

Evaluation of the inhibition efficiency of acetylenic halo-derivatives by electrochemical methods and solution analysis

A. FRIGNANI, C. MONTICELLI, M. TASSINARI, G. TRABANELLI

Corrosion Study Centre "A. Daccò", Chemistry Department, University of Ferrara, 46 L. Borsari, 44100 Ferrara, Italy

Received 23 December 1993; revised 15 August 1994

The behaviour of some 3-methyl-1-butyne halo-derivatives towards Armco iron corrosion in 0.5 M H_2SO_4 was examined by the analysis of dissolved iron and electrochemical methods. Their inhibitive performance was determined in relation to the introduced halogen atom with respect to the duration of the tests and temperature. At the same time, these effects were compared to those of 1-octyn-3-ol. In general, the results of the electrochemical methods were found to be in good agreement with those of solution analysis. The possibility of obtaining reliable corrosion data from electrochemical impedance spectroscopy measurements by simply applying the Stern–Geary equation is discussed.

1. Introduction

The influence exerted on the inhibitive performances of some 3-methyl-1-butyne (3M1B) derivatives by the substitution of the acetylenic hydrogen atom with halogen atoms (chlorine, bromine, iodine) was investigated. Their inhibition efficiencies are compared to that of 1-octyn-3-ol (OCT), a potential inhibitor for practical applications.

The actual corrosion rate of Armco iron in 0.5 M H_2SO_4 in the presence of the various compounds was evaluated by an analytical determination of dissolved iron as a function of time (solution analysis: SA). Subsequently, the corrosion process was studied by various electrochemical techniques (polarization curves: PC; electrochemical impedance spectroscopy: EIS). A comparison of the different results was carried out in order to verify the reliability of EIS measurements in the presence of inhibitors acting through the formation of a surface polymeric film [1–9].

In our laboratory EIS was applied to evaluate the inhibitive effects towards Armco iron corrosion in 0.5 M H_2SO_4 at 25°C of various organic compounds, acting through a surface adsorption process, (quaternary ammonium derivatives [10], or S-containing additives [11, 12]). The inhibition performances and the mechanism of action of some acetylenic compounds, mainly propargyl alcohol (PA) have already been studied by EIS [13–18].

2. Experimental details

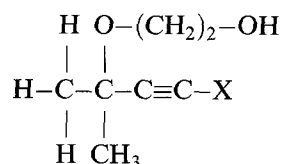
The electrodes were Armco iron cylinders ($\sim 3 \text{ cm}^2$ of exposed lateral surface), which were mechanically prepared and then heat treated at 700°C \times 14 h in an argon atmosphere. Before testing, their surfaces

were prepared using emery papers from 150 to 600 grit.

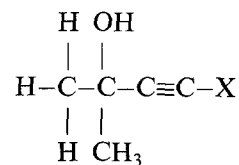
The test solution was nitrogen gas purged 0.5 M H_2SO_4 , usually at 70°C, owing to the increased film forming tendency of acetylenic derivatives at elevated temperatures.

The following substances were tested as inhibitors.

(i) 3-methyl-1-butyne (3M1B) derivatives:



where X = H (H1); Cl (C1); Br (B1); I (I1).



where X = Cl (C2); Br (B2); I (I2).

(ii) 1-octyn-3-ol (OCT), as a reference due to its use in industrial applications [19].

Potentiodynamic (0.5 mV s^{-1}) polarization curves were recorded by means of an AMEL Metalloscan, and EIS spectra by means of a Solartron apparatus (FRA 1250, EI 1286; five frequencies per decade from 10^4 to 10^{-2} Hz; 10% standard deviation). The latter tests were performed in the linear conditions of the electrochemical system, by applying a sinusoidal perturbation of $\pm 5 \text{ mV}$ r.m.s. amplitude.

