



Inhibitory mechanism of low-carbon steel corrosion by mimosa tannin in sulphuric acid solutions

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Abstract

Mimosa tannin was investigated as inhibitor of low-carbon steel sulphuric acid corrosion in concentrations from 10^{-5} to 10^{-1} mol L⁻¹, at the temperature of 298 K in the solutions of pH 1, 2 and 3. The inhibitor effectiveness increases with increase in concentration. The adsorptive behaviour of mimosa tannin in solutions of pH 1 and 2 may be approximated, both by Temkin and Frumkin type isotherms, probably due to the chemisorption of tannin molecules on the metal surface. The free energies of adsorption are in the range from -35.1 to -39.5 kJ mol⁻¹. At pH 3, a Freundlich type isotherm is obeyed, probably due to the physisorption of ferric-tannate that forms at this pH, both on the metal surface and in the bulk electrolyte. The free energy of adsorption at pH 3 is -11.8 kJ mol⁻¹. The activation energy of the iron dissolution process at pH 1 was found to be 51.4 kJ mol⁻¹ and decreased to 48.0 kJ mol⁻¹ on the addition of 1.25×10^{-2} mol L⁻¹ mimosa tannin. The addition of the same amount of mimosa tannin into solutions of pH 2 and 3, increased the activation energy of iron dissolution from 15.6 to 34.3 kJ mol⁻¹ and from 12.0 to 19.2 kJ mol⁻¹, respectively.

List of symbols

A	corrosion rate constant (A cm ⁻²)
a	Frumkin isotherm attraction constant
B	adsorption–desorption equilibrium constant (mol ⁻¹ L)
b_a	anodic Tafel slope (mV dec ⁻¹)
b_c	cathodic Tafel slope (mV dec ⁻¹)
c	concentration (mol L ⁻¹)
E_a	activation energy (J mol ⁻¹)
f	energetic inhomogeneity parameter
ΔG_{ads}	free energy of adsorption (J mol ⁻¹)

k	corrosion rate (A cm ⁻²)
n	Freundlich isotherm constant
R	universal gas constant (J mol ⁻¹ K ⁻¹)
T	thermodynamic temperature (K)
w_{blank}	specimen mass-loss in blank solution (g)
w_{inh}	specimen mass-loss in solution containing inhibitor (g)
w_{sat}	specimen mass-loss in inhibited system at surface saturation (g)

Greek symbols

θ	surface coverage
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1. Introduction

The use of tannins as low cost eco-friendly corrosion inhibitors is of special interest from the environmental point of view. Tannins are mixtures, mostly of hydroxy aromatic compounds. For example, mimosa tannin (MT) has a polymeric structure containing on the average four flavanoid units, (Figure 1) [1]. The *o*-dihydroxy phenolic groups of the B-ring are capable of chelating with Fe²⁺ and/or Fe³⁺ giving ferrous and ferric tannates.

A full understanding of the inhibitory mechanism of natural tannins is currently unavailable. It is well known

that tannins inhibit corrosion in acidic electrolytes [1–4]. However, controversy exists as to the mechanism of their inhibitory action [5, 6]. Even in very acidic electrolytes, inhibitory properties of tannins have been ascribed to the formation of a passivating layer of ferric-tannates on the metallic surface [5]. In our previous study [4], we have shown, both by ionic equilibrium calculation and spectrophotometric measurements, that tannates do not form at and below pH 1. Therefore, it is highly unlikely that a continuous protective layer of tannates would form on a bare, freely corroding electrode surface, in a highly acidic solution. Other results of our previous study may be summarized as follows:

