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Inhibition of the hydrogen evolution reaction on aluminium covered by 'spontaneous' oxide

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The electrochemical behaviour of aluminium covered by a thin 'spontaneous' oxide film was studied as a function of temperature and electrolyte composition at pH 1.3 The rectification mechanism of the charge transfer reactions is discussed on the basis of E/I characteristics. Tafel plots for the hydrogen evolution reaction showed anomalous slopes between $2.3 \times 3RT/F$ and $2.3 \times 4RT/F$, depending on temperature. The inhibiting effects of 1 and 2-naphthylamines on the corrosion kinetics of aluminium in acid media ($HClO_4$ and NaCl + HCl) were determined using electrochemical methods. Consideration of the protonation of amines and the effects of the positively charged surface suggest that the observed excellent inhibition is due to the planar orientation (with π-electron bonds) of the adsorbed inhibitor molecules and the existence of synergetic effects. The degree of surface coverage was found to increase with temperature up to 40 °C. At approximately 40 °C the adsorbed molecules probably change their orientation becoming vertically adsorbed on the surface with strong lateral repulsion.

List of symbols

b	Tafel slope (mV (decade)$^{-1}$)
c	concentration (M)
E	potential (V)
E_{app}	activation energy (kJ mol^{-1})
F	Faraday constant (C mol^{-1})
I	Current (A)
j	current density (A cm^{-2})
R	gas constant (J K mol^{-1})
T	temperature (K)
z	number of electrons

Greek letters

β	symmetry factor
ν	sweep rate (mV s^{-1})
θ	protective efficiency (%)
η	overvoltage (V)

Sub/superscripts

a	anodic
c	cathodic
corr	corrosion
f	fraction

1. Introduction

Aluminium, because of the nature of its oxide, can be included in the so-called valve metal group. In contact with moist air or immersed in water, the metal is always spontaneously covered by an oxide film, the thickness of which is between 3 to 5 μm and which protects the metal from further oxidation [1]. The film thickness and its protective properties can be increased by anodic polarization. In almost neutral solutions the aluminium surface is covered by an insoluble barrier type oxide film, while, in contrast, a porous oxide film forms in non-oxidizing acid solutions [2]. Aluminium oxide dissolves in strong alkaline and non-oxidizing acid solutions due to the covalent character of the chemical bond. In the presence of halogen-ions, especially chloride ions, corrosion of aluminium occurs predominantly by localized attack (pitting corrosion) [3, 4].

The corrosion of aluminium, can be effectively prevented or retarded by the addition of various organic additives in corrosive media. The interaction of the molecules of organic additives with the metallic surface changes the nature of the corroding metal surface and influences the mechanism of the electrochemical processes that occur at the metal–solution interface.

Acid solutions are used to clean aluminium surfaces, aluminium foils and lithographic panels which substitute metallic zinc [5]. Since the metal dissolution in such solutions is rather large, it is necessary to inhibit it by the addition of additives, which should provide a good quality pickled metal surface.

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Numerous organic compounds containing nitrogen functional atoms act as good corrosion inhibitors in acid media. In addition such inhibitors kinetically change the cathodic and/or anodic processes and are important additives in technological processes metal deposition [6, 7]. Investigations of various aliphatic and aromatic amines, as well as nitrogen-heterocyclic compounds [8–12], showed that their inhibitory action is connected with several factors such as: (i) the structure of molecules, (ii) the number and type of absorption sites, (iii) the distribution of charge in the molecule, and (iv) the type of interaction between organic molecules, and the metallic surface.

The adsorption of organic compounds has been the subject of many investigations because of its influence on the understanding of the electrical double layer, the kinetics of electron transfer, the general field of corrosion (including inhibition), and the mechanism of electrode processes, especially the role of intermediates. Many papers have appeared on the adsorption of organic compounds on aluminium [13–15]. The performance of the effective inhibiting action [16] of more than 400 organic compounds at 10^{-2} M in 1 M HCl + 2.5% NaCl on the corrosion of aluminium has been investigated.

