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Non-toxic organic zinc corrosion inhibitors in hydrochloric acid

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The efficiency of some substituted N-arylpyrroles as zinc corrosion inhibitors in hydrochloric acid was examined by electrochemical (d.c. and a.c.) and gravimetric methods. The influence of the structure and composition of a molecule on the inhibition characteristics was observed by investigation of the action of the functional group located on the pyrrole ring (–CHO) and at the ortho position of the benzene ring (–H, –Cl, $-CH_3$). The results have shown that all the organic compounds investigated possess good inhibiting properties. In contrast to most commercial acid corrosion inhibitors, which are highly toxic and very hazardous products, substituted N-arylpyrroles are nontoxic compounds with good environmental characteristics.

1. Introduction

The corrosion inhibition efficiency of organic compounds is connected with their adsorption properties. The role of the adsorbed inhibitor is to isolate the metal from the corrosive medium and/or to modify the electrode reactions which cause dissolution of the metal. In the case of heterocyclic nitrogen compounds in acid media the adsorption is ascribed to the effects of the aromatic rings which are adsorbed parallel to the metal surface [1]. It has been observed that the adsorption depends mainly on the electronic structure of the molecules [2, 3] as well as on the surface morphology of the metal [4].

Zinc is an active metal which dissolves readily in acid media. Therefore, there is a strong necessity for protection of zinc by organic inhibitors [5–13].

A remarkable efficiency of substituted N-arylpyrroles as corrosion inhibitors for iron in hydrochloric acid has been shown by a previous investigation [14–17]. The aim of this work is to study the influence of structure and composition of some substituted pyrroles on their inhibitory properties against zinc corrosion in hydrochloric acid media. In contrast to most commercial corrosion inhibitors, which are toxic and dangerous products, in the case of substituted N-arylpyrroles there is no danger to people or the environment.

2. Experimental details

The material used for the investigation was 99.98% zinc. Electrodes were prepared from cylindrical zinc rods, isolated with a Teflon band so that a circular cross section ($0.628\,cm^2$) only was exposed. Prior to every experiment the electrode was polished with 600 grit silicon carbide emery paper, degreased with ethanol and rinsed with triply distilled water.

Measurements were taken in a conventional electrolytic cell with a platinum counter electrode using a saturated calomel electrode as reference. The electrodes were immersed in the solution consisting of 0.5 M hydrochloric acid containing the organic inhibitors at a concentration of 5×10^{-3} M.

The following substituted N-arylpyrroles were studied:

(1) 1–(2-chlorophenyl)–2,5-dimethylpyrrole–3-carbaldehyde
(2) 1–(2-methylphenyl)–2,5-dimethylpyrrole–3-carbaldehyde
(3) 1–phenyl–2,5-dimethylpyrrole–3-carbaldehyde
(4) 1–(2-chlorophenyl)–2,5-dimethylpyrrole–3,4-dicarbaldehyde
(5) 1–(2-methylphenyl)–2,5-dimethylpyrrole–3,4-dicarbaldehyde
(6) 1–phenyl–2,5-dimethylpyrrole–3,4-dicarbaldehyde

The investigated compounds were synthesized by Knorr–Paal condensation of 2,5-hexadione with the corresponding anilines, according to the standard method [18]. The products were purified by distillation or recrystallization and were analysed spectroscopically before being added to the solution. The inhibiting characteristics of the compounds were examined by electrochemical d.c. and a.c. techniques as well as by weight loss measurements.

Kinetic data were obtained directly from steady state polarization measurements analysed on the basis of the Tafel extrapolation method and on the 'linear' polarization measurements of polarization resistance in the vicinity of the corrosion potential

