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Pyridine and its derivatives as inhibitors of aluminium corrosion in chloride solution

M. KLIŠKIĆ, J. RADOŠEVIĆ, S. GUDIĆ

Faculty of Technology, Laboratory of Electrochemistry and Materials Protection, Teslina 10/V, 21000 Split, Croatia

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Pyridine and its selected derivatives (symmetric collidine and 2,5-dibrompyridine) have been studied as corrosion inhibitors for high purity aluminium in a 2 M NaCl solution at 25 °C and 35 °C using d.c. polarization techniques. The investigations were carried out with a wide range of concentrations of the compounds examined (from 0.5×10^{-5} M to 1×10^{-3} M). The results show that the derivatives are adsorbed on aluminium according to the Freundlich isotherm. The values of the standard free energy of adsorption suggest that the adsorptive properties of the compounds under consideration approach the physical type. The polarization curves show that the compounds act as cathodic-type inhibitors.

1. Introduction

Aluminium and its alloys have high resistance to corrosion in nearly neutral aqueous solutions owing to the presence of the passive film. In such solutions the surface film is insoluble but may be locally destroyed by aggressive anions, primarily chlorides, and corrosive attack takes place [1]. Many authors [2–7] accept that the mechanism of pit initiation involves: (i) adsorption of chlorides on the oxide surface due to the influence of the electric field at the oxide–solution interface [8]; (ii) formation of a hydroxychloride aluminium salt, which goes into the solution; and (iii) dissolution of the oxide at places where the film is thinner.

Propagation of pitting then takes place with dissolution of the underlying metal. As a result of adsorption or adsorption-reaction of the inhibitor at the oxide covered metal surface, there may be different inhibition mechanisms. According to Thomas [9] the mechanism of action of both inorganic and organic inhibitive anions on corrosion of various metals such as Fe, Al and Zn in near neutral solutions involves the following: (i) stabilization of the passivating oxide film by reducing its dissolution rate; (ii) repassivation of the surface due to repair of the oxide film by promoting reformation of the oxide; (iii) repair of the oxide film by formation of insoluble surface compounds and consequent plugging of pores; and (iv) prevention of adsorption of aggressive anions because of the competitive adsorption of inhibitive anions.

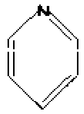
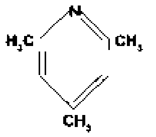
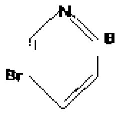
Inhibition of localized corrosion by organic compounds usually involves chemical adsorption at the oxide covered metal surface as a primary step [10], but the exact mechanism of adsorption of inhibitor molecules or ions is not clear. Determination of the type of adsorption isotherm corresponding to the adsorption on the metal–electrolyte phase boundary gives much valuable information as to the adsorption process, since it makes possible to determine such quantities as the standard free energy of adsorption, its dependence on the degree of surface coverage, the character of the adsorption layer on the metal–electrolyte phase boundary, the magnitude and character of interactions between the molecules of the adsorbed substance or between these molecules and the surface atoms of the metal. Therefore, the accurate determination of the type of adsorption isotherm corresponding to the investigated adsorption process is of primary importance [11].

The aim of this work is to study the effect of pyridine and its derivatives on the corrosion of high purity aluminium covered with a 'natural' oxide film in a 2 M sodium chloride solution. Organic compounds were chosen whose molecular structure was likely to lead to adsorption on the aluminium surface. They are characterized by the presence of nitrogen atoms which act as reaction centres for adsorption on the metal surface.

2. Experimental details

The experiments were carried out using high purity aluminium (99.999%), obtained by courtesy of Alcan International. The Al sample was cut into cubes and made into electrodes by inserting insulated copper wires and protecting all sides but one with epoxy resin. The exposed geometric area was 0.57 cm^2. To obtain reproducible and comparable results, special attention was paid to the surface pretreatment. After trying different methods, the most accurate results were achieved by mechanical polishing of the electrode surface up to a mirror finish, followed by its immersion in alcohol and doubly distilled water, and exposure to air in order for the 'natural' oxide layer to be formed, prior to immersion into the solution. A

Table 1. Structures, names and abbreviations of the studied inhibitors

PYRIDINE	SYMMETRIC COLLIDINE	2,5-DIBROM PYRIDINE
		
PYR	COL	DBP

new electrode surface was used for each run. The measurements were performed at least twice.