The object of the present investigation was to study the inhibiting effect of 1-naphthylamine (1-NA) and 2-naphthylamine (2-NA) on the corrosion of aluminium (99.6%) in acid solutions; a 1 M perchloric acid solution and a 3% NaCl solution at pH 1.3, in a temperature range from 20 to 70 °C. The use of 1-NA as a corrosion inhibitor was inspired by the fact that it had shown excellent adsorption properties (it acts as an excellent surface active substance in polarography) in acid solutions. The influence of some amines as capillary active substances on polarographic electrode processes of some metallic cations was studied by d.c. and a.c. methods in acid media [17]. The inhibition efficiency of the electrode processes was found to increase in the following order: methylamine < n-buthylamine < pyridine < aniline < quinoline < naphthylamine.

In spite of the fact that polarographic and corrosion processes are not identical, a parallelism of these effects may exist, since in both cases the adsorbed organic additive retards the electrochemical reaction.

2. Experimental details

The aluminium sample selected for the study had the following composition by percent weight: Al, 99.6; Cu, 0.01; Si, 0.09; Fe, 0.27; Ti, 0.15; V, 0.09. Disc electrodes suitable for the EG&G PARC model 616 system were machined from a cylindrical rod with a diameter of 8 mm. The electrode surface was abraded with emery paper to an 800 metallographic finish, degreased in trichloroethylene and rinsed with triply distilled water. Prior to each electrochemical experiment, the electrode was left for 5 min in the atmosphere and then for 10 min in a solution at the open circuit potential. This procedure gave good reproducibility of results. In all measurements the counter electrode was a platinum gauze and the reference electrode was a saturated calomel electrode (SCE). All potential are referred to the SCE.

Measurements were performed in two basic solutions; 1 M perchloric acid and 3% NaCl at pH 1.3, adjusted by concentrated HCl, alone, and in the presence of the inhibitors; 1 and 2-naphthylamines (NA). All solutions were deaerated by argon. The measurements were carried out in a standard electrochemical cell with a separate compartment for the reference electrode connected with the main compartment via a Luggin capillary. The cell was a water-jacketed version, connected to a constant temperature circulator.

The polarization *E* against *I* curves were obtained by means of the linear potential sweep technique with a sweep rate of $2\,\mathrm{mV\,s^{-1}}$, and with rotation rates of 500 and $2000\,\mathrm{min^{-1}}$. All measurements were performed using a PAR potentiostat, model 273A with an IBM computer.

3. Results and discussion

3.1. *The polarization properties of aluminium*

As previously mentioned, the influence of the electrolyte composition and temperature on the electrochemical behaviour of aluminium was investigated. Polarization measurements were performed on the rotating disc electrode by sweeping the potential from the region of hydrogen evolution to the anodic side at a sweep rate of $2\,\mathrm{mV\,s^{-1}}$.

Figure 1, curve (a) denotes the polarization curve obtained in a 3% NaCl solution, pH 1.3. It confirms the valve behaviour of aluminium, i.e. the rectification mechanism of electron transfer reaction (blocked anodic, but not cathodic electron transfer). The cathodic current value of $1.5\,\mathrm{mA\,cm^{-2}}$ is achieved at polarization of −200 mV (going from the potential of zero current), and shows a further steep increase. At the same polarization on the opposite side,

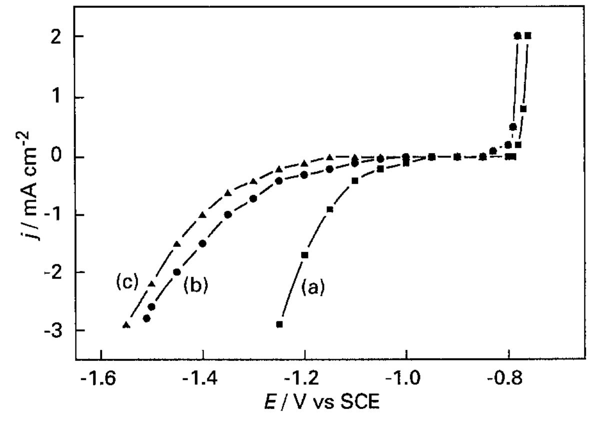

Fig. 1. Potentiodynamic polarization curves for an aluminium electrode in 3% NaCl solution at pH 1.3 without (■) and with the presence of: (▲) 0.001 M 1-naphthylamine, (●) 0.001 M 2-naphthylamine, at $t = 20\,°\mathrm{C}$, $n = 2000\,\mathrm{min^{-1}}$, $\nu = 2\,\mathrm{mV\,s^{-1}}$.

