I) and K_I the equilibrium constant for the adsorption of the inhibitor. "y" is a parameter known as the active site occupancy parameter and represents the number of inhibitor molecules adsorbed on a given active site on the metal.

In the presence of added sulfate ions the HSO_4^- ions are formed due to the weak acid properties of the latter species. This results in the reduction of the hydrogen ion activity of the solution. The experimental determination of k_{obs} in varying perchloric acid concentrations showed, however, that both the specific acid (H^+ ions) and the general acid (HSO_4^-) ions contribute to the overall corrosion rate.

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دراسات كيناتيكية على تآكل معدن الألمنيوم في الأوساط الحمضية التي تحتوي على أنيونات غير عضوية

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المستخلص . تمت دراسة كيناتيكية تحفيز أيون الكلوريد ، وتثبيط أنيونات غير عضوية لعملية تآكل معدن الألمنيوم في محاليل حمضية عند درجة ٣٠م وتركيزات $0 \leq NO_3^- \leq 0.18 \text{ mol L}^{-1}$ ، $0 \leq Cl^- \leq 0.8 \text{ mol L}^{-1}$ ، $0 \leq S_T \leq 1.0 \text{ mol L}^{-1}$ حيث S_T تمثل مجمـــوع أيونات SO_4^{2-} و HSO_4^- بثابت قوة $I = 2.0, \text{NaClO}_4$. وقد وجد أن التفاعل يتم على عدة خطوات اتزان تتنافس فيها أنيونات $Cl^-, NO_3^-, HSO_4^-, SO_4^{2-}$ والأكسجين الذائب O_2 ، للامتـزاز على سطح المعدن . كـما وجد إن معدل سرعة التآكل له الرتبة الصفرية وأن ثابت سرعة التفاعل المشاهد يعتمد على تركيز Cl^- حسب المعادلة الآتية :

$$(k_{obs} - k_0) = \frac{kK_2K_3[Cl^-]^2}{K_1[O_2] + K_2[Cl^-] + K_2K_3[Cl^-]^2}$$

حيث K_1 هو ثابت الاتزان لامتـزاز $O_2(g)$ و $K_2 \& K_3$ هما ثوابت امتزاز أنيونات Cl^- . وقد وجد أن إضافة أنيونات النترات تؤدي إلى تثبيط تآكل الألمنيوم . وقد نوقشت النتائج على ضوء تنافس خطوات الاتزان المتعددة والتي تحجب فيها أنيونات النترات والكبريتات سطح المعدن من مهاجمة أنيونات الكلوريد . وفي كل الأحوال فقد اقترحت آلية مكونة من ثلاثة اتزانات متنافسة هي امتزاز الأكسجين الجزيئي ، امتزاز أيونات الكلوريد ثم امتزاز المثبط ويتبع ذلك الخطوة المحددة لسرعة التفاعل .