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Sinapinic acid as Al–2.5Mg alloy corrosion inhibitor in sodium chloride solution

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Abstract

Sinapinic acid was studied for possible use as an Al–2.5Mg alloy corrosion inhibitor in a 0.5 mol dm^{-3} NaCl solution. Measurements were performed on a rotating disc electrode in a quiescent solution and at different electrode rotation rates and electrolyte temperatures. Electrochemical parameters for the Al–2.5Mg alloy were determined using polarization techniques and electrochemical impedance spectroscopy (EIS). The investigated compound acts as a cathodic-type inhibitor and the inhibition is ascribed to the adsorption of the inhibitor onto the electrode surface. The electrode coverage follows the Freundlich adsorption isotherm.

1. Introduction

Due to the various industrial applications and remarkable economic importance of aluminium and its alloys, their protection against corrosion in different media has attracted much attention [1–6]. The importance and wide application of aluminium–magnesium alloys in chemical-processing industry and food-handling equipment, shipbuilding and automotive industry [7], have provided an initiative for examination the possibility of corrosion inhibition of Al–2.5Mg alloy. One of the available methods is the use of corrosion inhibitors. Unfortunately, some compounds used as corrosion inhibitors have toxic properties and must be replaced with other non-toxic compounds. The inhibiting properties of amino acids, carboxylic and fatty acids and other non-toxic organic compounds are being examined [8–12]. Organic compounds that can be obtained from plant material such as vanillin [13], catechin [14], ferulic acid [15] and different plant extracts [16–18] are of interest.

Sinapinic acid (3,5 dimetoxy-4-hidroxy cinnamic acid) belongs to the group of phenolic acids, substances that naturally occur in fruit, vegetables, nuts, seeds, flowers and some herb beverages [19, 20]. Sinapinic acid is the main phenolic compound of rapeseed constituents [21], and it is also found in the first acidic sub-fraction of the aqueous extract of Rosemary leaves. The procedure of obtaining acidic sub-fractions from the aqueous extract of Rosemary leaves has been described previously [15]. This phenolic acid shows good antioxidant activity [21, 22] and also antibacterial and weak anti-fungal activity [23].

The aim of this work is to study the effect of sinapinic acid on the corrosion of Al–2.5Mg alloy in a 0.5 mol dm^{-3} NaCl solution using polarization and impedance techniques.

2. Experimental

A disc working electrode suitable for a rotating disc system was made from the Al–2.5Mg alloy with an exposed geometric area of 0.5 cm^2. Prior to each electrochemical experiment, the electrode surface was abraded with emery paper to a 1200 metalographic finish, degreased in ethanol, rinsed with doubly distilled water and left for a few minutes in air to develop the natural oxide film before being immersed in the solution.

The basic solution was 0.5 mol dm^{-3} NaCl, to which sinapinic acid was added in concentrations of 1×10^{-6}, 1×10^{-5}, 5×10^{-5}, 1×10^{-4} and 5×10^{-4} mol dm^{-3}. Commercial sinapinic acid (obtained from the Aldrich Chemical Co.) was used in this study. Figure 1 shows the structure of the sinapinic acid.

The pH of the solutions was adjusted to 6 using sodium hydroxide solution. The electrochemical glass cell used was of the usual type with a double-jacketed device allowing thermostatic experiments to be performed. The counter electrode was platinum foil and the reference electrode was a saturated calomel electrode (SCE) in contact with the working electrode via a Luggin capillary. The experiments were performed in a quiescent solution in the temperature range from 20 °C to 50 °C, and at the electrode rotation rates 150 rpm and 2000 rpm.

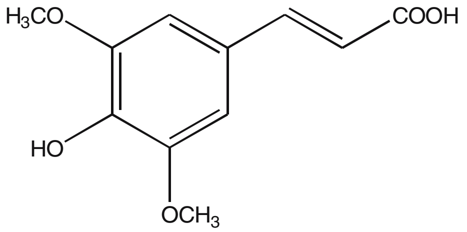

Fig. 1. Structural formula of sinapinic acid.