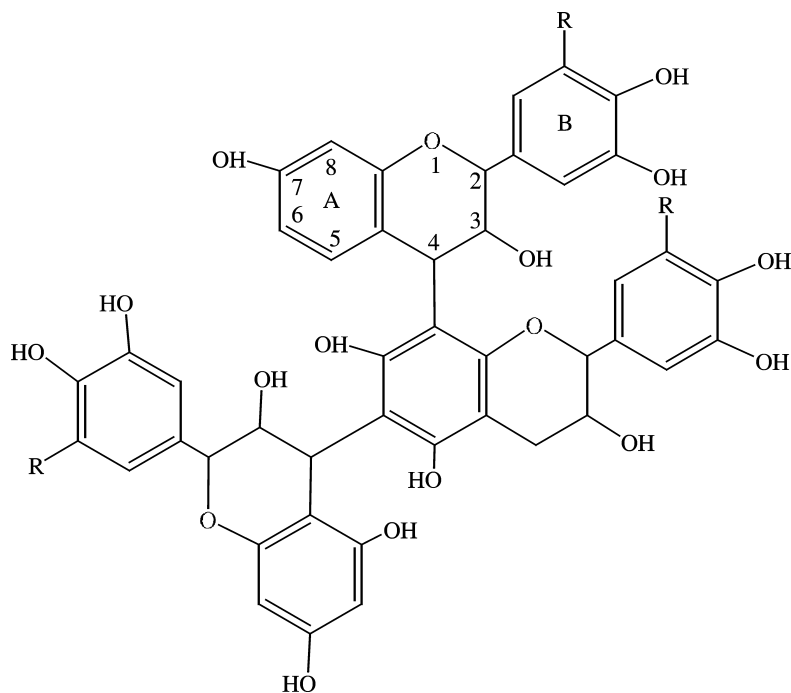


Fig. 1. Polymeric structure of mimosa tannin (R=OH for pyrogallol and R=H for pyrocatechol).

(i) The addition of MT to sulphuric acid solutions of pH 1, 2 and 3 induced a decrease in both cathodic and anodic currents, but had no significant effect on the corrosion potential which was approximately -520 , -565 and -605 mV vs SCE, respectively. The presence of MT did not significantly affect either the cathodic or the anodic Tafel slopes. At pH 1, the S-shape and hysteresis of anodic polarization curves were observed, indicating an adsorption-desorption process occurring at the electrode. Both the S-shape and hysteresis were gradually lost with increasing pH.

(ii) The protection efficiency, calculated from gravimetric measurements, increased with increasing the MT concentration and decreased with increasing pH.

(iii) Ionic equilibrium calculation revealed that formation of ferric-tannate monochelate starts above pH 1 and reaches its maximum at pH 3, when, for the case of the MT concentration higher than the Fe^{3+} concentration, all the ferric ions in the solution are present in the form of ferric-tannate monochelate. Monochelate is gradually transformed to bichelate at higher pH. Ferric-tannate formation at pH 3 was confirmed by spectrophotometric measurements, while no chelate formation was observed at lower pH. No surface layer formation was observed in gravimetric experiments at pH 1 and 2, while at pH 3 a blue-black, noncontinuous and loosely adherent tannate layer was formed.

The aim of this work was to further investigate the MT inhibitory mechanism of low-carbon steel corrosion in sulphuric acid solutions of pH 1–3. Particularly, the change in the inhibitory mechanism introduced by the ferric-tannate formation was considered.

2. Experimental details

Gravimetric experiments were conducted on low-carbon steel plates of size $2 \text{ cm} \times 4 \text{ cm}$. The samples were polished with grade 600 emery paper, degreased with methanol, rinsed with distilled water and dried. Sulphuric acid (Merck AR grade) solutions of pH 1, 2 and 3 were used as the blank corrosion test solutions.

Commercial mimosa tannin extract (Tannin Sevnica) was used in the concentration range 10^{-5} – $10^{-1} \text{ mol L}^{-1}$. Experiments were performed at temperatures between 20 and 50 °C and the experimentation time was 24 h. Three to six measurements were performed for each data point. The reproducibility of the experiments was higher than 90%.

3. Adsorption isotherms and free energies of adsorption

It is widely acknowledged that adsorption isotherms provide useful insight into the mechanism of corrosion inhibition. Often, classical adsorption isotherms of Temkin, Frumkin and Freundlich [7,8], respectively, given by

$$Bc = \frac{e^{f\theta} - 1}{1 - e^{-f(1-\theta)}} \quad (1)$$

$$Bc = \frac{\theta}{1 - \theta} e^{-2a\theta} \quad (2)$$

and

$$\theta = Bc^n \quad 0 < n < 1 \quad (3)$$

have been used for representing the adsorption behaviour of organic substances on metals of the iron group. c in Equations 1 to 3 is the inhibitor concentration, θ , is the surface coverage, a is the attraction constant, f is the factor of energetic inhomogeneity of the surface and n is a constant. B in Equations 1–3 is the adsorption–desorption equilibrium constant linked to the free energy of adsorption by the following relation [8]:

$$B = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{\text{ads}}}{RT}\right) \quad (4)$$