The iron corrosion rates were determined by analysis of dissolved iron as a function of time (SA), by the extrapolation of the Tafel lines and finally by impedance measurements (EIS) by applying the Stern–Geary (S–G) equation [20–22].

Table 1. Comparison of the corrosion rates of Armco iron, electrochemical parameters and percentage i.e.'s of the various acetylenic compounds in 0.5 M H₂SO₄ at 70° C, obtained with the different techniques

Additive	Conc. /mM	SA		PC		EIS					
		i_{corr} / $\mu\text{A cm}^{-2}$	i.e. /%	b_a /mV (dec) ⁻¹	b_c /mV (dec) ⁻¹	B /mV	i_{corr} / $\mu\text{A cm}^{-2}$	i.e. /%	R_t / $\Omega\text{ cm}^2$	i_{corr} / $\mu\text{A cm}^{-2}$	i.e. /%
none	—	5500	—	40	190	14	5500	—	5	2800	—
H1	1	3880	29.5	30	190	11	4000	27.3	6.8	1618	42.2
C1	1	2600	52.7	40	180	14	3200	41.8	12	1170	58.2
B1	1	1040	81.1	40	180	14	600	89.1	28	500	82.1
I1	1	45	99.2	150	180	36	10	99.8	1740	21	99.3
C2	1	2812	48.9	20	125	7.5	3000	45.5	5.2	1442	48.5
B2	1	1580	71.3	30	125	10.5	1800	67.3	11	955	65.9
I2	1	30	99.5	110	120	25	15	99.7	3360	7.4	99.7
OCT	0.5	723	86.9	75	~∞	33	32	99.4	1362	24	99.1
OCT	1	256	95.3	65	~∞	28	29	99.5	1750	16	99.4
OCT	10	245	95.5	30	~∞	13	25	99.6	1585	8	99.7

3. Results

3.1. Solution analysis

In the inhibited solutions, the iron dissolution rates diminished during the first hours of immersion, probably owing to the formation of the protective polymeric surface film. An evident coloured film formation was, in fact, optically observed on iron specimens after some hours following their immersion in the acid solution inhibited by the iodo-derivatives. After a variable time interval, depending on the type and concentration of the additive (for instance 4–6 h for 1 mM 3M1B derivatives, 2–3 h for 1 mM OCT), an almost constant value of dissolution rate was attained.

The corrosion rate values from SA, and the corresponding inhibiting efficiencies, shown in Tables 1 and 2, refer to conditions of full inhibitive performance.

H1 showed poor inhibitive effects, but the substitution of the acetylenic hydrogen atom with chlorine, bromine and, particularly, iodine, in that sequence, improved the inhibitive characteristics of the molecules. In fact, the iron dissolution rate in the uninhibited acid solution (5500 $\mu\text{A cm}^{-2}$) was decreased to 45 (I1) or 30 (I2) $\mu\text{A cm}^{-2}$ at 1 mM additive concentration, and the corresponding inhibiting efficiencies (i.e.) were higher than 99%.

Table 2. Comparison of the % i.e. values at various temperatures from SA and EIS measurements

	50° C		25° C	
	SA	EIS	SA	EIS
1 mM H1	—	—	26.8	22.5
1 mM C2	35.4	31.3	57.4	47.5
1 mM B2	70.4	50	60.4	53.5
1 mM I2	86.7	97.4	73.6	70.8
1 mM OCT	86.4	99.5	—	—
0.3 mM OCT	—	—	89.8	98.8

* Iron corrosion rates/ $\mu\text{A cm}^{-2}$ in 0.5 M H₂SO₄: SA 1014; EIS: 1000 at 50° C and SA: 235; EIS: 178, at 25° C.

OCT did not afford a protective action as high as iodo-derivatives, although it was highly efficient and its action persistent. Its efficiency did not greatly improve by increasing the concentration from 1 to 10 mM.

By decreasing the temperature, similar trends were observed (Table 2), although lower efficiencies were obtained. In these conditions, longer induction times were experienced, in the case of the most efficient compounds also.