The electrochemical glass cell was of the usual type with provision for purging with purified nitrogen and thermostating. Aluminium electrodes were introduced through the lid close to a Luggin capillary for connection with an SCE reference electrode. A platinum wire, enclosed in a tube with a glass frit, was introduced into the same solution as the counter electrode.

The basic solution was 2 M NaCl of pH 6.5 to which organic compounds were added in different concentrations (from 0.5×10^{-5} M to 1×10^{-3} M). Table 1 lists the additives used. The experimental temperatures were 25 °C and 35 °C. Potentiodynamic polarization curves were produced using a potentiostat (PAR M273) driven by a computer (PC: 386SX). Anodic and cathodic branches of polarization curves were recorded with the potential change rate of $2\,\mathrm{mV\,s^{-1}}$. Anodic and cathodic curve branches were joined by a computer into a Tafel diagram. The least squares method was used to extrapolate Tafel straight lines and to determine the electrochemical parameters.

3. Results and discussion

Various corrosion parameters such as corrosion potential, E_{corr}, corrosion current density, i_{corr}, anodic and cathodic Tafel slopes are recorded in Table 2 for aluminium in 2 M NaCl. The table does not list the values for DBP at 25 °C because this derivative does not dissolve completely at this temperature, so that it was not possible to trace the changes in corrosion parameters with concentration.

Figure 1 shows the potentiodynamic polarization curves for aluminium in a 2 M NaCl solution at 25 °C, both containing and not containing the organic additives. Both additives shifted the corrosion potential in the negative direction. The polarization curves showed no inhibitive reactions of these substances on anodic processes. Moreover, the lower the corrosion potential, the higher the anodic currents, even if such currents never exceed $10\,\mu\mathrm{A\,cm^{-2}}$. The cathodic cur-

Table 2. Effect of inhibitors on the various corrosion parameters of aluminium in 2 M NaCl solution

Inhibitor	*concentration* / M	E_{corr} / mV		i_{corr} / μA cm^{-2}		b_a / mV dec^{-1}		b_c / mV dec^{-1}	
		25 °C	*35 °C*	*25 °C*	*35 °C*	*25 °C*	*35 °C*	*25 °C*	*35 °C*
	none	−833	−891	1.58	2.33	515	288	278	376
PYR	0.5×10^{-5}	−982	−968	0.74	1.47	314	201	156	323
	1.0×10^{-5}	−982	−960	0.72	1.39	210	145	241	379
	0.5×10^{-4}	−993	−1090	0.67	1.18	186	255	176	321
	1.0×10^{-4}	−990	−1137	0.55	1.12	120	166	148	356
	0.5×10^{-3}	−1018	−1073	0.44	1.06	116	212	130	306
	1.0×10^{-3}	−978	−1126	0.35	1.00	69	174	116	254
COL	0.5×10^{-5}	−911	−876	0.91	1.64	372	174	340	204
	1.0×10^{-5}	−958	−871	0.85	1.54	268	195	310	252
	0.5×10^{-4}	−943	−864	0.75	1.39	258	145	288	276
	1.0×10^{-4}	−928	−840	0.65	1.18	163	167	309	213
	0.5×10^{-3}	−968	−1121	0.55	1.09	127	207	215	324
	1.0×10^{-3}	−925	−866	0.42	1.00	196	120	204	308
DBP	0.5×10^{-5}	–	−983	–	1.13	–	250	–	314
	1.0×10^{-5}	–	−979	–	1.11	–	178	–	292
	0.5×10^{-4}	–	−1008	–	1.09	–	172	–	259
	1.0×10^{-4}	–	−1009	–	1.04	–	193	–	313
	0.5×10^{-3}	–	−1007	–	1.00	–	234	–	262
	1.0×10^{-3}	–	−986	–	0.98	–	152	–	214