+200 mV, the anodic current is very low and potential-independent, indicating the existence of an oxide layer on the electrode surface. An abrupt current rise at about −0.8 V is correlated with a breakdown of passivity and the initiation of pitting [3–18]. Local metal dissolution prevents further polarization of the electrode. The addition of organic compounds, 1 and 2-naphthylamines, affects only the cathodic polarization curve, increasing the overvoltage of the cathodic process, as can be seen from curves (b) and (c) in Fig. 1. The current value of 1 mA cm^{-2} is achieved at −1.2 V and −1.4 V without and with the presence of additives, respectively.

The influence of temperature on the shape of the polarization curves can be seen in Fig. 2. With increasing temperature the anodic and cathodic current densities also increase, indicating that the rate of the corresponding electrode processes (metal dissolution and hydrogen evolution) increases, while the overvoltage of both reactions decreases.

Figure 3 represents the polarization curves obtained in a perchloric acid solution with and without the addition of additives. Comparing the results in Fig. 3 with those in Fig. 1 (in a 3% NaCl solution, pH 1.3), it can be seen that the range of small anodic currents is broader in a perchloric acid solution, and the current gradually increases with polarization until its final sharp rise. The presence of organic additives in the solution only changes the cathodic part of the polarization curves.

To obtain the kinetic parameters necessary for examining the corrosion process mechanism of the systems investigated, the current potential relationships have been analysed in the so-called Tafel region. Figure 4 represents the Tafel plots for aluminium in a 1 M perchloric acid solution alone and in the presence of different concentrations of inhibitors. By using the least-squares fit procedure with a correlation coefficient greater than 0.99, Tafel straight lines were obtained for all systems investigated, indicating the good applicability of the Butler–Volmer equation [19, 20]. The intersections of Tafel straight lines were found to be very close to the corresponding rest potential values.

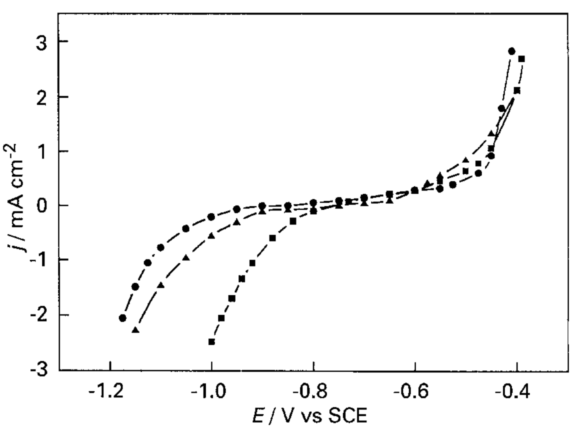

Fig. 3. Potentiodynamic polarization curves for an aluminium electrode in 1 M $HClO_4$ solution without (■) and in the presence of: (▲) 0.001 M 1-naphthylamine, (●) 0.001 M 2-naphthylamine, at $t = 20\,°C$, $n = 500\,min^{-1}$ and $\nu = 2\,mV\,s^{-1}$.