In the present study, the performance of MT as corrosion inhibitor has been evaluated for a broad range of concentrations. The results of 24 h gravimetric experiments performed at 25 °C are shown in Table 1. Electrochemical parameters from our previous investigation [4] suggest that MT probably decreases the dissolution of iron and evolution of hydrogen by blocking the metal surface. In that case, the corrosion rate in the presence of inhibitor is representative of the number of available corroding sites remaining after blockage of some sites due to inhibitor adsorption [9]. This assumption enables computation of the degree of surface coverage, θ , according to the equation:

$$\theta = \frac{w_{\text{blank}} - w_{\text{inh}}}{w_{\text{blank}} - w_{\text{inh}}^{\text{sat}}} \quad (5)$$

where w_{blank} , w_{inh} and $w_{\text{inh}}^{\text{sat}}$ are the specimen mass-losses in the uninhibited system, inhibited system and in the inhibited system at surface saturation, respectively. Variation of θ with MT concentration is shown in Figure 2. Temkin, Frumkin and Freundlich adsorption constants were deduced by application of a nonlinear least squares fitting procedure implemented in the programming system *Mathematica*. It was found that the adsorptive behaviour of MT in solutions of pH 1 and 2 may be approximated by both Temkin and Frumkin type isotherms while in the solution of pH 3, the Freundlich type isotherm is obeyed. The adsorption

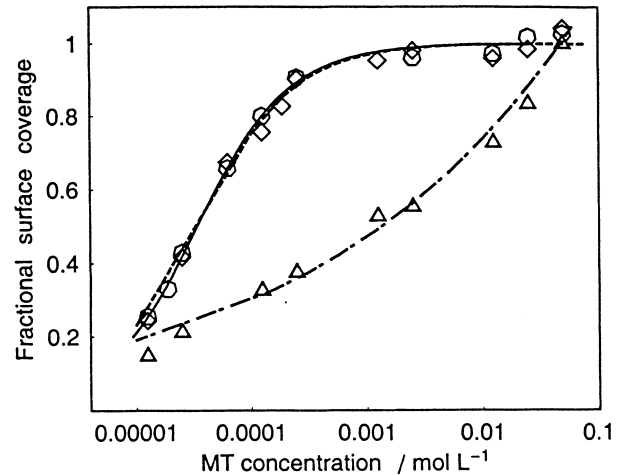


Fig. 2. Frumkin (---), Temkin (—) and Freundlich (- · - · -) isotherms for adsorption of mimosa tannin on low-carbon steel in sulphuric acid solutions of pH 1 (◇), 2 (○) and 3 (△).

constants along with the corresponding free energies of adsorption are shown in Table 2.

4. Inhibitory mechanism in solutions of pH 1 and 2

It is well known that the logarithmic adsorption isotherm in the range of medium surface coverage may be deduced by assuming, both adsorption on an energetically uniform, inhomogeneous metal surface (Temkin model) and adsorption on a homogeneous surface with an interaction in the adsorption layer (Frumkin model) [10]. A relatively low value of the energetic inhomogeneity factor f obtained from the Temkin model, in the solution of pH 1 (Table 2) would signify a weak dependence of the free energy of adsorption on the surface coverage [11]. On the other hand, the positive value of a obtained for the solution of pH 1 would provide evidence for attraction forces in the adsorption layer [8]. This would agree with the fact that the flavanoid units of tannin are capable of forming a polymeric structure by cross-linking on the metal surface [1]. However, to distinguish between these two models, the dependence of the adsorption enthalpy on surface coverage would have to be determined. The Temkin model would yield a decrease in the absolute value of the adsorption enthalpy with surface coverage while the Frumkin model would give an increase in the absolute value of the adsorption enthalpy with surface coverage when the attraction forces act among the molecules of the adsorbed layer [12, 13].

The values of the free energy of adsorption obtained by both models, at pH 1 and 2, indicate strong adsorption, which is probably chemisorption. The negative values of free adsorption energies show that MT adsorption is a spontaneous process. The chemisorptive bond could be formed by sharing a pair of electrons, from the organic inhibitor, with iron. The organic inhibitor polar units, containing S, N, O, Se or P, are usually regarded as the

Table 1. Inhibitor efficiencies of mimosa tannin at 25 °C from 24 h gravimetric experiments in sulphuric acid solutions of pH 1, 2 and 3

