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Butyl substituents in *n*-butylamine and their influence on mild steel corrosion inhibition in hydrochloric acid

J. M. BASTIDAS, J. DE DAMBORENEA, A. J. VÁZQUEZ

Centro Nacional de Investigaciones Metalúrgicas, CSIC, Avda. Gregorio del Amo 8, 28040-Madrid, Spain

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This paper describes a study of the influence of the butyl group as substituent in *n*-butylamine used as a mild steel corrosion inhibitor in hydrochloric acid solution. An inhibition mechanism is proposed. *n*-Butylamine, dibutylamine and tributylamine were studied in concentrations from 10^{-4} to 1 M and in the temperature range 278–308 K using electrochemical, gravimetric and surface roughness techniques. The three inhibitors adsorbed on the mild steel according to a Frumkin isotherm.

1. Introduction

Inhibiting the electrochemical corrosion of mild steel in acid media is of great scientific and economic importance. Amines are widely used as corrosion inhibitors in the steel making process and the inhibition mechanism is poorly understood [1].

In a recent paper the authors have shown that *n*-alkyl amines have good qualities for inhibiting the corrosion of mild steel in an acid medium [2]. It is known that low molecular weight amines are not good corrosion inhibitors and that if the atom attached to C in a ring (usually one or more hydrogen atoms) is replaced by substituent groups ($-NH_2$, $-NO_2$, –CHO or –COOH) inhibition usually improves [3].

The aim of this work is to study the influence of the butyl group, as substituent in *n*-butylamine, on the corrosion properties and inhibition mechanism of mild steel in a hydrochloric acid solution using different experimental techniques.

2. Method

The mild steel used had the following composition (weight %): 0.08 C, <0.02 P, 0.21 Mn, <0.02 S, 0.05 Si, with the balance in Fe. The specimens were mechanically polished with different grades of emery paper (down to 600), degreased with acetone and dried. The working electrode surface area was 10 cm^2. A 2 M HC1 acid was used as the corrosion test solution.

The inhibitors used were: n-Butylamine $C_4H_{11}N$ (BAM), dibutylamine $C_8H_{19}N$ (DBAM) and tributylamine $C_{12}H_{27}N$ (TBAM), Merck AR grades, in concentrations of 10^{-4}–1 M. The working temperatures were 278, 288, 298 and 308 K. The experimentation times were 2, 24, 48, 72 and 96 h, with a maximum of 48 h for the highest temperature tested.

Three electrochemical techniques were used: (i) polarization curves, (ii) polarization resistance (R_p) and (iii) electrochemical impedance spectroscopy (EIS). The first two techniques were performed using an electrochemical interface (Solartron 1286) in the three-electrode configuration. Tafel plots were obtained with a potential sweep rate of 5 mV s^{-1}, beginning at the rest potential (E_{corr}) up to ±60 mV. R_p measurements were obtained starting at the E_{corr} up to ±20 mV. EIS involved the imposition of 10 mV r.m.s. using a Solartron 1250 frequency response analyser connected to Solartron 1186 electrochemical interface. All the impedance measurements were made at the E_{corr}, using a logarithmic sweeping frequency of 5 steps $decade^{-1}$, the frequency range was from 10 kHz to 1 mHz. Gravimetric measurements (in triplicate) were carried out. Finally, the surface roughness was measured with a Kontron IBAS 2 image analyser. To do this the ratio L_t/L' was obtained, where L_t is the true length of the curve (of the corroded sample), and L' the projected length, measured along a selected reference direction. For additional information see [4].

3. Results

Figure 1 shows four typical polarization curves of mild steel immersed in 2 M HC1 acid solution inhibited with BAM 288 K. These curves are representative of those obtained for the other inhibitors used. The Figure describes a series of BAM concentrations whose curves are highly similar and one higher concentration in which the current density diminishes approximately by one order of magnitude. Table 1 summarizes anodic (β_a) and cathodic (β_c) slope values for the various experimental conditions of each inhibitor.

Figure 2 depicts a representative example of the polarization resistance results for the three amines studied as a function of experimentation time. The $1000(R_p)^{-1}$ parameter is directly related with the corrosion rate. This Figure refers to mild steel in 2 M HC1 acid solution in the presence of TBAM.