3.2. Polarization curves

The polarization curves showed that the inhibiting action of the tested acetylenic compounds improved as a function of time (from 2 to 24 h). The data in Table 1 and Figs 1 and 2 refer to 24 h testing.

Among 3M1B derivatives, only the iodo-compounds markedly inhibited the cathodic hydrogen

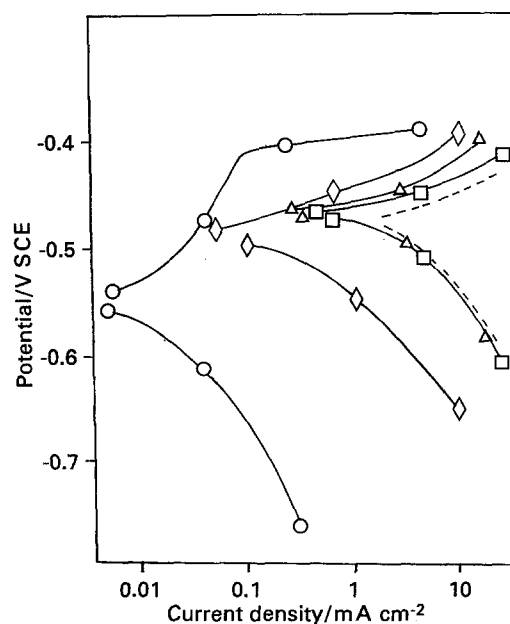


Fig. 1. Polarization curves of Armco iron in 0.5 M H₂SO₄ at 70° C, in the presence of: (□) 1 mM H1; (△) 1 mM C1; (◇) 1 mM B1; (○) 1 mM I1, after 24 h immersion. Blank test after 3 h (— — —).

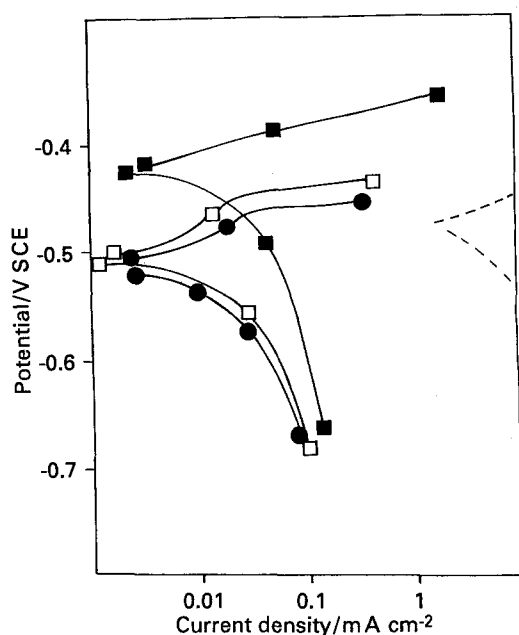


Fig. 2. Polarization curves of Armco iron in 0.5 M H_2SO_4 at 70°C, in the presence of OCT. OCT concentration: (●) 0.5 mM; (□) 1 mM; (■) 10 mM.

evolution reaction (h.e.r.), and the calculated values of the cathodic Tafel slopes (b_c) were similar, or close to, that of the blank test ($180\text{--}120\text{ mV}(\text{dec})^{-1}$, Fig. 1). Moreover, with these derivatives, the anodic reaction was inhibited according to the following sequence of increasing efficiency. $\text{H} < \text{C} < \text{B} \ll \text{I}$. The corresponding anodic Tafel slopes were usually close to that of the uninhibited solution ($\sim 40\text{ mV}(\text{dec})^{-1}$) but the most efficient compounds (I1 and I2), gave 150 and 110 $\text{mV}(\text{dec})^{-1}$, respectively.