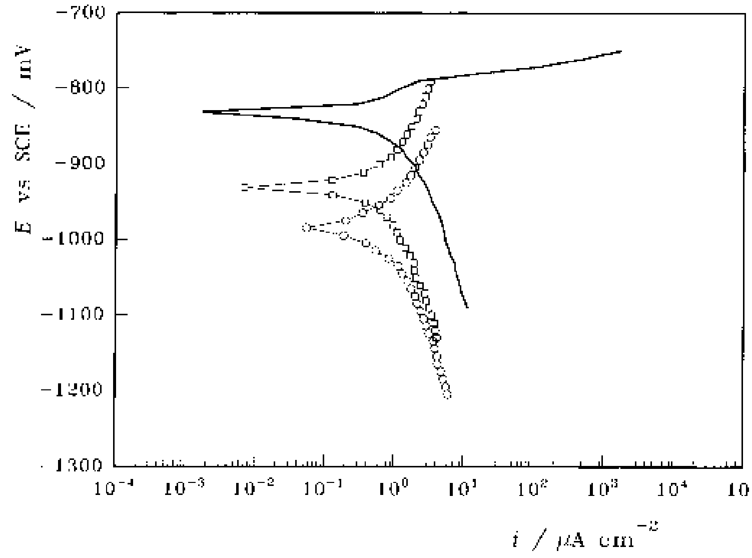


Fig. 1. Potentiodynamic polarization curves for Al in 2 M NaCl in the absence (——) and the presence of 1×10^{-3} M inhibitors at 25 °C. Key: (○) PYR and (□) COL.

rent densities were lower than in the case of pure NaCl solution.

Figure 2 shows the potentiodynamic polarization curves obtained at 35 °C. The DBP derivative did not dissolve completely at this temperature, and as well as the other two derivatives, caused the cathodic current densities to decrease and the corrosion potential to shift. The most remarkable decrease in E_{corr} (about 230 mV) was caused by pyridine. Lower corrosion potentials involve higher passive currents. The electrochemical tests indicate that the compounds examined do not affect the pitting potential of the metal, which in this case depends upon the chloride concentration under the adopted experimental conditions. Rather they cause a negative shift in the metal corrosion potential. The most negative shifts are caused by those substances which inhibit the localized attack [12]. In solutions of these compounds, the difference $E_{\text{pit}} - E_{\text{corr}} = \Delta E$ is as an appropriate parameter to rate the inhibiting efficiency of the substances against localized corrosion. The added substances have no effect on the mechanism of dissolution of aluminium, but cause only inactivation of a part of the surface with respect to the corrosive medium.

The inhibition efficiency of the additives, *E*, and surface coverage, Θ, were determined from the corrosion current density obtained by the intersection of cathodic and anodic Tafel lines, according to the equation:

$$E = \Theta \times 100 = \frac{i_{\text{corr}} - (i_{\text{corr}})_{\text{inh}}}{i_{\text{corr}}} \times 100 \qquad (1)$$

where i_{corr} is the corrosion current density of the uninhibited solution, and $(i_{\text{corr}})_{\text{inh}}$ the corrosion current density of the inhibited solution. The values obtained are presented in Table 2. When the values of