Figure 3 shows typical Nyquist plots for mild steel in 2 M HC1 acid solution obtained at different times

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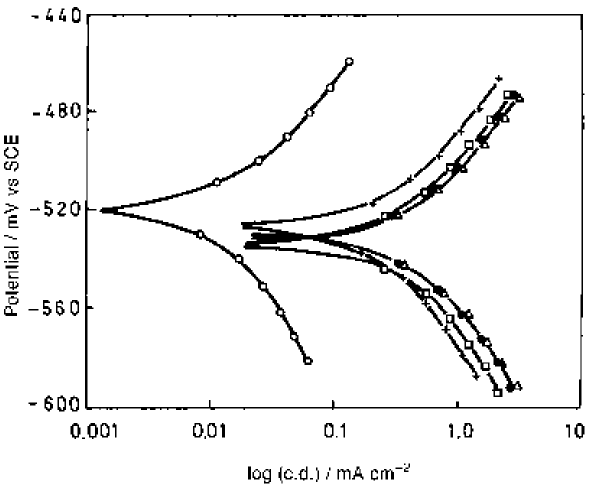

Fig. 1. Polarization curves for mild steel in 2 M HCl acid solution inhibited with butylamine (BAM) at 288 K. Concentration: (●) 1×10^{-3}, (△) 1×10^{-2}, (□) 5×10^{-2}, (+) 1×10^{-1} and (○) 1 M.

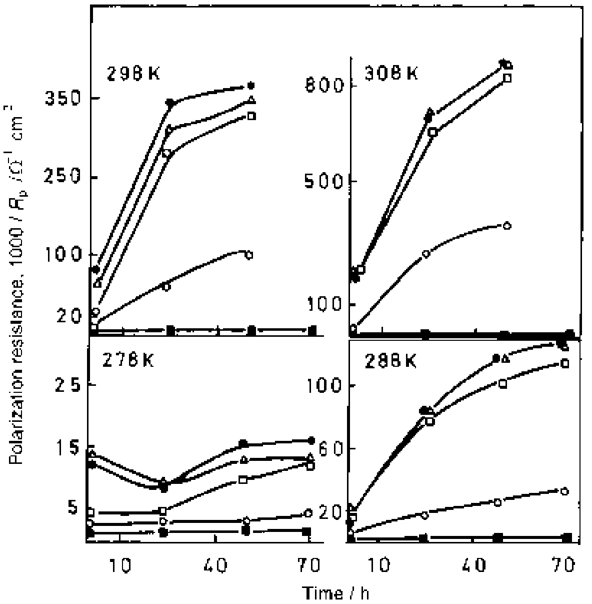

Fig. 2. Polarization resistance against time at different temperatures for mild steel in 2 M HCl acid solution inhibited with tributylamine (TBAM). Concentration: (●) 5×10^{-4}, (△) 1×10^{-3}, (□) 5×10^{-3}, (○) 5×10^{-2} and (■) 1 M.

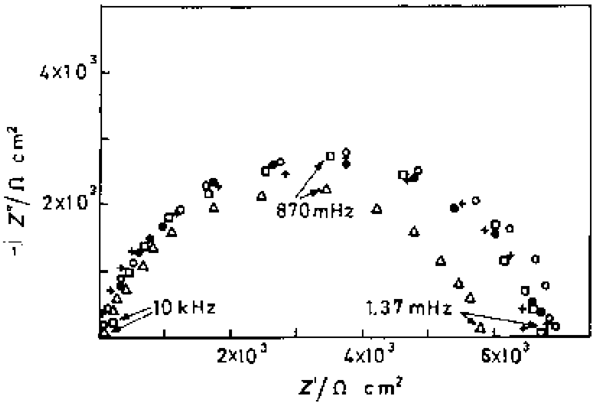

Fig. 3. Nyquist plots for mild steel in 2 M HCl acid solution inhibited with 1 M concentration of tributylamine (TBAM) at 288 K. Time: (●) 2, (+) 24, (△) 48, (○) 72 and (□) 96 h.

when adding TBAM with a concentration of 1 M at 288 K. As can be seen, the Nyquist plot always appears as a semicircle, this also being the case when the other two inhibitors studied, BAM and DBAM, were used.

Figure 4 shows the inhibitor concentration against mild steel corrosion rate in 2 M HC1 acid solution at 288 K. The corrosion rate of mild steel increases as the inhibitor concentration decreases.