OCT also considerably inhibited the HER, and, at

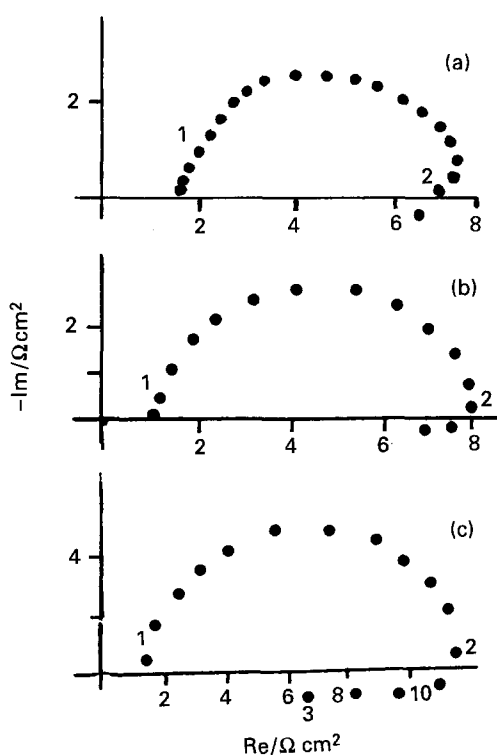


Fig. 3. Impedance diagrams of Armco iron in 0.5 M H_2SO_4 at 70°C: (a) blank test after 1 h, (b) +1 mM H1, after 24 h and (c) +1 mM B2, after 24 h. Frequency: (1) 1 kHz; (2) 1 Hz; (3) 10 mHz.

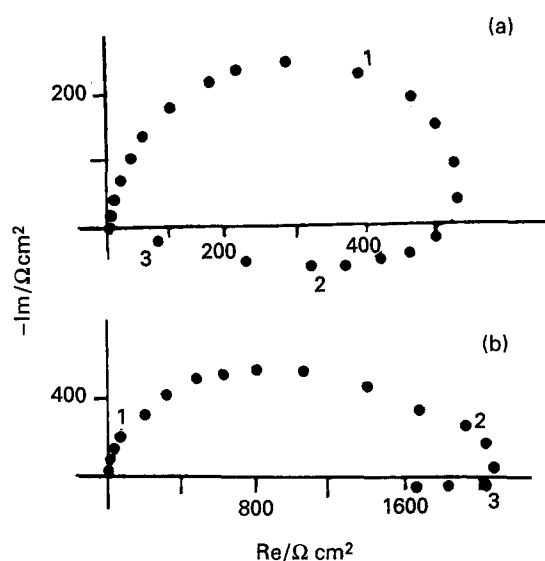


Fig. 4. Examples of impedance diagrams of Armco iron in 0.5 M H_2SO_4 at 70°C, in the presence of 1 mM H1. Test time: (a) 6 h and (b) 23 h. Frequency: (1) 100 Hz; (2) 1 Hz; (3) 10 mHz.

70°C, after 24 h, cathodic current density values almost independent of concentration were recorded (Fig. 2), with slopes of the cathodic Tafel lines tending to infinity. This additive also inhibited the anodic reaction, although not as efficiently as the iodo-compounds did, and b_a values of about $70\text{ mV}(\text{dec})^{-1}$ were calculated.

It must be emphasized that all the tested acetylenic derivatives inhibited the anodic reaction within a narrow potential range, beyond which a region of unpolarizability (due to the inhibitor desorption process) followed, depending on the type and concentration of the additives.

3.3. Electrochemical impedance spectroscopy

Some examples of complex plane impedance diagrams, obtained at 70°C, are reported in Fig. 3 (uninhibited solution, and H1 or B2 inhibited solutions), Fig. 4 (H1 inhibited) and Fig. 5 (OCT inhibited). Small differences were found between the blank and H1, C1, C2, B1 or B2 spectra, whereas much higher differences were displayed in the case of iodo-compounds or OCT.