The potentiodynamic polarization measurements were performed using a potentiostat (PAR M 273A), with a scanning rate of 0.2 mV s^{-1}. Anodic and cathodic branches of polarization curves were recorded. Corrosion current densities from the polarization curves were determined by extrapolation of cathodic Tafel lines to corrosion potential. The polarization resistance, R_p, was determined from the slope of polarization curves obtained by measurements in the potential range from −10 mV to + 10 mV from the corrosion potential and at a scanning rate of 0.2 mV s^{-1}. Impedance measurements were carried out using a lock-in amplifier (PAR M5210), at the open circuit potential (E_{OCP}) in quiescent solution, 30 min after the electrode had been immersed into the test solution. The a.c. amplitude was ± 10 mV with five data points per decade. The frequency range studied was from 50 kHz to 30 mHz.

3. Results and discussion

3.1. *Polarization measurements*

Figure 2 shows the potentiodynamic polarization curves for Al–2.5Mg alloy in a 0.5 mol dm^{-3} NaCl solution without and with the addition of sinapinic acid in different concentrations at 20 °C. The addition of sinapinic acid induces changes in the polarization behaviour of the alloy examined. The added substance reduces the cathodic current density and shifts the corrosion potential in the negative direction. These changes indicate that the sinapinic acid acts as a cathodic corrosion inhibitor of Al–2.5Mg alloy, under the given conditions. Lowering the inhibitor concentration decreases the changes mentioned. Table 1 show the corrosion parameters for the investigated alloy in a NaCl solution without and in the presence of different concentrations of sinapinic acid at different electrode rotation rates, and also lists the percentage of inhibition efficiency calculated using equation 1:

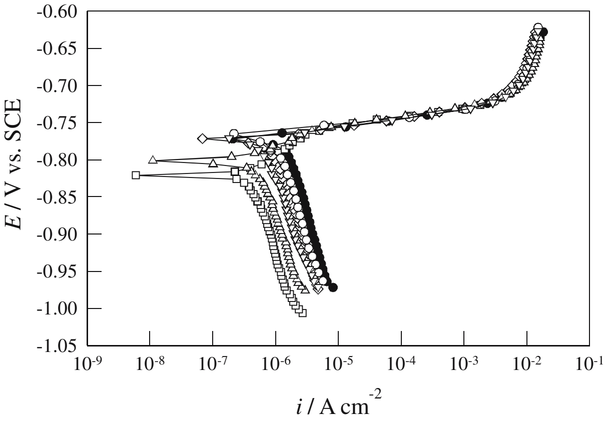

Fig. 2. Potentiodynamic polarization curves for the Al–2.5Mg alloy in quiescent 0.5 mol dm^{-3} NaCl solution at 20 °C without (●) and in the presence of sinapinic acid in the concentration of 1×10^{-6} mol dm^{-3} (○), 1×10^{-5} mol dm^{-3} (◇) 5×10^{-5} mol dm^{-3} (∇), 1×10^{-4} mol dm^{-3} (Δ) and 5×10^{-4} mol dm^{-3} (□).

$$\eta = \frac{i_{\rm corr} - (i_{\rm corr})_{\rm inh}}{i_{\rm corr}} \times 100 \tag{1}$$

where $i_{\rm corr}$ and $(i_{\rm corr})_{\rm inh}$ represent corrosion current densities in the absence and presence of inhibitor. The data from Table 1 show that the efficiency of the sinapinic acid increases with increase in concentration but decreases with increase in electrode rotation rate.

In order to study the relationship between inhibitor adsorption on the electrode surface and its concentration, the degree of surface coverage Θ, defined by Θ = η/100, was plotted as a function of the sinapinic acid concentration (Figure 3). The Freundlich adsorption isotherm [24] is

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

where $0 < n < 1$, or

$$\ln \Theta = \ln K + n \ln c \tag{3}$$

K and *c* represent the equilibrium constants of adsorption and the inhibitor concentration. A plot of ln Θ against ln *c* would give the straight line of intercept ln *K* if Equation 3 were applicable. The plot obtained is linear, which suggests that the Freundlich adsorption