Figure 5 shows the dependence of inhibitor efficiency on the temperature when different amounts of amines are added. The percentage inhibitor efficiency (*PIE*) is given $PIE = [\,(CR - CR_o / CR] \times 100$, where CR and CR_o are the corrosion rate in the absence and presence of inhibitor, respectively. In general, the PIE decreased as the temperature increased, this influence being particularly intense at low inhibitor concentrations. The three amines tested proved to be highly efficient when high concentrations were added.

4. Discussion

The polarization curves indicate that the values found for β_a are smaller than those found for β_c. In the case of the highest concentration β_c reaches a value of 111 mV dec^{-1} for BAM, 97 mV dec^{-1} for DBAM, and 157 mV dec^{-1} for TBAM (see Table 1).

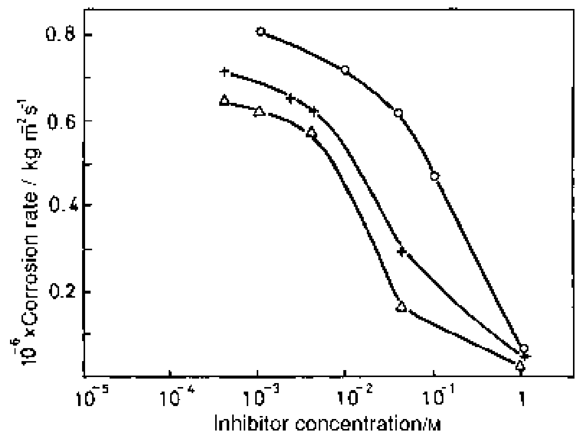

Fig. 4. Corrosion rate of mild steel against inhibitor concentration at 288 K. Key: (○) BAM, (+) DBAM and (△) TBAM.

Table 1. Anodic (β_a) and cathodic (β_c) slopes (mV dec^{-1}) from polarization curves for mild steel in 2 M HCl solution in presence of inhibitor

Concentration / M	*n-Butylamine (BAM)*		*Dibutylamine (DBAM)*		*Tributylamine (TBAM)*	
	β_a	β_c	β_a	β_c	β_a	β_c
1×10^{-4}	79	81	77	78	73	75
5×10^{-4}	78	80	76	77	70	75
1×10^{-3}	79	81	78	79	72	77
2.5×10^{-3}	78	78	77	77	70	76
5×10^{-3}	80	81	78	79	68	88
1×10^{-2}	80	82	79	78	72	85
5×10^{-2}	79	80	71	83	68	78
1×10^{-1}	76	86	74	80	69	83
1	74	111	70	97	60	157

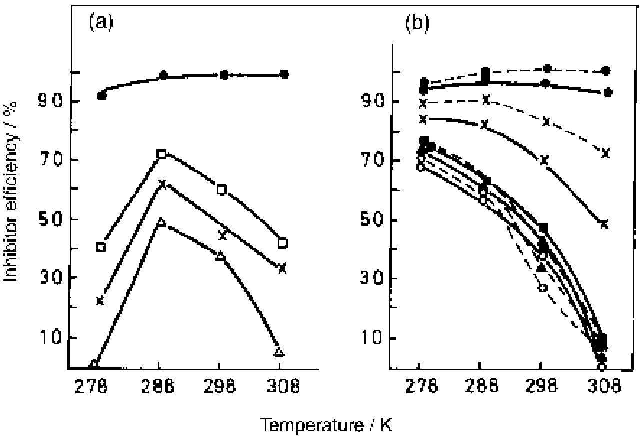

Fig. 5. Inhibitor efficiency against temperature. (a) Butylamine; (b) dibutylamine (——) and tributylamine (- - - -). Concentration: (○) 5×10^{-4}, (▲) 2.5×10^{-3}, (■) 5×10^{-3}, (△) 1×10^{-3} and (×) 5×10^{-2}, (□) 0.1 and (●) 1 M.

The fact that the β_c are slightly higher when the concentration increases suggests a cathodic action of the inhibitor. However, these differences are so small that their nature is not significant. This could be interpreted as an action of mixed inhibitor control over the electrochemical semireactions.

Figure 2 shows that for the smallest concentrations of TBAM studied there is a rapid increase in the corrosion rate which after 24 h seems to be stabilized. In contrast, for 1 M TBAM concentration the corrosion rate remains practically constant from the beginning of the experiment.

The Nyquist plot in Fig. 3 shows that the mild steel–TBAM system is under charge transfer resistance (R_{ct}) control with no existence of loops that might indicate inductive behaviour, from which it could possibly be inferred that the inhibitor is selectively adsorbed in specific places on the metal surface.