Inhibitor concentration / mol L ⁻¹	Inhibitor efficiency/%		
	pH 1	pH 2	pH 3
1.25 × 10 ⁻⁵	21.7	19.5	9.73
1.88 × 10 ⁻⁵	28.1	—	—
2.50 × 10 ⁻⁵	36.3	33.3	13.9
6.25 × 10 ⁻⁵	55.9	53.9	—
1.25 × 10 ⁻⁴	67.9	60.5	21.5
1.88 × 10 ⁻⁴	—	66.1	—
2.50 × 10 ⁻⁴	76.8	72.1	24.7
1.25 × 10 ⁻³	—	76.2	34.7
2.50 × 10 ⁻³	81.6	78.4	36.4
1.25 × 10 ⁻²	82.8	76.7	48.0
2.50 × 10 ⁻²	86.5	78.8	55.5
5.00 × 10 ⁻²	87.3	83.4	66.1

Table 2. Isotherm parameters and free energies of adsorption of mimosa tannin in sulphuric acid solutions of pH 1, 2 and 3

H ₂ SO ₄ solution	<i>f</i>	<i>a</i>	<i>n</i>	<i>B</i> /mol ⁻¹ L	Adsorption energy /kJ mol ⁻¹
Temkin isotherm					
pH 1	5.89×10 ⁻⁴	–	–	3.02 × 10 ⁴	–35.5
pH 2	3.08	–	–	1.49 × 10 ⁵	–39.5
Frumkin isotherm					
pH 1	–	0.147	–	2.54 × 10 ⁴	–35.1
pH 2	–	–0.372	–	4.66 × 10 ⁴	–36.6
Freundlich isotherm					
pH 3	–	–	0.22	2.14	–11.8

reaction centre for the chemisorption process. Natural tannins are oxygen-containing inhibitors; therefore, formation of iron–oxygen bond is possible.

When considering adsorption via the oxygen free pair of electrons, the possibility of protonation of –OH groups should be taken into account as this would remove one of the free electron pairs and lower the basicity of the remaining pair. Tannin in acid solution can be presented both as a molecular and a protonated species:



Equilibrium between these two forms is characterized by an equilibrium constant. According to Martell [14], p*K*_a values for –OH group protonation are lower than one (e.g., p*K*_a = –6.7 for phenol [15]), therefore, no significant effect of inhibitor protonation should be expected in sulphuric acid solutions of pH 1 to 3. Consequently, it is possible that the inhibitory effect of MT is more likely due to the adsorption of tannin molecular species than to the adsorption of protonated species.

5. Inhibitory mechanism in the solution of pH 3

At pH 3, tannin undergoes chemical transformation in the electrolyte and on the surface of the metal, reacting with Fe³⁺ produced at anodic sites to form ferric tannate species (Figure 3) [4, 16]. According to Seawell [1], ferrous tannates are not formed in acidic solutions. At pH 3, the Freundlich type isotherm is obeyed (Figure 2). Inhibitor efficiencies are considerably lower than those at pH 1 and 2 (Table 1). The interpretation is that the surface adsorbed tannin, at this pH, is trans-

formed into ferric-tannate monochelate which, being a cation, is expected to be poorly adsorbed on the steel surface in sulphuric acid solutions at the steady state potential, in the absence of the specifically adsorbed anions [7]. The free energy of adsorption calculated from the isotherm equation, is –11.76 kJ mol⁻¹. Under these circumstances, ferric-tannate is probably physically adsorbed on the surface. A blue–black layer covering the specimen surface was observed showing multilayer adsorption of ferric-tannate. A ferric-tannate film has been proposed to exist as a highly cross linked network of ferric ions and tannin molecules [17, 18].

6. Activation energies of metal dissolution process

A study of the influence of temperature on the protective effect of an inhibitor is important in elucidation of its inhibitory action. For example, apparent activation energies, *E*_a of the metal dissolution reaction can be determined from the Arrhenius relation [8]:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (7)$$

that is, by determination of the slopes of the straight lines that depict the linear dependence of the logarithm of the corrosion rate, ln(*k*), on the reciprocal value of the absolute temperature.