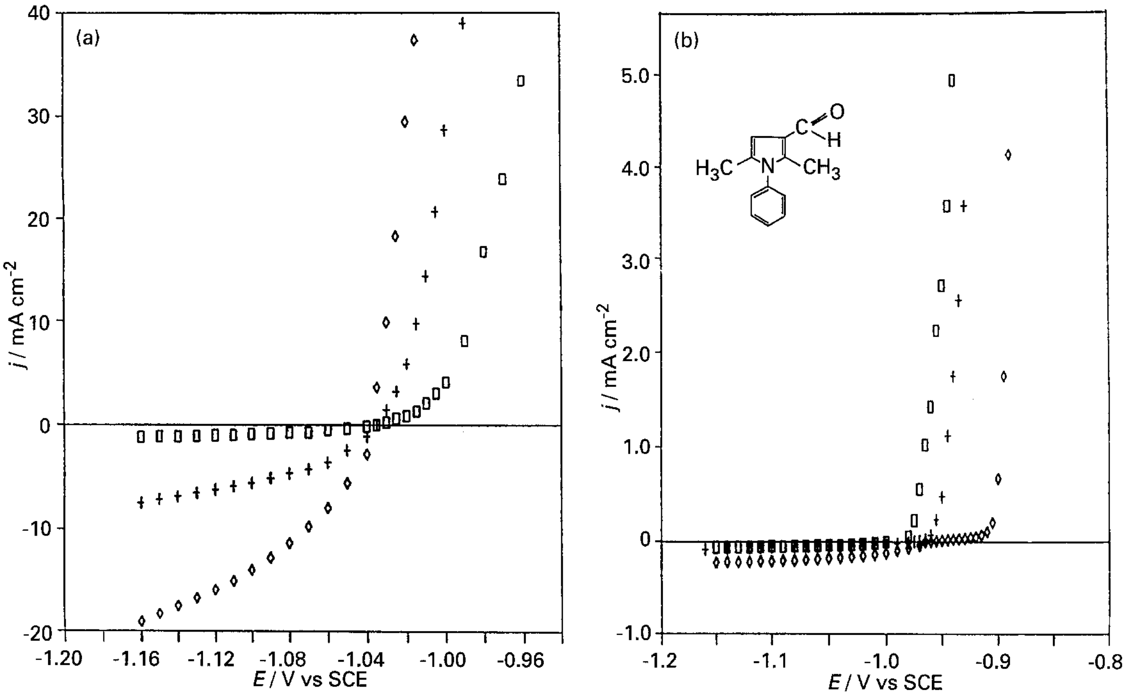

Fig. 1. Current density–potential curves on zinc in 0.5 M hydrochloric acid. (a) At (○) 20, (+) 40 and (◇) 60° C. (b) As (a) with the addition of 5×10^3 M 1-phenyl–2,5-dimethylpyrrole–3-carbaldehyde.

($E = E_{\mathrm{corr}} \pm 15\,\mathrm{mV}$) according to the procedure described by Mansfeld [19].

However, in corrosion systems with a discontinuous polarization curve in the vicinity of E_{corr} under steady state conditions, the determination of polarization resistance from electrochemical d.c. measurements:

$$R_{\mathrm{p}} = \left(\frac{\mathrm{d}E}{\mathrm{d}i}\right)_{E=E_{\mathrm{corr}}} \tag{1}$$

and from measurements by a.c. impedance techniques according to

$$R_{\mathrm{p}} = \lim_{\omega \to 0} Re\{Z_{\mathrm{f}}\}_{E=E_{\mathrm{corr}}} \tag{2}$$

has been found to be problematic. In those systems the corrosion currents cannot be determined according to

$$i_{\mathrm{corr}} = \frac{b_{\mathrm{a}} b_{\mathrm{c}}}{2.303(b_{\mathrm{a}} + b_{\mathrm{c}})} \frac{1}{R_{\mathrm{p}}} = \frac{B}{R_{\mathrm{p}}} \tag{3}$$

In such cases, where the usual polarization techniques fail, the corrosion current has been determined from the charge transfer resistance, R_{ct}, according to Epelboin and coauthors [20]:

$$i_{\mathrm{corr}} = \frac{B}{R_{\mathrm{ct}}} \tag{4}$$

$$R_{\mathrm{ct}} = \lim_{\omega \to \infty} Re\{Z_{\mathrm{f}}\}_{E=E_{\mathrm{corr}}} \tag{5}$$

where R_{ct} was determined at the intercept of the capacitive loop of the a.c. impedance diagram with the real axis at medium frequencies.

The results obtained have shown excellent agreement with the results obtained by the Tafel extrapolation method. The inhibition efficiency, z, was calculated using the equation:

$$z = \frac{i_0 - i_{\mathrm{i}}}{i_0} 100 \tag{6}$$

where i_{i} and i_0 denote corrosion current densities with or without the inhibitor, respectively.