Table 1. Corrosion parameters for the Al–2.5Mg alloy in a 0.5 mol dm^{-3} NaCl solution with addition of different concentration of sinapinic acid, at 20 °C and different electrode rotation rates

c (inhibitor)/ mol dm^{-3}	ω/ rpm	$-b_c$/ V dec^{-1}	$i_{\rm corr}$/ μA cm^{-2}	$E_{\rm corr}$/V	η/%
0	0	0.276	1.44	−0.771	–
1×10^{-6}		0.224	0.86	−0.767	40.3
1×10^{-5}		0.254	0.72	−0.770	50.0
5×10^{-5}		0.253	0.62	−0.771	56.9
1×10^{-4}		0.257	0.51	−0.800	64.6
5×10^{-4}		0.258	0.38	−0.820	73.6
0	150	0.293	2.28	−0.776	–
1×10^{-6}		0.240	1.63	−0.768	28.5
1×10^{-5}		0.257	1.40	−0.768	38.6
5×10^{-5}		0.257	1.22	−0.775	46.5
1×10^{-4}		0.250	1.02	−0.772	55.3
5×10^{-4}		0.258	0.79	−0.806	65.4
0	2000	0.283	2.84	−0.773	–
1×10^{-6}		0.275	2.32	−0.771	18.3
1×10^{-5}		0.282	2.10	−0.773	26.1
5×10^{-5}		0.257	1.93	−0.776	32.0
1×10^{-4}		0.268	1.68	−0.773	40.8
5×10^{-4}		0.265	1.40	−0.774	50.7

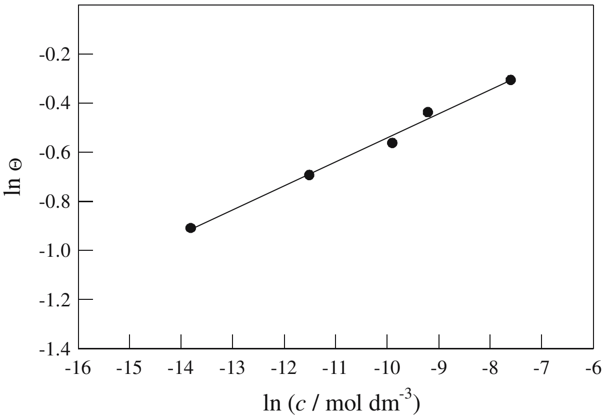

Fig. 3. Adsorption isotherm for the sinapinic acid.

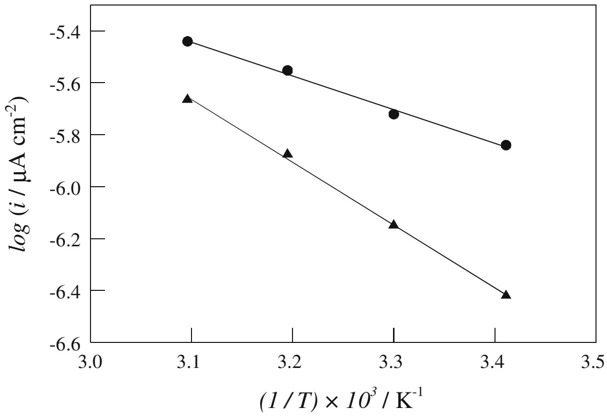

Fig. 4. Activation energy determination for the Al–2.5Mg alloy in 0.5 mol dm^{-3} NaCl solution without (●), and in the presence of sinapinic acid in the concentration of 5×10^{-4} mol dm^{-3} (▲).

isotherm is obeyed. The equilibrium constant of adsorption, K, was determined to be 1.55 dm^3 mol^{-1}.

The equilibrium constant of adsorption is related to the standard free energy of adsorption, ΔG^0_{ads} by

$$K = \frac{1}{55.5}\exp\left(\frac{-\Delta G^0_{ads}}{RT}\right) \tag{4}$$

The value of 55.5 is the concentration of water in the solution in mol dm^{-3}, R is the gas constant and T is the absolute temperature.

The value of ΔG^0_{ads} calculated according to Equation 4 was -10.85 kJ mol^{-1}. The negative value of ΔG^0_{ads} indicates that the adsorption process proceeds spontaneously. The value obtained indicates physical adsorption of organic matter on the metal surface.

The dependence of the corrosion current on temperature can be regarded as an Arrhenius-type process, the rate of which is:

$$i_{\mathrm{corr}} = A\exp\left(-\frac{E_{\mathrm{a}}}{RT}\right) \tag{5}$$

where i_{corr} is the corrosion current density, A is the Arrhenius preexponential constant and E_{a} is the apparent activation energy.