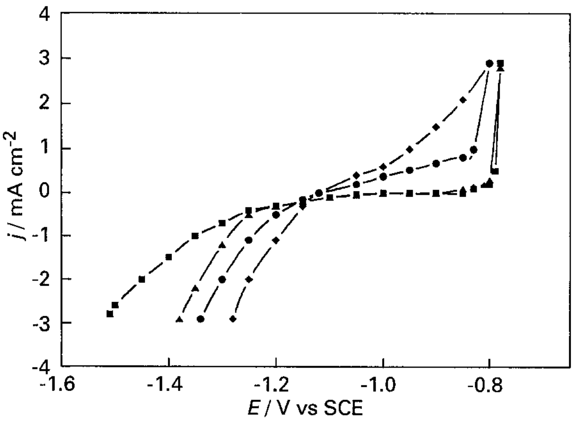

Fig. 2. Influence of temperature on the potentiodynamic polarization curves for an aluminium electrode in 3% NaCl solution containing 0.001 M 1-naphthylamine at pH 1.3 and at: (■) 20, (▲) 40, (●) 60, and (◆) 70 °C; $n = 2000\,min^{-1}$, $\nu = 2\,mV\,s^{-1}$.

The protective efficiency, θ, of additives investigated on corrosion of aluminium in both acid solutions was calculated using the equation:

$$\theta = \frac{(j_{corr})_o - (j_{corr})_i}{(j_{corr})_o} \times 100\% \qquad (1)$$

where $(j_{corr})_o$ and $(j_{corr})_i$ are the corrosion current densities in solutions without and with a given inhibitor, respectively. The kinetic parameters E_{corr}, j_{corr}, b_c, b_a, together with the protective efficiency, θ, are listed in Tables 1 to 6. These results indicate that 1 and 2-naphthylamines act as cathodic inhibitors on aluminium corrosion in the electrolytes used. Their protective efficiency depends on temperature and electrolyte composition. The protective efficiency is greater in a chloride solution than in perchlorate, and in the two electrolytes it is greatest at 40 °C. As an example, the influence of 2-naphthylamine, $c = 0.001\,M$, on the protective efficiency at different temperatures is presented in Fig. 5.

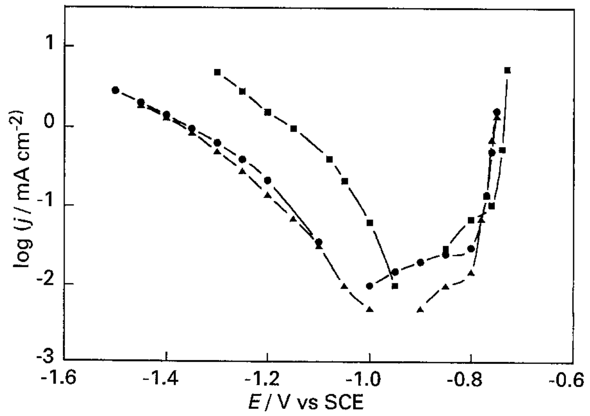

Fig. 4. Tafel plots for an aluminium electrode in 1 M $HClO_4$ solution without (■) and in the presence of: (▲) 0.001 M 1-naphthylamine, (●) 0.001 M 2-naphthylamine at $t = 20\,°C$, $n = 500\,min^{-1}$ and $\nu = 2\,mV\,s^{-1}$.

Table 1. Kinetic parameters for aluminium in 3% NaCl solution at pH 1.3 obtained in the temperature range 20 to 70 °C at $n = 2000\,min^{-1}$ *and* $v = 2\,mV\,s^{-1}$

t/°C	E_{corr}/mV	j_{corr}/mA cm^{-2}	$-b_c$/mV	b_a/mV
20	−790	0.0080	181	29
30	−786	0.0110	195	29
40	−862	0.0631	187	25
50	−938	0.0940	173	30
60	−928	0.0933	183	111
70	−917	0.0970	199	101

3.2. *H.e.r. kinetics on an aluminium covered electrode by thin 'spontaneous' oxide: analomous Tafel slopes*

The experiments were performed in argon-deareated electrolyte solutions, to eliminate the influence of oxygen electroreduction on the shape of polarization curves. Therefore the only cathodic process that occurred at the metal solution interface was hydrogen evolution. Tables 1 to 6 show that the Tafel slopes are greater than expected $2.3 \times (2RT/F)$ (118 mV at 25 °C) for the Volmer–Tafel mechanism. The Tafel slopes greater than $2.3 \times (2RT/F)$ are usually regarded as anomalous since they cannot be predicted for any mechanism by the two well-known theoretical procedures, namely, the steady-state method and the quasi-equilibrium approach, without making assumptions which are easily contestable. Preparation of the working electrode involved 5 min exposure to air and therefore the electrodes undoubtedly had a thin oxide film on their surface before being introduced into the cell. It is clear, however, that the presence of a film can markedly influence the reduction process at the surface by affecting the energetics of the reaction at the double layer, or by imposing a barrier to charge transfer through the film, or both.