Electrochemical measurements were made at temperatures from 20 to 60° C under stirred, aerated conditions.

The inhibiting efficiency was also examined by a gravimetric method of weight loss measurements. The corrosion rate was determined according to the relation:

$$K = \frac{\Delta m}{S \Delta t} \tag{7}$$

where Δm is the weight loss of metal, S is the surface of exposed metal and Δt is the time of exposure of the metal to the aggressive medium. Gravimetric measurements were also performed at temperatures of 20, 40 and 60° C.

3. Results

The inhibiting properties of substituted N-arylpyrroles with one or two carbaldehyde groups in the pyrrole ring and different radicals in the benzene ring (–H, $-CH_3$, –Cl) were investigated using electrochemical and nonelectrochemical methods.

Preliminary measurements with different concentrations of organic compounds investigated from 1×10^{-4} to 1×10^{-2} M showed that the concentration of 5×10^{-3} M is optimal and all the subsequent measurements were performed with this concentration of inhibitor in 0.5 M hydrochloric acid.

Figure 1(a) shows overall current density-potential potentiostatic curves obtained on zinc in 0.5 M hydrochloric acid, without the addition of inhibitor, while Figure 1(b) shows the curves obtained on zinc in 0.5 M hydrochloric acid with the addition of 5×10^{-3} M 1-phenyl–2,5-dimethylpyrrole at 20, 40 and 60° C.

Based on the results of potentiostatic polarization measurements the corrosion currents and corrosion

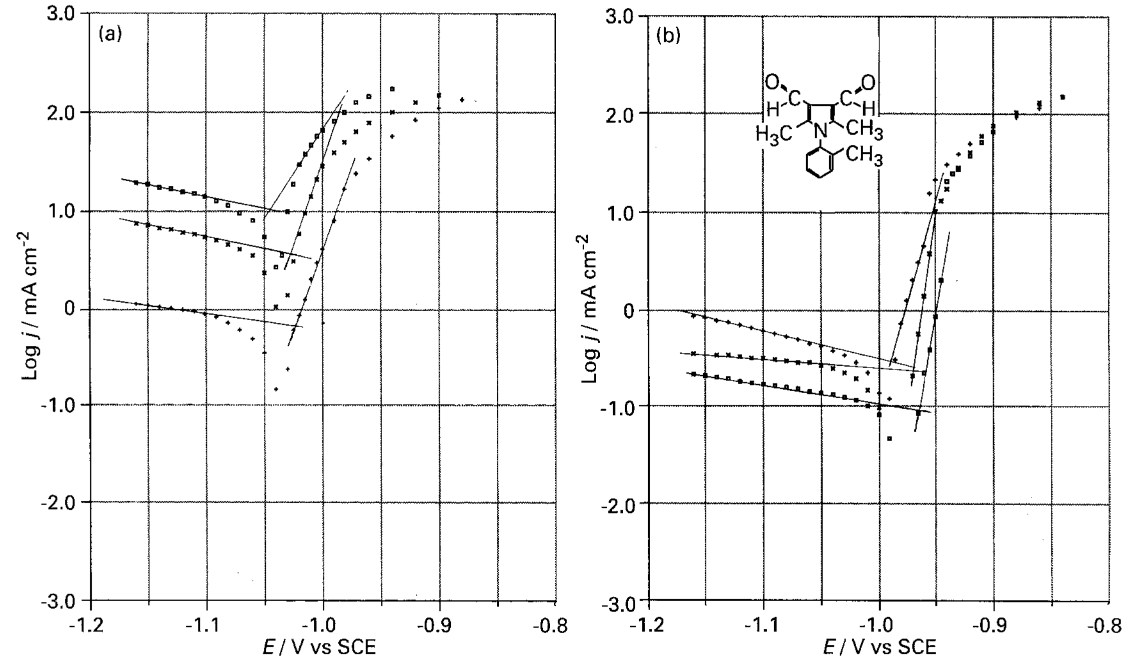

Fig. 2. Extrapolated Tafel plots for the overall current potential curves for zinc in 0.5 M hydrochloric acid. (a) At (+) 20, (×) 40 and (□) 60° C. (b) As (a) with the addition of 5×10^3 M 1–(2-methylphenyl)–2,5-dimethylpyrrole–3,4-dicarbaldehydes.

potentials were estimated from the intersections of the anodic and cathodic Tafel lines. Typical results of Tafel extrapolation are presented in Fig. 2. Figure 2(a) is related to zinc in the uninhibited hydrochloric acid solution and Fig. 2(b) to zinc in the solution of 0.5 M hydrochloric acid with the addition of 5×10^{-3} M 1–(2-methylphenyl)–2,5-dimethylpyrrole–3,4-dicarbaldehydes at 20, 40 and 60° C.