In this work, corrosion rates were calculated from gravimetric measurements performed in the systems of pH 1, 2 and 3 with MT concentration equal to 0 and 1.25 × 10⁻² mol L⁻¹ and with temperature of the corrosion medium ranging from 20 to 60 °C. The corrosion rates increase with temperature increase, both for the

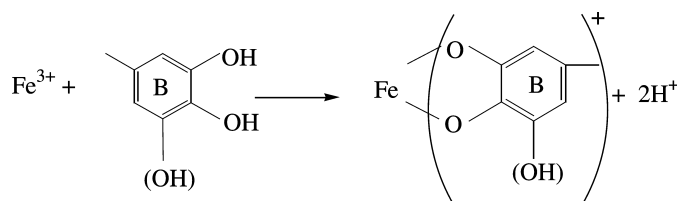


Fig. 3. Formation of ferric-tannate monochelate in the chelation process between a ferric ion and a tannin molecule.

supporting electrolytes and for the inhibited solutions. Arrhenius plots for pH 1, 2 and 3 are shown in Figure 4 (a), (b) and (c), respectively. The straight lines have coefficients of correlation in the range from 0.962 to 0.986. The activation energy of 51.4 kJ mol^{-1} obtained in the inhibitor-free system at pH 1 agrees well with literature activation energy data [19–21] for steel dissolution in sulphuric acid. In the presence of MT at pH 1, the activation energy is slightly reduced and is approximately 48.0 kJ mol^{-1} . This result confirms the previous assumption of tannin chemisorption based on the magnitude of the adsorption energy because unchanged

or lowered activation energy may be interpreted as being indicative of chemisorption [22, 23]. Although the relatively high value of free energy of adsorption at pH 2 indicates strong adsorption, a rise in activation energy from 15.6 kJ mol^{-1} in the inhibitor free solution to 34.3 kJ mol^{-1} in the presence of the inhibitor indicates that the adsorbed tannin is probably partially transformed into ferric-tannate. This also accounts for the negativity of the Frumkin parameter a at pH 2, as the charged tannate species would introduce repulsive Columbic forces into the adsorption layer. On the other hand, the relatively low value of the adsorption energy and rise in the activation energy from 12.0 to 19.2 kJ mol^{-1} , observed in the system at pH 3, may be linked to the existence of physical adsorption [23].

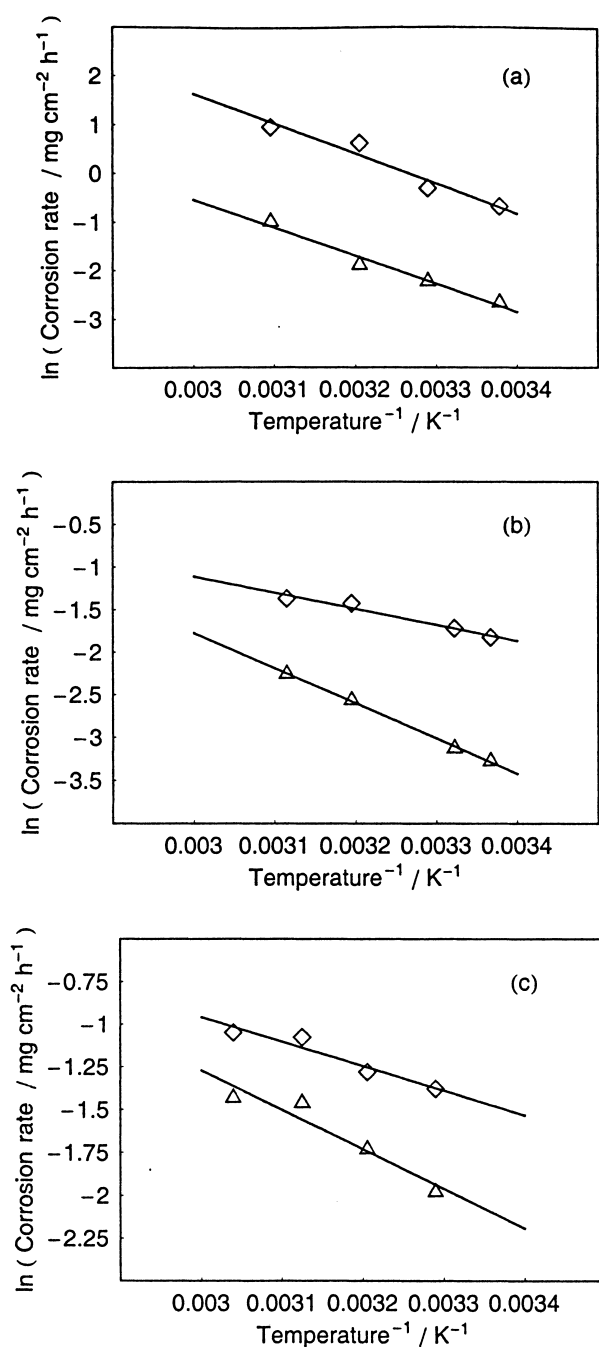


Fig. 4. Arrhenius plots for the low-carbon steel dissolution process in the sulphuric acid solutions of: (a) pH 1, (b) pH 2 and pH 3, containing 0 mol L^{-1} MT (\diamond) and $1.25 \times 10^{-2} \text{ mol L}^{-1}$ MT (Δ).