According to this inhibition mechanism the amine could be adsorbed in active places referring to either of the semireactions or even referring to both, thus causing the corrosion rate to drop. The corrosion reaction is affected by the existence of less active points blocked by the inhibitor.

This behaviour can be ascertained both from analysis of the polarization curves (Fig. 1) and from the values of the capacitance of the organic coating (C_{oc}). This has been roughly estimated, since the semicircles are not centred on the real axis, from the relationship $C_{oc}=(R_{ct}\omega_c)^{-1}$ where the characteristic angular frequency: $\omega_c=2\pi f_c$, f_c is the frequency on the Nyquist plot at which the imaginary component is a maximum (Fig. 3). In the first case, the polarization curves change towards lower values of current density without the appearance of a clear modification in the value of the Tafel slopes, which remain practically constant (~76 mV dec^{-1}).

Likewise, in the second case, the C_{oc} is located between 20–30 μF cm^{-2} for all cases, which does not indicate the formation of a continuous film on the metal surface. In general, for the highest inhibitor concentration tested (1 M) the C_{oc} value was ~20 μF cm^{-2} for the entire time. On the other hand, for lower inhibitor concentrations, C_{oc} increased with experimentation time. For example, for 5×10^{-3}–10^{-4} M concentration of TBAM between 2–48 h experimentation, a linear increase in C_{oc} value was obtained from 20 to 200 μF cm^{-2}. This apparent contradiction may be explained by an increase in the metal surface area.

Figure 6(a) depicts the results of mild steel dissolution, expressed as the surface roughness parameter (SRP) against the inhibition efficiency of BAM, at 308 K and 72 h immersion time. It can be seen that as SRP increased the inhibition efficiency decreased. Finally, Fig. 6(b) shows experimental evidence of this

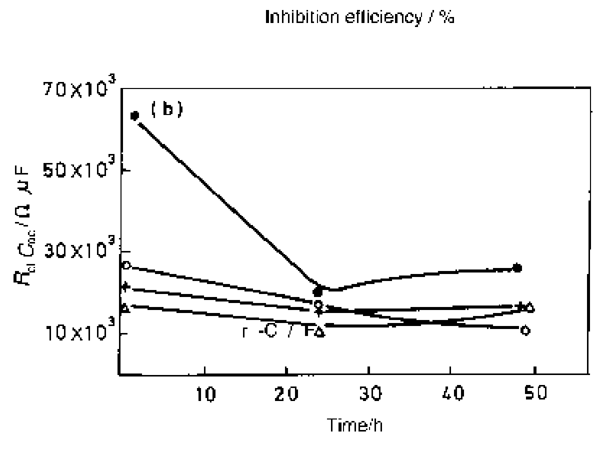

Fig. 6. (a) Surface roughness parameter against inhibition efficiency for mild steel in 2 M HCl acid solution in presence of butylamine (BAM) and (b) $R_{ct}C_{oc}$ against time for mild steel in 2 M HCl acid solution inhibited with TBAM. Conditions: (a) 308 K, 72 h; (b) temperature: (●) 278, (+) 288, (△) 298 and (○) 308 K.

increase in the metal surface with time; R_{ct} was obtained by measuring the diameter of the semicircle in the Nyquist plots (Fig. 3). Except for the lowest temperature tested, the $R_{ct}C_{oc}$ product is independent of time (see Fig. 6(b)).

The decrease in the corrosion rate by means of a mechanism of selective adsorption does not appear, however, to the same extent in each of the inhibitors tested. As may be seen in Fig. 4 the variation in the corrosion rate with inhibitor concentration is different for each case, except for the highest concentrations.

Figure 7 (solid line) shows isotherm plots, that is, the degree of surface coverage (θ) against the concentration of the inhibitor. The θ was calculated from the inhibitor efficiency relationship: $(CR-CR_o)/CR$. The Frumkin isotherm can be written [5] as $kc=[\theta/(1-\theta)]\ [\exp(-2a\theta)]$, where c is the concentration of inhibitor, a is the interaction parameter, k is the equilibrium constant of the adsorption reaction given by $k=(1/55.5)\ [\exp(-\Delta G^{\circ}_{ads}/RT)]$, the value 55.5 is the concentration of water in the solution in mol dm^{-3}, ΔG°_{ads} is the adsorption energy, R is the universal gas constant, and T the absolute temperature.