Owing to the nonlinear behaviour of the current-potential curve in the vicinity of the corrosion potential, E_{corr}, there was no possibility of determining the polarization resistance, R_p, from d.c. measurements according to Mansfeld [19], neither was it possible to determine it from impedance spectroscopy in the low frequency range from the intercept of the extrapolated induction loop at zero frequency. The corrosion current density was determined from a.c. impedance spectroscopy using Relation 4, according to Epelboin [20].

The charge transfer resistance, R_{ct}, was determined at the intercept of the capacitive loop of the a.c. impedance diagram with the real axis at medium frequencies.

Figure 3a shows impedance spectroscopy diagrams for zinc in 0.5 M hydrochloric acid at 20, 40 and 60° C and Fig. 3(b) impedance diagrams for zinc in 0.5 M hydrochloric acid solution inhibited with the addition of 5×10^{-3} M 1–(2-chlorophenyl)–2,5-dimethylpyrrole–3-carbaldehyde.

Figure 4 shows Tafel line intersections in the system zinc–0.5 M hydrochloric acid with the addition of 5×10^{-3} M 1–(2-chlorophenyl)–2,5-dimethylpyrrole–3-carbaldehyde.

As well as the electrochemical methods, the gravimetric method was used in determining the inhibiting characteristics of substituted N-aryl-pyrrole. To compare the results of the investigating methods used, Table 1(a, b, c) shows the results of corrosion parameters obtained for zinc in hydrochloric acid without an inhibitor and with the addition of 1–(2-chlorophenyl)–2,5-dimethylpyrrole–3-carbaldehyde.

Table 1(a) shows the kinetic parameters of zinc in uninhibited hydrochloric acid and in hydrochloric acid inhibited with 1–(2-chlorophenyl)–2,5-dimethylpyrrole–3-carbaldehyde obtained using the Tafel

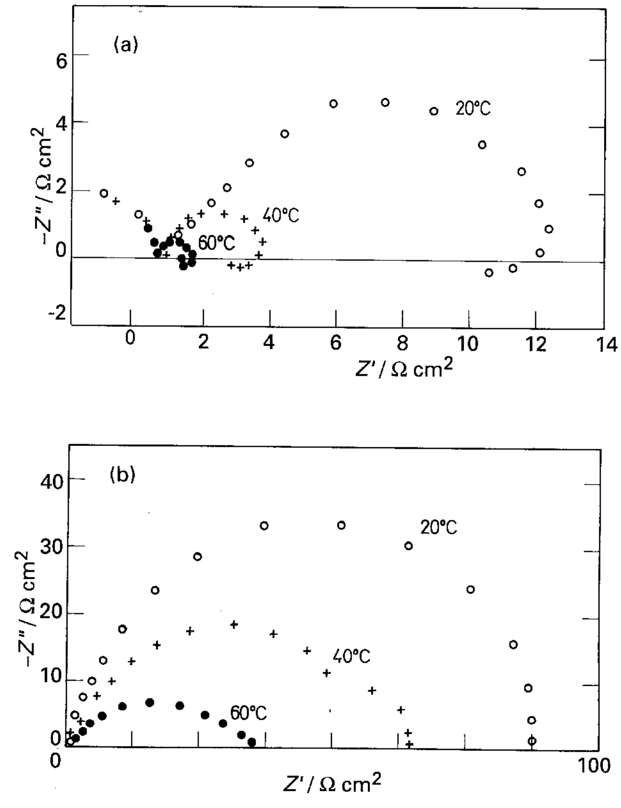

Fig. 3. Impedance spectroscopy diagrams for zinc in 0.5 M hydrochloric acid. (a) At (□), 20, (+) 40 and (· · ·) 60° C. (b) As (a) with the addition of 5×10^3 M 1–(2-chlorophenyl)–2,5-dimethylpyrrole–3-carbaldehyde.