7. Conclusions

(i) Mimosa tannin performs well as a mixed type inhibitor of steel corrosion in sulphuric acid solutions of pH 1 and 2. The adsorptive behaviour may be approximated by both Temkin and Frumkin type isotherms verifying the assumption of a monolayer adsorption. The value of the free adsorption energy suggests a chemisorption-based mechanism that is probably due to the chemisorption of tannin molecules on the metal surface via the oxygen free pair of electrons.

(ii) The adsorption of ferric-tannate at pH 3, obeys the Freundlich adsorption isotherm. Relatively low value of the free adsorption energy suggests the physisorption-based mechanism.

(iii) The activation energy does not change significantly with the presence of $1.25 \times 10^{-2} \text{ mol L}^{-1}$ mimosa tannin at pH 1, thus, indicating that the mechanism of its inhibition probably occurs via blocking of the metal surface by the chemisorbed tannin molecules.

(iv) The activation energy increases by the presence of mimosa tannin at pH 3, indicating that inhibition probably occurs via formation of a physisorbed ferric-tannate multilayer on the metal surface.

References

1. A.J. Seawell, *J. Oil Col. Chem. Assoc.* **61** (1978) 439.
2. M. Favre and D. Landolt, Proceedings of the 7th European symposium on 'Corrosion Inhibitors', Ann. Univ. Ferrara (1990), p. 787.
3. J. Iwanow and Yu.I. Kuznetsow, Proceedings, *op. cit.* [2], p. 795.
4. S. Martinez and I. Štern, *Chem. Biochem. Eng. Q.* **13** (1999) 191.
5. R.M. Saleh, A.A. Ismail and A.A. El Hosary, *Br. Corros. J.* **17** (1982) 131.
6. I.H. Farooqi, A. Hussain, M.A. Quaraishi and P.A. Saini, *Anti-Corros.* **46** (1999) 328.
7. I.L. Rozenfeld, 'Corrosion Inhibitors' (McGraw-Hill, New York, 1981), p. 97.
8. A.E. Stoyanova, E.I. Sokolova and S.N. Raicheva, *Corros. Sci.* **39** (1997) 1595.
9. M.M. Osman, A.M.A. Omar and A.M. Al-Sabagh, *Mat. Chem. Phys.* **50** (1997) 271.

10. W. Durnie, R. De Marco, A. Jefferson and B. Kinsella, *J. Electrochem. Soc.* **146** (1999) 1751.
11. B.I. Podlovchenko and B.B. Damaskin, *Elektrochimia* **8** (1972) 297.
12. B.E. Conway, 'Principles of Electrode Processes' (Ronald Press, New York, 1965), p. 78.
13. D.D. Do, 'Adsorption Analysis: Equilibria and Kinetics' (Imperial College Press, London 1998), p. 10.
14. A.E. Martell and M. Calvin, 'Chemistry of Metal Chelates Compounds' (Prentice-Hall, New York, 1953) p. 28.
15. S.H. Pine, 'Organic Chemistry' (McGraw-Hill, New York, 1987), p. 100.
16. M. Favre and D. Landolt, Proceedings, *op. cit.* [2], p. 787.
17. P.J. DesLauriers, *Mater. Perform.* **26** (1987) 35.
18. E. Knowles and T. White, *J. Oil. Colour Chem. Assoc.* **41** (1958) 10.
19. M. Metikoš-Huković, R. Babić, Z. Grubač and S. Brinić, *J. Appl. Electrochem.* **26** (1996) 443.
20. D. Altura and K. Nobe, *Corrosion* **29** (1973) 433.
21. F. Bentiss, M. Traisnel, L. Gengembre and M. Lagrenee, *Appl. Surf. Sci.* **152** (1999) 237.
22. T. Szauer and A. Brandt, *Electrochim. Acta* **26** (1981) 943.
23. S. Sankarapavinasan, F. Pushpanaden and M. Ahmed, *Corros. Sci.* **32** (1991) 193.