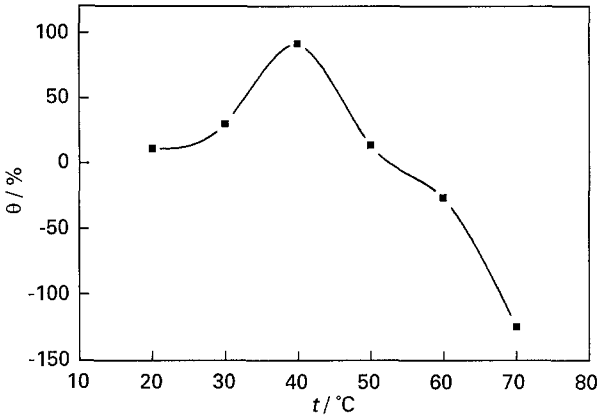

Fig. 5. Influence of temperature on the protection efficiency of 2-naphthylamine for aluminium in 3% NaCl solution at pH 1.3.

Table 2. Kinetic parameters for aluminium in 3% NaCl solution at pH 1.3 with the presence of 0.001 M 1-naphthylamine in the temperature range 20 to 70 °C at $n = 2000\,min^{-1}$ *and* $v = 2\,mV\,s^{-1}$

t/°C	E_{corr}/mV	j_{corr}/mA cm^{-2}	$-b_c$/mV	b_a/mV	θ/%
20	−809	0.0029	223	22	63.75
30	−849	0.0034	175	41	69.09
40	−870	0.0036	171	43	94.29
50	−944	0.0096	150	81	89.78
60	−933	0.0233	157	107	76.09
70	−1073	0.0729	143	209	24.84

The first systematic explanation of anomalous Tafel slopes on oxide-covered electrodes was presented by Meyer [21]. He suggested that for a typical electrode reaction, e.g. hydrogen evolution reaction on an oxide-covered electrode, two potential energy barriers exist which are kinetically significant. First, the charge carriers, H_3O^+ ions in the present case, must negotiate the barrier in the Helmholtz double layer to reach the reaction site at the oxide–electrolyte interface; and second, the electrons from the metal must negotiate the potential energy barrier within the oxide to reach the oxide–solution interface where the two charge carriers, H_3O^+ and e^-, subsequently neutralize each other. This model is frequently referred to as the 'dual-barrier model'. Quantitatively, the simplest way to express this effect is as follows. For the discharge of H_3O^+ on a metal covered by a semiconducting oxide; for conditions of constant concentration of H_3O^+ and electrode coverage, the rate equation is

$$j = \text{constant} \times \exp\left(-\frac{\beta(\eta - \eta_f)}{RT} \times zF\right) \qquad (2)$$

where β is the charge transfer symmetry factor with the usual value of 0.5, η is the total metal–(oxide)–solution overpotential, η_f is the fraction of η which operates across the semiconducting oxide film and R is the gas constant.

In general, it may be assumed that η_f, the potential drop across the semiconducting oxide film of given thickness and properties, is the same function of the total overpotential η. By taking logarithms of Equation 2:

$$\log j = \text{constant} - \frac{\beta(\eta - \eta_f)}{2.3RT} \times zF \qquad (3)$$

On rearrangement and differentiation of Equation 3 the Tafel slope may be deduced as

$$\partial\eta/\partial \log j = \frac{2.3RT}{\beta zF(1 - \partial\eta_f/\partial\eta)} \equiv \text{Tafel slope} \qquad (4)$$

In the absence of an oxide film and with the usual values of $\beta(-0.5)$ and $z(=1)$, the Tafel slope is 118 mV at 25 °C, as theoretically predicted by the Volmer–Tafel mechanism, which suggests that the rate-controlling step is the Volmer discharge step followed by the Tafel recombination step. However, the identification of the reaction mechanism by the Tafel slope is only possible in very limited cases [22].