Arrhenius plots (i.e., the logarithms of the corrosion current density against 1/T) are presented in Figure 4. Straight lines are obtained both for pure NaCl solution and for NaCl solutions with inhibitor added. The E_{a} values were determined from the slopes of these plots, and calculated to be: $E_{a1} = 24.94$ kJ mol^{-1} in a noninhibited 0.5 mol dm^{-3} NaCl solution, $E_{a2} = 46.29$ kJ mol^{-1} with the addition of 5×10^{-4} mol dm^{-3} sinapinic acid. Higher values of E_{a} in the presence of inhibitor indicate that a higher energy barrier is attained for the reaction [25]. According to Popova et al. [26], the temperature dependence of the inhibitor efficiency and the comparison of the values of E_{a} both in the absence and in the presence of inhibitor lead to some conclusions concerning the mechanism of the inhibiting action. The temperature dependence of the inhibition efficiency for the sinapinic acid is shown in Table 2. The inhibition efficiency decreases with increasing temperature, which suggests that the inhibitor molecules are physically adsorbed.

Figure 5 shows "linear" parts of polarization curves obtained by the linear polarization method for Al–2.5Mg alloy in a 0.5 mol dm^{-3} NaCl solution in the presence of sinapinic acid in concentration 5×10^{-4} mol dm^{-3} at different electrode rotation rates. The results indicate that increase in electrode rotation rate leads to a reduced slope of the "linear" parts of the curve i.e. reduced values of the polarization resistance. The same has been observed when the electrolyte temperature increases.

The values of the polarization resistance, R_{p}, were determined from the slope of the "linear" polarization curves near E_{corr}:

$$R_p = \left(\frac{dE}{dI}\right)_{E=E_{\mathrm{corr}}} \tag{6}$$

R_{p} values were used to calculate the inhibiting efficiency, η, using the equation:

$$\eta = \left(\frac{R_{\mathrm{pi}} - R_{\mathrm{p}}}{R_{\mathrm{pi}}}\right) \times 100 \tag{7}$$

where R_{p} and R_{pi} are the polarization resistances without and with the addition of inhibitor.

The values of the polarization resistance and the inhibitor efficiency calculated using Equation 7 are shown in Table 3.

Table 2. Temperature dependence of inhibitor efficiency for sinapinic acid in quiescent NaCl solution

T/K c (inhibitor)/mol dm^{-3}	293 η/%	303 η/%	313 η/%	323 η/%
0	–	–	–	–
1×10^{-6}	40.3	32.6	21.4	11.6
1×10^{-5}	50.0	44.7	31.4	20.4
5×10^{-5}	56.9	50.5	36.1	26.2
1×10^{-4}	64.6	55.8	43.6	33.4
5×10^{-4}	73.6	62.6	52.5	42.0

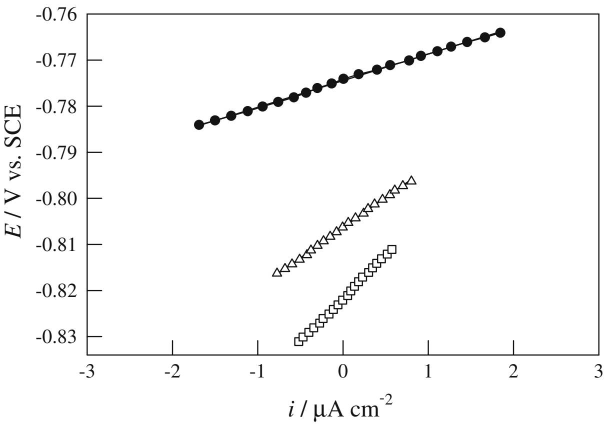

Fig. 5. "Linear" polarization curves for determination of polarization resistance of the Al–2.5Mg alloy in 0.5 mol dm^{-3} NaCl solution in the presence of sinapinic acid in concentration of 5 × 10^{-4} mol dm^{-3} at 20 °C and at the electrode rotation rates ω_1 = 0 rpm (□), ω_2 = 150 rpm (Δ) and ω_3 = 2000 rpm (•).

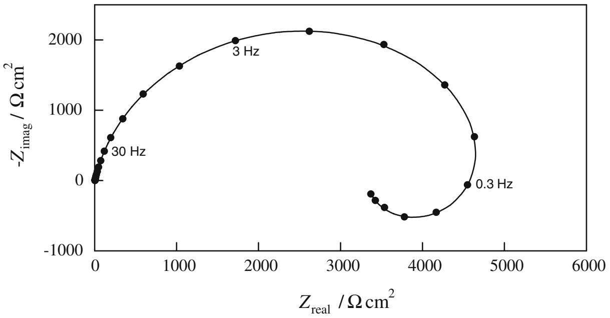

Fig. 6. The Nyquist plot of the Al–2.5Mg alloy in 0.5 mol dm^{-3} NaCl solution at open circuit potential.