The impedance spectra of 3M1B derivatives were characterized by one capacitive semicircle, although, in the case of iodo-derivatives, particularly at long testing times, very depressed capacitive arcs were recorded. The following sequence of increasing additive efficiency was found valid for both series of 3M1B derivatives: $\text{H} < \text{C} < \text{B} \ll \text{I}$.

In the presence of OCT two capacitive loops are observed, even though poorly resolved at short immersion times.

The evolution of the protective characteristics of the most efficient inhibitors was clearly shown by the noticeable increase in the intercept of their capacitive loops with the real axis as a function of time (Figs 4 and 5). For instance, in the case of I1, this intercept increased from ~ 500 (6 h) to $\sim 1800\ \Omega\text{ cm}^2$ (23 h). In

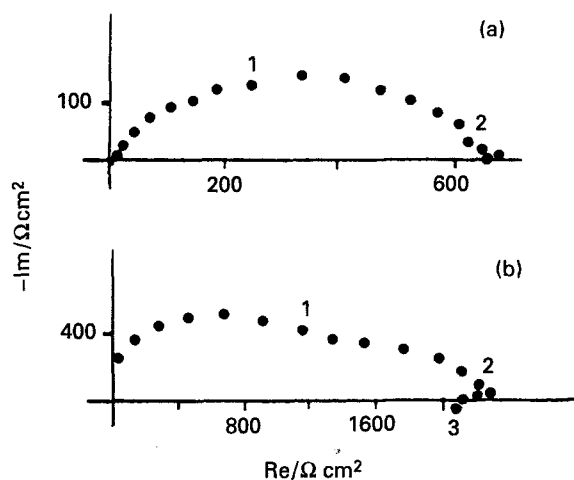


Fig. 5. Example of impedance diagrams of Armco iron in 0.5 M H_2SO_4 at 70°C, in the presence of 1 mM OCT. Test time: (a) 3 h and (b) 24 h. Frequency: (1) 1 kHz; (2) 1 Hz; (3) 10 mHz.

the case of OCT, its concentration (0.5; 1; 10 mM) did not markedly affect this steady-state (24 h) value.

The above trends were confirmed by tests performed at lower temperatures. In fact, iodo-compounds again presented much wider capacitive loops than the blank test or H1, C2, B2 ones, and their dimensions increased as a function of immersion time; with OCT, two well defined capacitive loops were still observed at 25°C, at a concentration as low as 0.3 mM, after 24 h immersion.

Moreover, the obtained impedance spectra showed a low frequency pseudo-inductive loop. This loop, also mentioned in the literature, was poorly reproducible in our case; as a rule, its extension tended to decrease by using the most efficient inhibitors, or by increasing the additive concentration or testing time.

Epelboin *et al.* have attributed the inductive loops found for PA [14] and for 2-butyne-1,4-diol [13] in H_2SO_4 solutions to the relaxation of the inhibitor coverage, whereas Growcock *et al.* [16] have ascribed the loop found in concentrated HCl solutions inhibited by OCT mainly to the amplitude of the applied potential perturbation.

4. Discussion

The efficiency of the tested 3M1B derivatives towards iron acid corrosion is improved by the substitution of the acetylenic hydrogen atom with chlorine, bromine or iodine, in that sequence, or by increasing the testing temperature. At 1 mM concentration, the iodo-compounds are more efficient than OCT. The chain length in position 3 plays a minor role.

Like other acetylenic compounds, the inhibitive performances of these derivatives have to be related to the formation of a polymeric surface film on iron, and this is particularly evident with I1, I2 or OCT. In the case of 3M1B derivatives this polymeric film acts through a blocking effect of the active metal surface, whereas, in the case of OCT, it acts as a physical barrier to H^+ discharge.