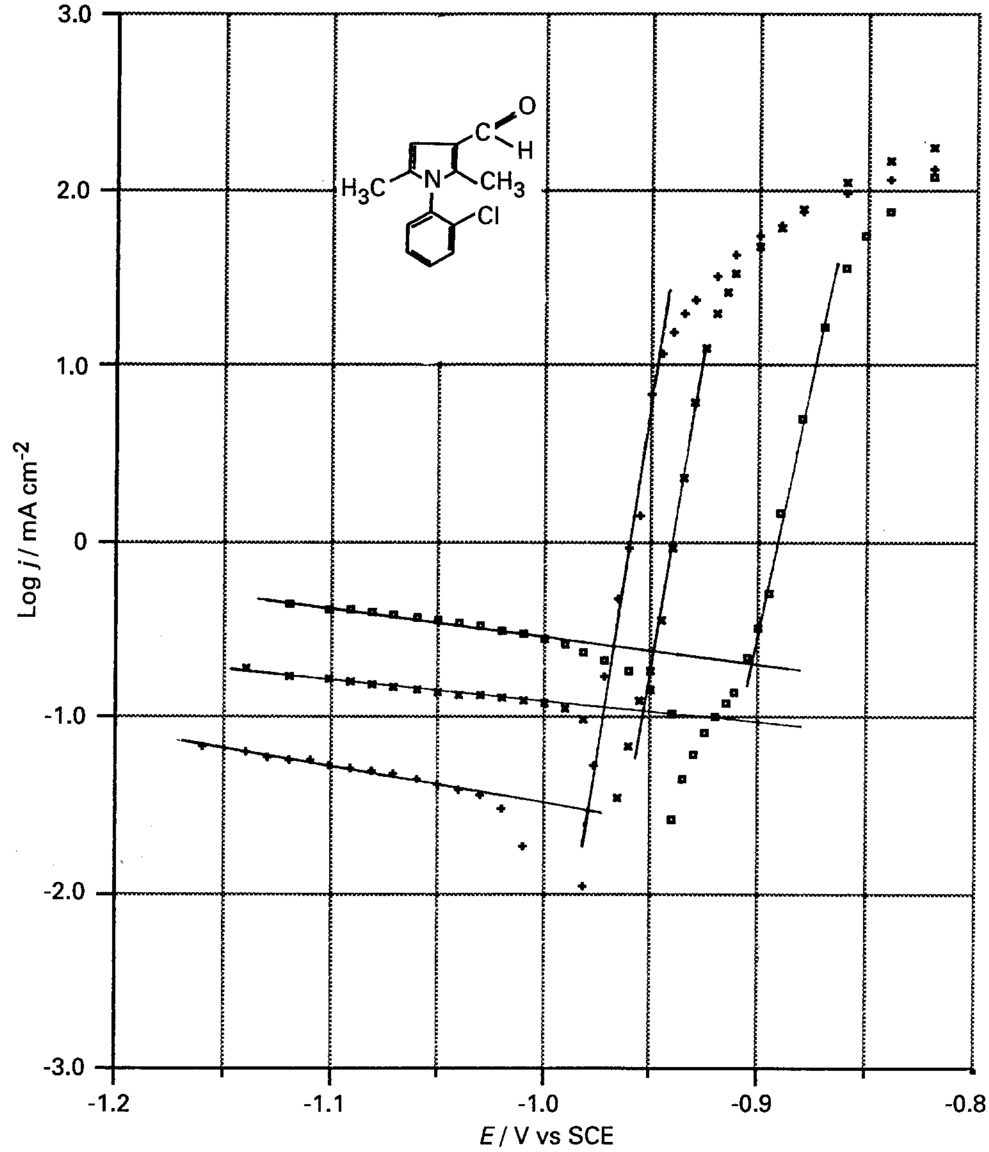

Fig. 4. Intersections of anodic and cathodic Tafel lines for zinc in 0.5 M hydrochloric acid with the addition of 5 × 10^3 M 1–(2-chlorophenyl)–2,5-dimethylpyrrole–3-carbaldehyde at 20, 40 and 60° C.

extrapolation method. Table 1(b) relates to the corrosion currents and the inhibition efficiency of 1–(2-chlorophenyl)–2,5-dimethylpyrrole–3-carbaldehyde calculated on the basis of determination of charge transfer resistance, R_{ct} from a.c. impedance spectroscopy measurements and using Relation 4, according to Epelboin [20].