If half the total metal–solution potential operates across the film i.e. if $\eta_f = 0.5\eta$, than the value of the Tafel slope from Equation 4 is 236 mV. In the present investigations the Tafel slopes lie between 180 mV (decade)$^{-1}$ ($2.3 \times 3RT/F$) and 236 mV (decade)$^{-1}$

Table 3. Kinetic parameters for aluminium in 3% NaCl solution at pH 1.3 with the presence of 0.001M 2-naphthalamine in the temperature range 20 to 70 °C at $n = 2000\,\mathrm{min}^{-1}$ and $\nu = 2\,\mathrm{mV\,s}^{-1}$

t/°C	E_{corr}/mV	j_{corr}/mA cm^{-2}	$-b_c$/mV	b_a/mV	θ/%
20	−795	0.0071	264	19	11.25
30	−795	0.0077	263	19	30.00
40	−886	0.0052	188	41	91.77
50	−1090	0.0810	181	145	13.82
60	−1015	0.1174	175	188	−25.83
70	−1042	0.2180	251	218	−124.74

Table 5. Kinetic parameters for aluminium in 1 M $HClO_4$ solution with the presence of 0.001 M 1-naphthylamine in the temperature range 20 to 70 °C at $n = 500\,\mathrm{min}^{-1}$ and $\nu = 2\,\mathrm{mV\,s}^{-1}$

t/°C	E_{corr}/mV	j_{corr}/mA cm^{-2}	$-b_c$/mV	b_a/mV	θ/%
20	−766	0.0013	251	254	27.77
30	−744	0.0095	222	188	58.51
40	−777	0.0184	119	242	74.26
50	−783	0.0610	103	421	28.95
60	−796	0.1053	115	555	13.68
70	−739	0.1416	60	295	−23.24

$(2.3 \times 4RT/F)$, depending on the temperature. At long polarization times ($\nu < 2\,\mathrm{mV\,s}^{-1}$), some cathodic ‘activation’ is manifested ($b_c \approx 2.3\,RT/F$). These results are in good agreement with the results obtained for hydrogen evolution on aluminium covered by a thin oxide film in buffered acetate solution at pH 5.5 [23].

Tables 1 to 6 show that the electrolyte composition and the presence of organic additives do not significantly influence the value of Tafel slope b_c. The electrolyte composition, as pointed out earlier, has a strong influence on the anodic part of the polarization curve and, therefore, on the value of the Tafel slope b_a (see Tables 1 to 6). In a perchloric acid solution, over a temperature range 20 to 70 °C, b_a ranges from 280 to 589 mV (decade)$^{-1}$, indicating growth of the oxide layer during anodic polarization. With increasing temperature the rate of oxide growth [2, 24], i.e. the film thickness, also increases. In the presence of chloride ions and over a temperature range from 20 to 40 °C the electrode is practically unpolarizable in the anodic range, see Fig. 1, because of the initiation of localized corrosion attack, i.e. pitting corrosion. b_a is close to 30 mV, and lower than the expected 40 mV corresponding to the uniform anodic dissolution of aluminium via hydrated Al^{3+} ions [2]. At temperatures higher than 40 °C the slope values are greater than 100 mV (decade)$^{-1}$, which can be attributed to the participation of side reactions in film growth and to the penetration of chloride ions into the film [12].