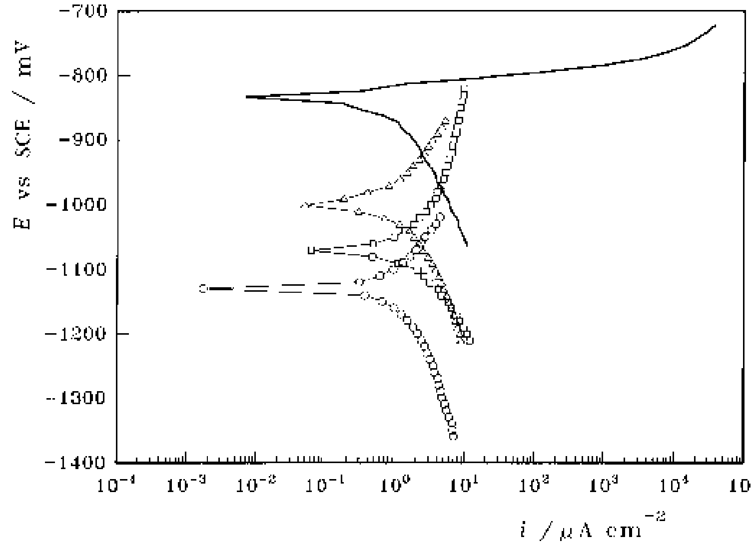


Fig. 2. Potentiodynamic polarization curves for Al in 2 M NaCl in the absence (——) and the presence of 1×10^{-3} M inhibitors at 35 °C. Key: (○) PYR, (□) COL and (△) DBP.

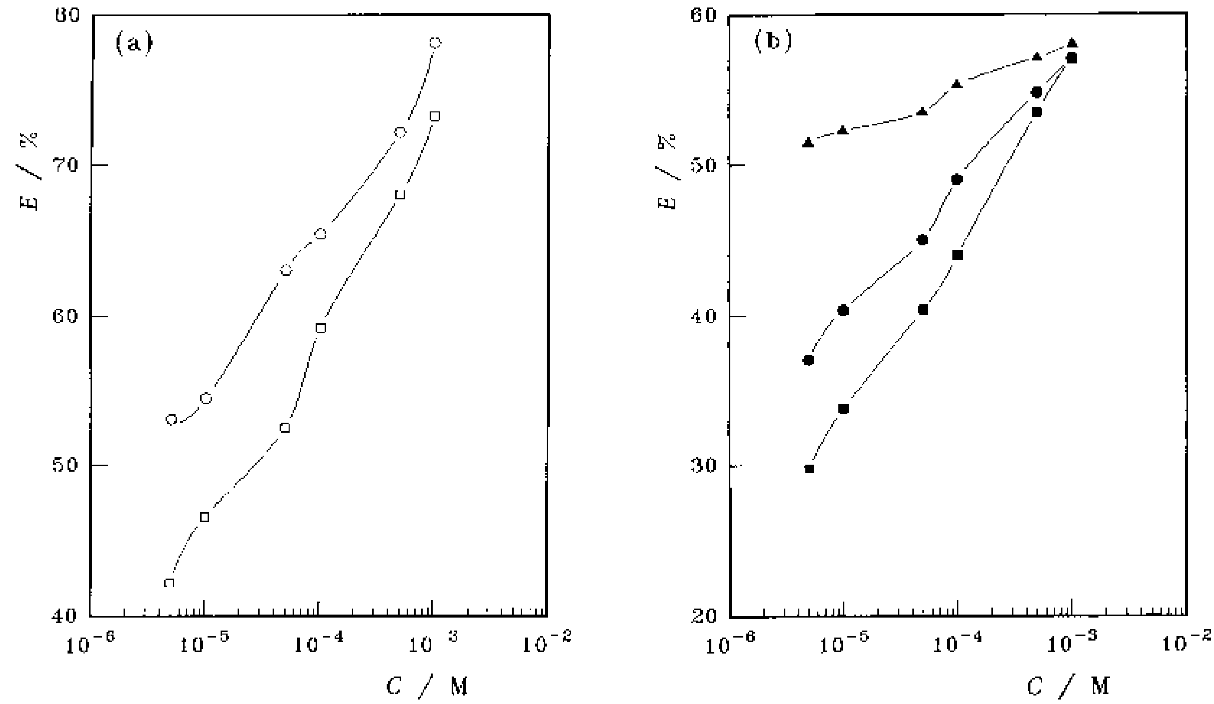


Fig. 3. Effect of the inhibitor concentration on the inhibition efficiency in 2 M NaCl solution at (a) 25 °C and (b) 35 °C. Key: (○, ●) PYR, (□, ■) COL and (▲) DBP.