Table 1(c) refers to the corrosion rate and the degree of protection obtained by the gravimetric method of weight loss measurements of zinc in the same system (shown in Table 1(a) and (b)).

Table 2 represents the values of corrosion potentials, corrosion currents and degrees of protection of zinc in all the solutions. The results show that all the investigated organic compounds have good inhibiting characteristics.

At low temperatures (20–40° C) the substituted N-arylpyrrole with one carbaldehyde group shows better inhibiting properties (86.0–99.3%) than dicarbaldehydes (38.6–97.7%) while dicarbaldehydes exhibit very good protection of zinc (97.8–98.8%) at higher temperatures (60° C).

4. Discussion

Most organic inhibitors contain at least one polar group with an atom of nitrogen, sulphur or oxygen, each of them as a chemisorption centre. The protective properties of such compounds depend on the electron densities around the chemisorption centre: the higher the electron density at the centre, the more effective is the inhibitor. Investigations of aliphatic and cyclic amines have shown that cyclic amines are better inhibitors than aliphatic ones [4].

The investigated substituted N-arylpyrroles having a nitrogen atom in the heterocyclic ring of the pyrrole with substituted carbaldehyde and a phenyl ring with substituted radicals (H, CH_3, Cl) are organic compounds whose composition and molecular structure represent good conditions for inhibition. The earlier investigation [14, 16], on inhibiting efficiency of substituted N-aryl pyrroles as iron corrosion inhibitors has shown that the introduction of one or two carbaldehyde groups in the pyrrole ring improves the inhibiting characteristics.

Table 1. Kinetic parameters of zinc in 0.5 M hydrochloric acid with and without the addition of 1–(2-chlorophenyl)–2,5-dimethylpyrrole–3-carbaldehyde

(a) *Obtained using Tafel extrapolation method*

Solution	b_a/mV dec^{-1}			b_c/mV dec^{-1}			j_{corr}/mA cm^{-2}			*z*/%		
	20° C	*40° C*	*60° C*	*20° C*	*40° C*	*60° C*	*20° C*	*40° C*	*60° C*	*20° C*	*40° C*	*60° C*
0.5 M HCl	30	30	30	–500	–462	–400	0.66	3.83	11.22	–	–	–
0.5 M HCl + inhibitor 2	10	18	38	–727	–727	–533	0.034	0.11	0.24	94.8	97.1	97.8

(b) *As* (*a*) *but calculated on basis of determination of* R_{ct} *from impedance spectroscopy measurements according to Epelboin et al. [20]*

Solution	*B*/mV			R_{ct}/Ω cm^2			j_{corr}/mA cm^{-2}			*z*/%		
	20° C	*40° C*	*60° C*	*20° C*	*40° C*	*60° C*	*20° C*	*40° C*	*60° C*	*20° C*	*40° C*	*60° C*
0.5 M HCl	13.86	13.93	14.08	12.3	3.5	1.3	1.13	3.98	10.83	–	–	–
0.5 M HCl + inhibitor 2	4.28	8.01	13.20	88	68	38	0.048	0.12	0.34	95.0	96.9	96.8

(c) *Corrosion rate and protection degree of zinc in 0.5 M hydrochloric acid with and without the addition of 1–(2-chlorophenyl)–2,5-dimethyl-pyrrole–3-carbaldehyde obtained by gravimetric method*

Solution	Δm/g			*K*/g cm^{-2} min^{-1}			*z*/%		
	20° C	*40° C*	*60° C*	*20° C*	*40° C*	*60° C*	*20° C*	*40° C*	*60° C*
0.5 M HCl	1.5×10^{-3}	1.14×10^{-2}	9.71×10^{-2}	4.68×10^{-6}	3.5×10^{-5}	3.03×10^{-4}	–	–	-
0.5 M HCl + inhibitor 2	3.0×10^{-4}	6.0×10^{-4}	2.2×10^{-3}	9.29×10^{-7}	1.85×10^{-6}	6.77×10^{-6}	80.1	94.8	97.8