The Frumkin isotherm equation adopts the form [5]: $y=c/c_{\theta=0.5}=[\theta/(1-\theta)]\ \{\exp[a(1-2\theta)]\}$ where y is the relative concentration: $y=c/c_{\theta=0.5}$. Figure 7 (dotted line) shows the variation in θ against y. The attraction constant, a, deduced from the latter equation is given by $a=[2.3/(1-2\theta)]\ \log[y(1-\theta)/\theta]$. The attraction constant was determined for each dotted line in Fig. 7. The values obtained were 0.88 for BAM, 1.33 for DBAM and 0.67 for TBAM.

The positive sign of the constant a, indicating highly attractive lateral interaction forces between the adsorbed molecules [6], contributes to the vertical adsorption of organic molecules, and the sigmoidal shape of the adsorption isotherm (Fig. 7, solid line) confirms the applicability of Frumkin's equation to describe the adsorption process [7].

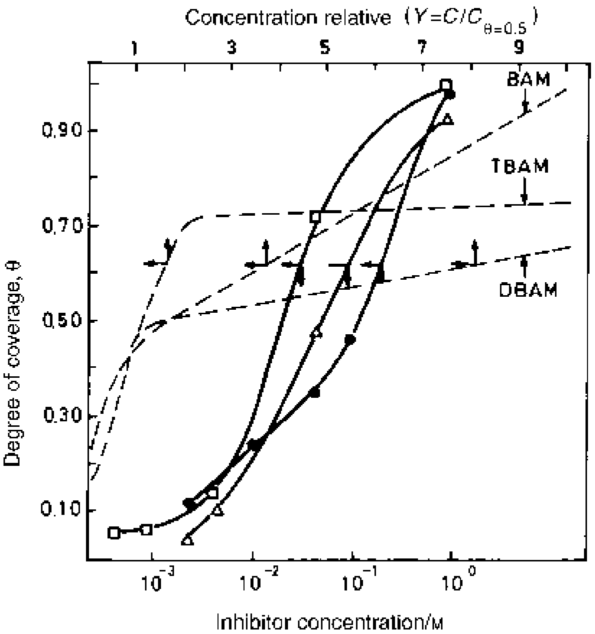

Fig. 7. Isotherm plots (solid line) and relative concentration, $y=c/c_{\theta=0.5}$, (dotted line) against inhibitor concentration for mild steel in 2 M HCl acid solution at 308 K. Key: (●) BAM, (△) DBAM and (□) TBAM.

The capacitance of the organic coating formed on mild steel is given by $C_{oc}=\epsilon\epsilon_o A(d)^{-1}$, where ϵ is the dielectric constant of the amine, $\epsilon_o=8.85\times10^{-14}$ F cm^{-1} is the dielectric constant of a vacuum, $A=1$ cm^2 is the exposed area of the mild steel test electrode and d is the thickness of the organic coating. For a value of C_{oc} of about 10^{-6} F cm^{-2} and a mean value for ϵ of 2 [8] the resulting thickness was 17.7×10^{-8} cm, which agrees very well with the value of the length of *n*-butylamine (~1 nm). This result corroborates the vertical adsorption pointed out above.

Figure 5 expresses the positive influence of the butyl group as substituent on the inhibition efficiency of the base molecule, BAM. In order to obtain a similar order of inhibition efficiency the BAM concentration has to be higher than DBAM and TBAM. The explanation of these results may be twofold. On the one hand, in this type of small length chain it seems apparent that the degree of substitution carries with it an increase in the electron density of the nitrogen atom responsible for adsorption on the metal, while on the other hand, as has been pointed out above, it is possible that side interactions may occur between the substituted groups which may screen wide areas of the metal surface, thus preventing a generalized attack [1].

Figure 8 depicts Arrhenius plots for mild steel immersed in 2 M HCl acid in the presence of different BAM and TBAM concentrations. The DBAM showed similar behaviour (data not included). The plots obtained are straight lines and the slope of each straight line gives its activation energy. Table 2 summarizes E_a values for the three amines tested.