Θ are determined from the corrosion current density and not directly from the results of measurements of the degree of coverage, it should be remembered that Equation 1 can be used only for the assumption that adsorbed molecules of the substance mechanically screen the coated part of the electrode surface and therefore protect it from the action of the corrosive medium [11].

The influence of inhibitor concentration on aluminium corrosion in a 2 M NaCl solution at 25 °C and 35 °C was investigated for all tested additives and the highest efficiency occurred at a concentration of 10^{-3} M (Fig. 3). Fig. 3a indicates that pyridine has a somewhat higher efficiency than collidine, while at 35 °C (Fig. 3b), and at the highest concentration, these two additives have almost the same efficiency. Pyridine and its derivatives are heterocyclic compounds containing nitrogen. This atom acts as an active adsorption centre at the metal surface. Molecules of additives examined adsorb at the aluminium surface by means of the free electron pair belonging to the sp^2 orbital, which gives pyridine its basic properties. The efficiency is lower at higher temperatures in both cases. The difference in efficiency of PYR and COL can be explained by the presence of methyl groups at positions 2, 4 and 6 in collidine. Although the electron donating characteristic of the methyl group makes the pyridine ring prone to electrophilic attack, the electron-attracting property of the pyridine ring on the methyl groups is much more prominent. Methyl groups at positions 2 and 4 of the pyridine ring are denuded of electrons by inductive and resonance effects of the nitrogen atom. A proton is easily lost from these activated methyl groups under suitable conditions [13]. Thus, the alkalinity is reduced and the capability of the metal surface to adsorb is reduced.

The efficiency of DBP, present even in the smallest quantities, exceeds 50% at 35 °C, and varies only slightly with increase in concentration. The explanation for the somewhat higher efficiency of DBP in comparison with PYR may lie in the –Br group introduced at positions 2 and 5. Owing to higher electronegativity [14] nitrogen attracts electrons from the outer shell of the bromine atom which increases the density of π-electrons of the nitrogen atom and the capability of adsorption to the positive metal surface.

The observed changes in Θ are shown in Figs 4–6 as functions of the logarithm of concentration of the examined organic compounds in a 2 M NaCl solution. The Freundlich isotherm [15] is

$$\Theta = KC^n \tag{2}$$

where $0 < n < 1$, or

$$\log\Theta = \log K + n\log C \tag{3}$$

K and C represent the equilibrium constants of adsorption and additive concentration, respectively.

A plot of $\log\Theta$ against $\log C$ would give a straight line of intercept $\log K$ if Equation 3 is applicable. These plots are shown for all compounds in Figs 4, 5 and 6, and are linear, which suggests that the Freundlich adsorption isotherm is obeyed.

The equilibrium constant of adsorption, K, is related to the standard free energy of adsorption, $\Delta G^\circ_{\text{ads}}$ by

$$K = \frac{1}{55.5}\exp\left(\frac{-\Delta G^\circ_{\text{ads}}}{RT}\right) \tag{4}$$

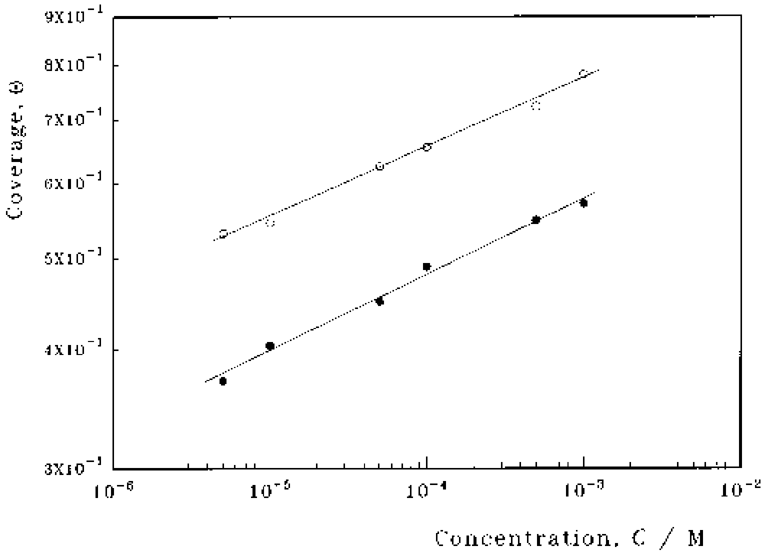


Fig. 4. Adsorption isotherms for PYR on Al in 2 M NaCl at 25 °C (○) and 35 °C (●).