3.3. *Adsorption of 1-naphthalamine and 2-naphthalamine*

The electrochemical behaviour of aluminium depends on its surface state. Aluminium immersed in water is covered by a ‘natural’ surface oxide film, which is stable in the pH range between 4 and 8.5 [25], and, even during a longer exposure to an acid or alkaline solution. Although the anhydrous oxide is a stable reaction product at room temperature, the free energy of dehydration is relatively small. Hence, species of different degrees of hydration (up to $Al_2O_3 \cdot 3H_2O$ or $Al(OH)_3$ may form during anodic oxidation, at least at the oxide–solution interface. The hydration of aluminium–oxygen bonds on the oxide film and the subsequent dissociation of the hydroxide leads to the development of a charge on the oxide surface. Therefore, an acid-base equilibrium establishes [2] with a characteristic value of pH of zero charge ($\mathrm{pH_{pcz}}$), which controls the surface charge and adsorption characteristics of an oxide covered electrode. The $\mathrm{pH_{pcz}}$ for aluminium is close to 9 [26, 27]. At pH lower than 9 the aluminium surface has a net positive charge and anions such as chloride are attracted to the surface and can adsorb. The adsorption of aggressive ions on the defect sites of the oxide layer leads to localized corrosion attack [28].

The high effectiveness of organic substances containing nitrogen functional atoms suggests the existence of a synergistic effect in acid solutions [29]. In the bulk of an acid solution, the predominant species are the cations. The adsorption of cations onto the positively charged metal surface is weak. Due to the chemisorption of anions (e.g. halogen ions), a negatively charged metal surface favours the adsorption of cations. A subsequent discharge of the ionic form along with the formation of molecules at the interface can also occur. Besides the electrostatic interaction between the cations and the anions, chemisorption of the molecular form through the electron pair of the nitrogen atom can also occur. The characteristics of the nitrogen-containing compounds, the concentration of the inhibitor and

Table 4. Kinetic parameters for aluminium in 1 M $HClO_4$ solution in the temeprature range 20 to 70 °C at $n = 500\,\mathrm{min}^{-1}$ and $\nu = 2\,\mathrm{mV\,s}^{-1}$

t/°C	E_{corr}/mV	j_{corr}/mA cm^{-2}	$-b_c$/mV	b_a/mV
20	−725	0.0018	198	287
30	−768	0.0228	149	398
40	−822	0.0715	124	584
50	−812	0.0860	120	589
60	−789	0.1220	98	546
70	−733	0.1149	80	190

Table 6. Kinetic parameters for Al in 1 M $HClO_4$ solution with the presence of 0.001 M 2-naphthylamine in the temperature range 20 to 70 °C at $n = 500\,\mathrm{min}^{-1}$ and $\nu = 2\,\mathrm{mV\,s}^{-1}$

t/°C	E_{corr}/mV	j_{corr}/mA cm^{-2}	$-b_c$/mV	b_a/mV	θ/%
20	−832	0.0005	185	267	72.22
30	−834	0.0110	192	482	51.97
40	−791	0.034	117	270	53.43
50	−895	0.1139	151	1089	−32.44
60	−919	0.1379	97	1032	−13.03
70	−902	0.1462	109	501	−27.33

the acid, the strength of the anion adsorption and many other factors determine which type of synergetic adsorption predominates [29].

In acid solutions, both 1 and 2-naphthylamine molecules are proton acceptors, and an equilibrium, occurs

$$R{-}NH_2 + H^+ = R{-}NH_3^+ \qquad (5)$$

It follows that with decreasing pH the concentration of the corresponding cations increases. Therefore the adsorption of aromatic amine compounds in acid solutions on a negatively charged metal surface will predominantly take place by functional group–metal surface interaction. However, it has been found that aromatic amine compounds in acid solutions are sometimes adsorbed in a planar layer as a result of π-electron interaction between the molecules and the electrode surface. Tkalčec [17] found that 1 and 2-naphthylamines strongly influenced the positive side of electrocapillary curves obtained on mercury in a perchloric acid solution, suggesting a planar orientation of adsorbed molecules and π-bonding. A similar observation was reported by Hackerman and Kaesche [12] for adsorption of organic amines on iron in hydrochloric acid solution.

The present results show an increase in protective efficiency up to 40 °C, and with further temperature increase protective efficiency decreases. It seems that this change may be correlated with a reorientation process, a change from π-bonding to adsorption via functional groups.