For the evaluation of the iron corrosion rates from

EIS data, the S-G equation was applied ($i_{corr} = (ba.bc)/((ba + bc)2.3R)$, R , considering the poor reproducibility of the pseudo-inductive loop, was taken as the intercept of the capacitive loop with the real axis (defined as R_t , the charge transfer resistance). This procedure was introduced by Epelboin *et al.* to evaluate the inhibition efficiency of PA in sulphuric solutions [14]. However, with certain inhibitors, Lorenz and Mansfeld found an empirical correlation between the iron corrosion rate and R_t , whereas, with an onium compound (TPBP⁺: triphenylbenzylphosphonium-chloride) the S-G equation was satisfied by R_p [15].

In the present case the trends of iron corrosion rates from EIS measurements agree with those from SA determinations, although the values from the former method tend to be lower than those of the latter with 3M1B derivatives, and strikingly lower with OCT. Such a trend was also observed at an OCT concentration as low as 0.3 mM, at 25°C.

With the former compounds, the S-G equation may be used to evaluate the iron corrosion rates with an acceptable approximation [23], although some uncertainty exists about the correct B value introduced into the S-G equation, since the evaluation of b_a can be very approximate owing to the tendency of the inhibitor to desorption, even at low anodic overpotentials, as experienced also with other organic compounds [12, 15]. Nevertheless, in the case of OCT the marked differences found between the EIS and SA corrosion rates cannot be attributed only to the adopted B value. It must be taken into consideration that OCT forms a more compact barrier film than 3M1B derivatives do, as shown by its cathodic curve, where h.e.r. is diffusion controlled. If, in this case, impedance spectra characterize the reaction taking place only in the fraction of the surface where the film protectivity fails, then the differences in the corrosion rate values can be, at least partially, attributed to the fact that R_t values were calculated considering the total exposed area and not its less protective fraction.

If $R_p(R_p = \lim_{f \rightarrow 0}(Z' - R_w))$ had been used, the differences between SA and EIS corrosion rates would have been much lower in the case of less efficient inhibitors, but not in the case of the most efficient ones, generally with OCT, owing to the limited extension of the above-described pseudo-inductive loops.

However, percentage inhibiting efficiencies values from electrochemical techniques are in good agreement with those from analytical measurements, as previously verified for some acetylenic compounds [14] and for other types of organic inhibitors of iron acid corrosion [10–12, 24–29].

Work is in progress to develop the equivalent circuit model for the corrosion process. Impedance spectra of some 3M1B derivatives may be suitably fitted by a R_t-C_{dl} network with a R_a-C_a combination in parallel, similarly to that experienced by [18] for PA. Nevertheless, to simulate impedance spectra in the presence of OCT, some other effects (dif-

fusion, non uniform corrosion, etc.) must be taken into account.

5. Conclusions

The substitution of the acetylenic hydrogen atom with halogen atoms, mainly iodine, favours the film forming tendency of 3MIB derivatives, thus improving their inhibitive performances. I.e.'s over 99% may be obtained with the corresponding iodo-compounds at 70° C.

In the presence of these derivatives, reliable corrosion rates may be evaluated by EIS measurements by applying the S-G equation, whereas this fails with OCT, when diffusion of reacting species through a more or less uniform and thick film controls the global corrosion process, as found by other authors in different systems [24, 30].

However, EIS can be used for screening the inhibitive performances of different acetylenic derivatives and for monitoring their evolution as a function of time.

Acknowledgement

This work was supported financially by the MURST 60% Fund.