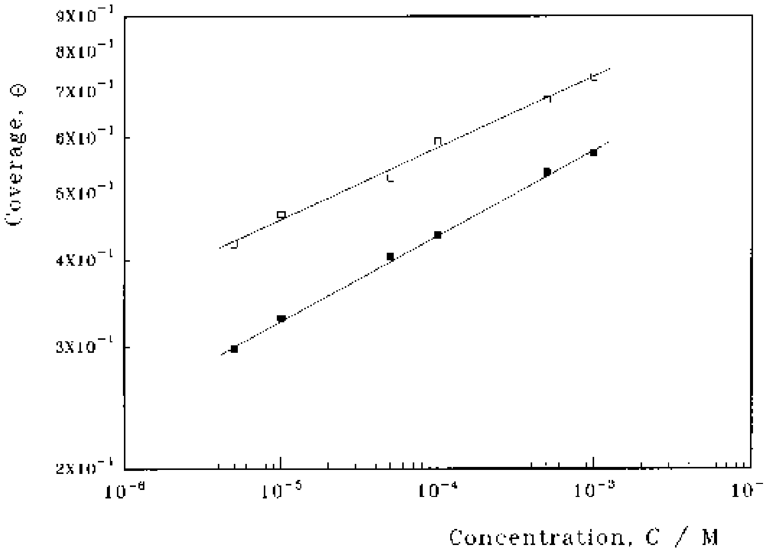


Fig. 5. Adsorption isotherms for COL on Al in 2 M NaCl at 25 °C (□) and 35 °C (■).

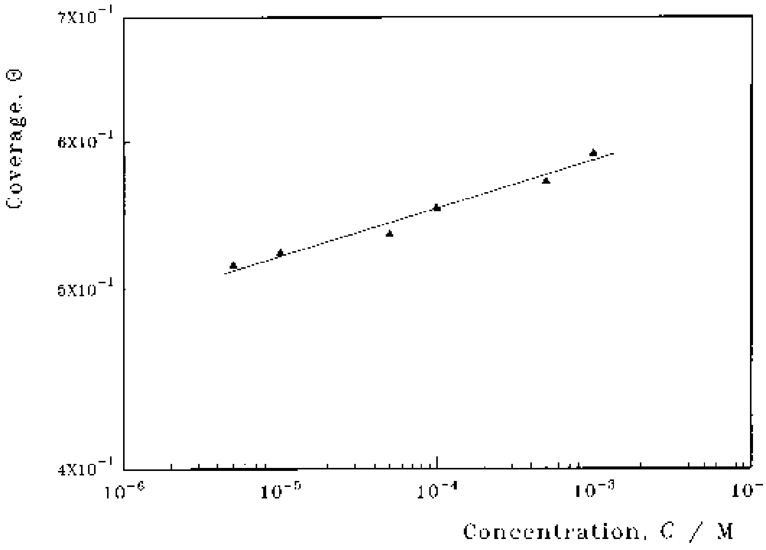


Fig. 6. Adsorption isotherm for DBP on Al in 2 M NaCl at 35 °C.

Table 3. Percentage inhibition efficiency, equilibrium constant and standard free energy for Al in 2 M *NaCl in presence of different inhibitors*