3.4. *Energy of activation*

The energy of activation of hydrogen evolution was calculated from the slope of $\log j_c$ against $1/T$ straight line, according to the equation:

$$\log j_c = \frac{E_{app}}{2.303RT} + \text{constant} \qquad (6)$$

where j_c is the cathodic current density, E_{app} is the activation energy, and T is the temperature. Typical plots for aluminium polarization in a 3% NaCl solution alone and in the presence of inhibitors ($c = 0.001$ M) at -1.3 V are presented in Fig. 6. Activation energies calculated for both electrolytes are listed in Table 7.

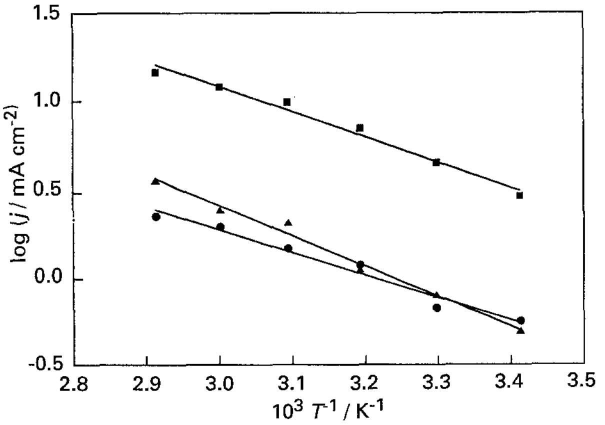

Fig. 6. Arrhenius plots of the cathodic currents obtained on aluminium electrode at -1.3 V in 3% NaCl solution at pH 1.3 without (■) and in the presence of: (▲) 0.001 M 1-naphthylamine, (●) 0.001 M 2-naphthylamine.

Table 7. Activation energies for aluminium in the solutions investigated

Solution	E_{app}/kJ mol^{-1}
3% NaCl	26.6
3% NaCl + 1-NA	33.8
3% NaCl + 2-NA	25.3
1 M $HClO_4$	30.6
1 M $HClO_4$ + 1-NA	59.0
1 M $HClO_4$ + 2-NA	58.9

In comparing the activation energies obtained it must be realized that they are only apparent values, i.e. they have been determined at constant bulk inhibitor concentrations. The protection efficiency and the degree of surface coverage θ change with temperature [30]. This change is incorporated in the value of E_{app}. The more sensitive the protection efficiency and the degree of surface coverage to temperature changes, the larger are the differences in activation energy between the inhibited and uninhibited solutions. To eliminate this effect, the activation energy should be determined at a constant surface inhibitor activity, i.e. at a constant degree of surface coverage.

4. Conclusions

Corrosion kinetics of aluminium covered by thin 'spontaneous' oxide film were studied in $HClO_4$ and NaCl + HCl solutions alone and in the presence of 1 and 2-naphthylamines by using potentiodynamic measurements in the temperature range 20 to 70 °C.

The shape of the polarization curves are typical for valve metal behaviour. E/I characteristics show the rectification mechanism of electron transfer reactions at the electrode–electrolyte interface and anomalous Tafel slopes between $2.3 \times 3RT/F$ and $2.3 \times 4RT/F$, depending on temperature.

1 and 2-naphthylamines inhibit hydrogen evolution via adsorption of both the protonated species and, predominantly, the molecular species. The protonated species inhibit via a zeta-potential effect in addition to its blocking effect, while the molecular species inhibit via interaction of π-electrons of the conjugated bonds of the aromatic nuclei with the electrode surface.

The inhibition efficiency of 1 and 2-naphthylamines on aluminium corrosion in acid media seems to be more likely due to specific adsorption of the molecular species. This conclusion is based on the facts: (i) the electrolytes are rather concentrated solutions of strong acids and zeta-potential must be small. This is in agreement with the observation that the presence of the inhibitor does not change the Tafel slope significantly, and (ii) at pH 1.3 the electrode surface is positively charged (pH_{pcz} is close to 9) and adsorption of cations is weak. The high effectiveness of inhibition in solutions containing Cl^- ions suggests the existence of synergetic affects. Due to the chemisorption of halide ions, a negatively charged metal surface favours the adsorption of protonated species.

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