The negative values of E_a indicate the spontaneous adsorption of organic compounds on the surface of the electrode. Thus, the increase in E_a may be interpreted as the physical adsorption which occurs in the first stage [9]. It can be seen that for a wide range of inhibitor concentrations E_a is higher in the presence

Table 2. Activation energy (E_a) of mild steel in presence of inhibitor

Concentration / M	*Activation energy, E_a, / kJ mol^{-1}* *n-Butylamine (BAM)*	*Dibutylamine (DBAM)*	*Tributylamine (TBAM)*
1×10^{-4}	70	93	90
5×10^{-4}	65	94	90
1×10^{-3}	53	92	93
2.5×10^{-3}	58	97	90
5×10^{-3}	60	97	93
1×10^{-2}	59	93	85
5×10^{-2}	59	89	83
1×10^{-1}	58	82	80
1	22	70	27

Activation energy for the blank solution (2 M HCl) is 70 kJ mol^{-1}

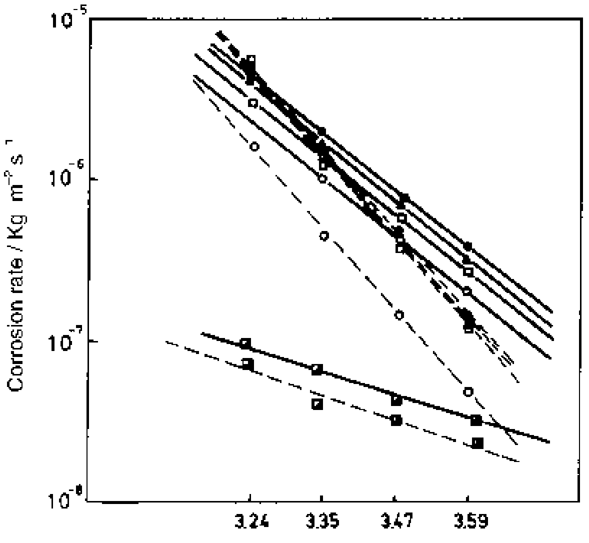

Fig. 8. Arrhenius plots for mild steel in 2 M HCl acid solution inhibited with BAM (——) and TBAM (- - - -). Concentration: (●) 1×10^{-3}, (△) 1×10^{-2}, (□) 5×10^{-2}, (○) 0.1 and (◪) 1 M.

of DBAM and TBAM inhibitors (83–97 kJ mol^{-1}) than in the absence of inhibitor (70 kJ mol^{-1}). In the presence of BAM E_a is lower (53–70 kJ mol^{-1}). A drop in E_a was found with the highest inhibitor concentration studied. Thus, the corrosion rate can be expressed by the sum of two constants: K_1 and K_2 which are the rate constants for the uninhibited reaction and completely covered surface, respectively [10]. These data agree with those reported for mild steel inhibited with *n*-alkyl amine with 6–12 carbon atoms in the chain [2].

5. Conclusions

The inhibition efficiency increased as a result of the beneficial influence of the base molecule of butylamine, when combined with one- or two- butyl groups. The inhibition efficiency decreased with increase in temperature.

The polarization results indicate that the amines studied acted as mixed inhibitors.

The inhibition mechanism of the three amines studied on mild steel in hydrochloric acid solution seems to be that of selective adsorption on active centres. The three amines tested were chemically adsorbed vertically on the mild steel surface according to a Frumkin isotherm.

6. References

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

[2] J. de Damborenea, J. M. Bastidas and A. J. Vázquez, *Electrochim. Acta*, in press.

[3] U. R. Evans, 'The Corrosion and Oxidation of Metals, Second Supplement', E. Arnold, London (1976) p. 104.

[4] E. E. Underwood, *in* 'Practical Applications of Quantitative Metallography' (edited by J. L. McCall and J. H. Steele, Jr.), ASTM STP 839, Philadelphia (1984) p. 170.

[5] B. B. Damaskin, O. A. Petrii and V. V. Batrakov, 'Adsorption of Organic Compounds on Electrodes', Plenum Press, New York (1971) p. 67.

[6] S. Muralidharan, K. L. N. Phani, S. Pitchumani, S. Ravichandran and S. V. K. Iyer, *J. Electrochem. Soc.* **142** (1995) 1478.

[7] R. Zvauya and J. L. Dawson, *J. Appl. Electrochem.* **24** (1994) 943.

[8] R. C. Weast (editor), 'Handbook of Chemistry and Physics', 66th edn CRC press, Boca Raton, FL (1985), p. E–50.

[9] T. Szauer and A. Brandt, *Electrochim. Acta* **26** (1981) 1219.

[10] O. L. Riggs, Jr and R. M. Hurd, *Corrosion* **23** (1967) 252.