Inhibitor concentration / M		E / %		K / M^{-1}		$\Delta G^{\circ}_{\mathrm{ads}}$ / kJ mol^{-1}	
		25 °C	*35* °C	*25* °C	*35* °C	*25* °C	*35* °C
PYR	0.5×10^{-5}	53	37	2.27	1.70	−11.98	−11.64
	1.0×10^{-5}	55	40				
	0.5×10^{-4}	63	45				
	1.0×10^{-4}	65	49				
	0.5×10^{-3}	72	55				
	1.0×10^{-3}	78	57				
COL	0.5×10^{-5}	42	30	1.84	1.40	−11.46	−11.14
	1.0×10^{-5}	47	34				
	0.5×10^{-4}	53	40				
	1.0×10^{-4}	60	44				
	0.5×10^{-3}	68	54				
	1.0×10^{-3}	73	57				
DBP	0.5×10^{-5}	–	52	–	2.44	–	−12.57
	1.0×10^{-5}	–	52				
	0.5×10^{-4}	–	54				
	1.0×10^{-4}	–	55				
	0.5×10^{-3}	–	57				
	1.0×10^{-3}	–	58				

The value 55.5 in the above equation is the concentration of water in the solution in mol dm^{-3}. Table 3 lists the thermodynamic data obtained from the adsorption isotherms. The standard free energy of adsorption, $\Delta G^{\circ}_{\mathrm{ads}}$, calculated from the isotherm equation vary from −11.14 to −12.57 kJ mol^{-1} which means that the organic compounds are physically adsorbed on the surface. In such cases the physically adsorbed film is several monolayers thick [16]. The higher the values for the equilibrium constant and the standard free energy of adsorption, the better the inhibitive activity of the substance. The values decrease with increase in temperature.

4. Conclusion

The additives examined have shown an inhibitive effect on aluminium corrosion in a 2 M NaCl solution. The inhibitor efficiency presents a maximum value for an additive concentration of 1×10^{-3} M. The values obtained for the standard free energy of adsorption indicate physical adsorption. All the substances examined have been shown to decrease the cathodic current density. The compounds induce a decrease in aluminium corrosion potentials and do not affect the pitting potential. The inhibitive effect of the compounds studied decreases with increase in temperature. All the inhibitors follow the Freundlich isotherm.

References

[1] D. J. Duquette, 'Mechanism of Corrosion Fatigue of Aluminium Alloys', AGARD Conference Proceedings no. 316, Corrosion Fatigue (1982).

[2] Z. A. Foroulis and M. J. Thubrikar, *J. Electrochem. Soc.* **122** (1975) 1296.

[3] *Idem*, *Werkst. Korros.* **26** (1975) 350.

[4] S. Dallek and R. T. Foley, *J. Electrochem. Soc.* **123** (1976) 1775.

[5] T. H. Nguyen and R. T. Foley, *ibid.* **126** (1979) 1855.

[6] *Idem*, *ibid.* **127** (1980) 2563.

[7] B. W. Samuels, K. Sotoudeh and R. T. Foley, *Corrosion* **27** (1981) 321.

[8] P. M. Natishan, E. McCafferty and G. K. Hubler, *J. Electrochem. Soc.* **135** (1988) 321.

[9] J. G. Thomas, *in* 'Corrosion', vol. 2 (edited by L. L. Shreir) Newnes–Butterworths, London (1976), p. 18.3.

[10] G. Trabanelli, 'Corrosion Mechanisms' (edited by F. Mansfeld), Marcel Dekker New York Basel (1987), p. 119.

[11] M. Kaminski and Z. Szklarska-Smialowska, *Corr. Sci.* **13** (1973) 557.

[12] C. Monticelli, G. Brunoro and G. Trabanelli, Proceedings of the 7th European Symposium on Corrosion Inhibitors, Ann. Univ. Ferrara, N.S., Sez. V, suppl. 9 (1990).

[13] R. M. Acheson, 'An Introduction to the Chemistry of Heterocyclic Compounds', Interscience Publishers, London (1960) p. 174.

[14] R. T. Morrison and R. N. Boyd, 'Organic Chemistry', Allyn and Bacon, New York (1973), p. 22.

[15] B. B. Damaskin, O. A. Petrii and V. V. Batrakov, Adsorption of Organic Compounds on Electrodes', Plenum Press, New York (1971).

[16] K. M. Ralls, T. H. Courtney and J. Wulff, 'Introduction to Materials Science and Engineering', Wiley & Sons, New York (1976), p. 214.