References

- [1] E. J. Duwell, J. W. Todd and H. C. Butzke, *Corros. Sci.* **4** (1964) 435.
- [2] I. N. Poutilova, Proc. 2° SEIC, Ann. Univ. Ferrara, (NS), Sez. V, Suppl. no. 4, Ferrara (I) (1965) p. 139.
- [3] S. B. Balezin, N. I. Podobayev, A. G. Voskresensky and V. V. Vasilyev, Proc. 3° I.C.M.C., vol. 2, Moscow (1966) p. 9.
- [4] G. W. Poling, *J. Electrochem. Soc.* **114** (1967) 1209.
- [5] R. J. Tedeschi, *Corrosion* **31** (1975) 130.
- [6] F. B. Growcock, W. W. Frenier and V. R. Lopp, Proc. 6° SEIC, Ann. Univ. Ferrara, (NS), Sez. V, Suppl. no. 8, Ferrara (I) (1985) p. 167; *ibid.* p. 183.
- [7] V. Jovancicevic, B. Yang and J. O'M. Bockris, *J. Electrochem. Soc.* **135** (1988) 94.
- [8] J. O'M. Bockris and B. Yang, *J. Electrochem. Soc.* **138** (1991) 2237.
- [9] B. Yang, N. G. Smart and J. O'M. Bockris, *Electrochim. Acta* **37** (1992) 317.
- [10] A. Frignani, M. Tassinari, L. Mészáros and G. TrabANELLI, *Corros. Sci.* **32** (1991) 903.
- [11] A. Frignani, M. Tassinari and G. TrabANELLI, *Electrochim. Acta* **34** (1989) 1259.
- [12] A. Frignani and M. Tassinari, Proc. 7° SEIC, Ann. Univ. Ferrara, (NS), Sez. V, Suppl. no. 9, Ferrara (I) (1990) p. 985.
- [13] I. Epelboin, M. Keddama and H. Takenouti, Proc. 3° SEIC, Ann. Univ. Ferrara, (NS), Sez. V, Suppl. no. 5, Ferrara (I) (1970) p. 237.
- [14] I. Epelboin, M. Keddama and H. Takenouti, *J. Appl. Electrochem.* **2** (1972) 71.
- [15] W. J. Lorenz and F. Mansfeld, *Corros. Sci.* **21** (1981) 647.
- [16] F. B. Growcock and R. J. Jasinski, *J. Electrochem. Soc.* **136** (1989) 2310.
- [17] T. Kristóf and T. Salamon, *Werkst. u. Korros.* **41** (1990) 519.
- [18] M. Bartos and N. Hackerman, *J. Electrochem. Soc.* **139** (1992) 3428.
- [19] F. B. Growcock and W. W. Frenier, CORROSION '84, paper 121.
- [20] M. Stern, *Corrosion* **14** (1958) 440t.
- [21] F. Mansfeld, 'Advances in Corrosion Science and Technology', vol. 6 (edited by M. G. Fontana and R. W. Stahele), Plenum Press, New York (1976), Chap. 3, p. 163.
- [22] A. Caprani, I. Epelboin, Ph. Morel and H. Takenouti, Proc. 4° SEIC, Ann. Univ. Ferrara, (NS), Sez. V, Suppl. no. 6, Ferrara (I) (1975) p. 517.
- [23] D. C. Silverman, *Corrosion* **46** (1990) 589.
- [24] A. Bonnel, F. Dabosi, C. Deslouis, M. Duprat, M. Keddama and B. Tribollet, *J. Electrochem. Soc.* **130** (1983) 753.
- [25] S. Brunet, G. Pinard-Legry, G. Plante and G. Turluer, Eurocorr 77, London, (1977) p. 357.
- [26] G. Schmitt and K. Bedbur, Proc. 9° ICMC, vol. 4, Toronto (1984) p. 112.
- [27] D. C. Silverman and J. E. Carrico, *Corrosion* **44** (1988) 280.
- [28] M. Mitzlaff, H. N. Hoffmann, K. Juttner and W. J. Lorenz, *Ber. Bunsenges. Phys. Chem.* **92** (1988) 1234.
- [29] K. Aramaki, M. Hagiwara and H. Nishihara, *J. Electrochem. Soc.* **135** (1988) 1364.
- [30] G. Mengoli, M. M. Musiani, C. Pagura and F. Paolucci, Proc. 7° SEIC, Ann. Univ. Ferrara, (NS), Sez. V, Suppl. no. 9, Ferrara (I) (1990) p. 61.