Generally, R_p values increase with increasing inhibitor concentration but decrease with the increase in electrode rotation rate and electrolyte temperature.

3.2. *Electrochemical impedance measurements*

The impedance response obtained for corrosion of the alloy investigated in a quiescent 0.5 mol dm^{-3} NaCl solution without the addition of sinapinic acid is presented in Figure 6 in the Nyquist format. In pure NaCl solution, the impedance scan has one capacitive loop in the high-frequency range and one inductive loop in the low-frequency domain.

The time constant at high frequencies has often been attributed to the formation of an oxide layer [27–29] or to an oxide layer itself. Some authors attribute its existence to the transport process through the aluminium oxide layer [30, 31]. The origin of the inductive loop can be ascribed to the relaxation of adsorbed species and alloy dissolution [29, 30, 32].

Table 3. Polarization resistance and inhibition efficiencies for the Al–2.5Mg alloy in a 0.5 mol dm^{-3} NaCl solution without and with addition of different concentration of sinapinic acid at 20 °C and different electrode rotation rates

c (inhibitor)/mol dm^{-3}	ω/rpm	R_p/kΩ cm^2	η/%
0	0	5.08	–
1 × 10^{-6}		8.69	41.5
1 × 10^{-5}		10.23	50.3
5 × 10^{-5}		11.72	56.7
1 × 10^{-4}		14.04	63.8
5 × 10^{-4}		18.70	72.8
0	150	4.36	–
1 × 10^{-6}		6.18	29.5
1 × 10^{-5}		6.90	36.8
5 × 10^{-5}		8.09	46.1
1 × 10^{-4}		9.76	55.3
5 × 10^{-4}		13.08	66.7
0	2000	2.81	–
1 × 10^{-6}		3.39	17.1
1 × 10^{-5}		3.80	26.1
5 × 10^{-5}		4.22	33.4
1 × 10^{-4}		4.84	41.9
5 × 10^{-4}		5.78	51.4

Figure 7 shows the impedance responses obtained for quiescent 0.5 mol dm^{-3} NaCl solution with the addition of different concentrations of sinapinic acid. The addition of sinapinic acid leads to growth in diameter and size of the capacitive semicircle, which probably reflects physical blocking of the alloy surface. Furthermore, at an inhibitor concentration higher then 1 × 10^{-6} mol dm^{-3} the inductive loop in the Nyquist complex plane completely disappears, which indicates the formation of a thicker protective film and therefore reduced corrosion.

Figure 6 and Figure 7 show that the semicircles obtained are depressed. Deviations of this kind, often referred to as frequency dispersions, have been attributed to nonhomogeneities of aluminium surface [33]. A practical way to represent distributed processes, such as corrosion of a rough and nonhomogeneous electrode surfaces, is with an element that follows its distribution - the constant phase element, CPE. The impedance, Z_{CPE}, of CPE is described by the expression:

$$Z_{\mathrm{CPE}} = [Q(j\omega)^n]^{-1} \tag{8}$$

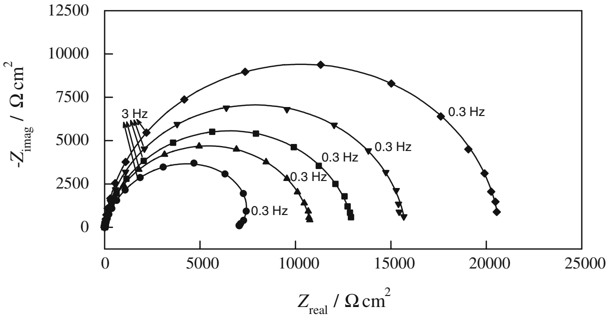

Fig. 7. The Nyquist plot of the Al–2.5Mg alloy in 0.5 mol dm^{-3} NaCl solution at open circuit potential in the presence of sinapinic acid in concentrations 1 × 10^{-6} (•), 1 × 10^{-5} (▲), 5 × 10^{-5} (■), 1 × 10^{-4} (▼) and 5 × 10^{-4} mol dm^{-3} (◆).