The effect of functional groups on the adsorption of organic molecules is very important. Molecules of organic substances containing functional groups – which are electron donors, like CHO, are chemically adsorbed on the surface of metals having unshared electron orbitals [4]. The adsorption of surface-active organic compounds increases with the molecular weight. Consequently, the high inhibition of N-aryl-2,5-dimethylpyrroles with carbaldehyde groups can be explained on the basis of the condensation characteristic of the carbaldehyde groups leading to the production of large molecules [16].

The results in Table 1(a–c) show that all experimental methods used are appropriate for the investigation of the efficiency of organic compounds as corrosion inhibitors. A good agreement between electrochemical and nonelectrochemical methods was obtained.

Substituted N-arylpyrroles with one carbaldehyde group in the pyrrole ring have very good protecting efficiency in the whole temperature range (20–60° C), while substituted N-arylpyrroles with two carbaldehyde groups have better inhibiting properties at higher temperatures (40 and 60° C).

The adsorption of surface active organic compounds increases with molecular weight. It is to be expected that compounds with two carbaldehyde groups show better inhibiting characteristics by reason of the enlarged condensation process. However, compounds with two carbaldehyde groups have excellent inhibiting characteristics only at higher temperatures, while their inhibiting properties at 20° C are insignificant (except 1–(2-chlorophenyl)–2,5-dimethylpyrrole–3,4-dicarbaldehyde). This leads to the conclusion that the adsorption of large condensate molecules at higher temperatures (60° C) is better.

The investigation of the influence of different radicals (–H, –Cl, $-CH_3$) substituted in the ortho position of benzene ring has shown that 1-phenyl–2,5-dimethylpyrrole–3-carbaldehyde possesses the best inhibiting characteristic. This can be explained by

Table 2. Values of corrosion potentials, corrosion currents and protection degrees of zinc corrosion in all examined solutions

Solution	E_{corr}/V			j_{corr}/mA cm^{-2}			*z*/%		
	20° C	*40° C*	*60° C*	*20° C*	*40° C*	*60° C*	*20° C*	*40° C*	*60° C*
HCl	–1.024	–1.030	–1.042	0.660	3.831	11.220	–	–	–
1	–1.008	–0.978	–0.910	0.028	0.026	0.118	95.3	99.3	98.9
2	–0.976	–0.955	–0.908	0.034	0.110	0.240	94.8	97.0	97.8
3	–0.992	–0.962	–0.910	0.085	0.093	0.175	86.0	97.1	98.4
4	–0.970	–1.000	–0.996	0.405	0.600	0.195	38.6	83.6	98.3
5	–0.987	–0.961	–0.917	0.056	0.082	0.145	91.5	97.8	98.7
6	–0.984	–0.970	–0.962	0.260	0.220	0.095	56.7	94.5	99.1

(1) 1-phenyl–5-dimethylpyrrole–3-carbaldehyde
(2) 1–(2-chlorophenyl)–2,5-dimethylpyrrole–3-carbaldehyde
(3) 1–(2-methylphenyl)–2,5-dimethylpyrrole–3-carbaldehyde
(4) 1-phenyl–2,5-dimetylypyrrole–3,4-dicarbaldehyde
(5) 1–(2-chlorophenyl)–2,5-dimethylpyrrole–3,4-dicarbaldehyde
(6) 1–(2-methylphenyl)–2,5-dimethylpyrrole–3,4-dicarbaldehyde

the influence of steric factors in the condensation of carbaldehydes.

The most commercial acid corrosion inhibitors are highly toxic and very hazardous products, dangerous to eyes and skin. Some may affect lungs, the central nervous system, visual ability and may lead to death upon high direct contact. Contamination of surface waters is a major cancer cause due to high toxicity in fish. All this is a reason for rigorous protection measures in handling commercial inhibitors.

In contrast to most acid corrosion inhibitors the investigated substituted N-aryl pyrroles are non-toxic compounds which, according to Maga [21] are found to be naturally occurring in foods such as coffee, chocolate, eggs, rice, tea, tobacco and potato.

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