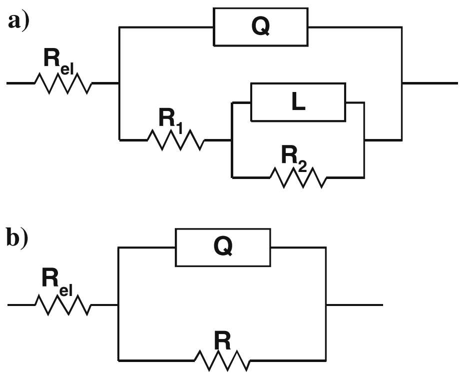

Fig. 8. Equivalent circuits for modelling impedance data of the Al–2.5Mg alloy (a) for the measurements in noninhibited NaCl solution and in the presence of sinapinic acid in concentration of 1×10^{-6} mol dm^{-3}. (b) for the measurements in NaCl solution in the presence of sinapinic acid in concentrations of 1×10^{-5} mol dm^{-3} to 5×10^{-4} mol dm^{-3}.

where Q and n are constants that can be used in data fitting when interpreting frequency dispersions. The exponent n has values between -1 and 1. A value of -1 is characteristic of an inductance, a value of 1 corresponds to a capacitor, a value of 0 corresponds to a resistor and a value of 0.5 can be assigned to diffusion phenomena.

Figure 8 shows the equivalent circuits used to fit the experimental data. The equivalent circuit marked with a) was found to fit the experimental data obtained in the NaCl solution without the addition of sinapinic acid, and with the addition of the lowest concentration of the inhibitor. This consists of a constant phase element Q related to the double layer capacity in parallel to the series resistors R_1 and R_2 and an inductance L in parallel to R_2. R_{el} corresponds to the electrolyte resistance. The value of the electrolyte resistance, R_{el}, was around 5 Ω in all experiments. The equivalent circuit marked b) is used for modelling the experimental data for measurements in the NaCl solution in the presence of sinapinic acid in concentrations higher then 1×10^{-6} mol dm^{-3}. It consists of a parallel RQ combination connected in series with the electrolyte resistance.

The parameters of the equivalent circuit were evaluated using the simple least squares fit procedure and are presented in Table 4. The increase in R_1 indicates an increase in corrosion resistance (corrosion inhibition) whereas the decrease in Q values can be correlated to a decrease in the corroded area by formation of a thicker protective film and an increase in electrode area covered by the inhibitor. The capacitive properties of the system considered in the presence of sinapinic acid are attributable to the dielectric properties of the surface (metal-oxide-inhibitor) adsorption layer.

Table 4. Impedance parameters for the Al–2.5Mg alloy in 0.5 mol dm^{-3} NaCl solution in the absence and in the presence of varied concentrations of the sinapinic acid

c/mol dm^{-3}	$Q_1 \times 10^6$/ Ω^{-1} s^n cm^{-2}	n_1	R_1/k Ω cm^{-2}	L/kH cm^{-2}	R_2/k Ω cm^{-2}
0	22.63	0.88	3.34	1.32	1.86
1×10^{-6}	19.78	0.87	7.08	0.83	2.24
1×10^{-5}	16.21	0.91	10.83		
5×10^{-5}	14.64	0.90	13.04		
1×10^{-4}	11.96	0.93	15.77		
5×10^{-4}	10.07	0.94	20.69		

4. Conclusions

The results of polarization measurements have indicated that the sinapinic acid acts as a cathodic inhibitor of the Al–2.5Mg alloy in a 0.5 mol dm^{-3} NaCl solution. The inhibiting efficiency decreased with increasing electrode rotation rate and increasing electrolyte temperature.

The adsorption behaviour of the sinapinic acid can be described by the Freundlich adsorption isotherm. The values determined for standard free adsorption energies indicate physical adsorption of an organic substance on the electrode surface.

The impedance measurements performed at E_{OCP} without inhibitor are characterized by a high-frequency capacitive loop related to dielectric properties of the oxide film and low-frequency inductive loop which was determined by a faradaic process and attributed to corrosion on the electrode surface. Increase in sinapinic acid concentration leads to an increase in diameter of the capacitive semicircle and to the disappearance of the inductive semicircle, which indicates the formation of a thicker protective surface film.

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