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Alcoholic *Mentha* extracts as inhibitors of low-carbon steel corrosion in aqueous medium

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Abstract This paper presents experimental evidence of the ability of alcoholic *Mentha* extracts to inhibit the corrosion of low-carbon steel in aqueous acid solutions. Alcoholic extracts of *Mentha spicata* L., *Mentha x gentilis* L., *Mentha crispa* L., *Mentha piperita* L., and *Mentha x piperita* L. were tested. The corrosion inhibition capability of these extracts was confirmed by means of weight loss experiments, cyclic voltammetry, chronoamperometry, polarization curves, and electrochemical impedance spectroscopy.

Keywords Corrosion inhibitors · Low-carbon steel · *Mentha* extracts

Introduction

Organic compounds are recognized as effective inhibitors of the corrosion of many metals and alloys [1–4]. The efficiency of an organic compound as a corrosion inhibitor is closely associated with its chemical adsorption [5]. Most organic compounds contain nitrogen, sulfur, oxygen, and multiple bonds in their molecules, through which they are adsorbed onto metal surfaces [6]. Some authors describe this interaction as a chelating reaction between the metal surface and the organic compound [7]. The planarity of the π orbital and the lone electron pairs in the heteroatom are important features that determine the adsorption of these molecules onto the metallic surface. Quantum chemical simulations have been applied to understand the processes involved in the interaction between the metallic surface and the structure of the organic compound, for instance, in relation to corrosion inhibition [8, 9]. Different classes of organic compounds have been used as corrosion inhibitors for iron and low-carbon (or mild) steel in acid solutions due to the fact that these metal materials are of fundamental importance in many industrial processes [10–13]. In this regard, organic compounds containing nitrogen have a notable influence on the corrosion inhibition of steel in acid solutions [14–17]. However, although these compounds provide good results, they are not environmentally safe substances. Thus, the investigation of natural organic compounds as corrosion inhibitors is particularly interesting for two reasons: they are not expensive and are ecologically acceptable. Natural honey has been tested as a corrosion inhibitor in highly saline water [18], ascorbic acid in aqueous Na_2SO_4 solutions [4], mimosa tannin in sulfuric acid [6], an extract of the plant *Zenthoxylum alatum* in aqueous orthophosphoric acid [19], holo-α-lactalbumin and β-casein in aqueous phosphate buffer solution [20], stearic acid in aqueous perchloric acid [21], and natural oil extracted from Pennyroyal Mint in chloridric acid [22]. Many alternative eco-friendly corrosion inhibitors have been developed for steel, and reviews of natural products as corrosion inhibitors for metals have recently been published [23–25]. Also, our laboratory has previously carried out studies which confirmed the adsorption of caffeine onto a copper surface in aqueous and ethanolic media [26–28].

Extracts of some plants have been reported to reduce the corrosion rate of different metals [29–32]. This paper reports electrochemical evidence of the ability of the alcoholic extracts of *Mentha spicata* L., *Mentha x gentilis* L., *Mentha crispa* L., *Mentha piperita* L., and *Mentha x piperita* L. to

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inhibit the corrosion of low-carbon steel in aqueous solutions. The corrosion inhibition capability of these *Mentha* alcoholic extracts was confirmed by means of weight loss experiments, cyclic voltammetry, chronoamperometry, polarization curves, and electrochemical impedance spectroscopy (EIS).

Experimental

Working electrodes for potentiodynamic, EIS, and chronoamperometric measurements were cut into a rectangular shape ($1.0 \times 0.5 \times 0.1$ cm) from a low-carbon steel sheet (C, 0.06; Mn, 0.31; P, 0.0104; S, 0.0114; Cr, <0.001; Ni, 0.0051; Al, 0.0332 wt.%). The electrodes were used without thermal treatment. The working electrodes were polished with 600 and 1,200 grit emery papers, rinsed with deionized water, and degreased with a p.a. grade acetone:chloroform mixture (1:1) prior to each experiment. Aerated aqueous solutions of pure sulfuric acid (0.20 mol L^{-1}) were used at room temperature as the aggressive medium. Distilled/de-ionized water was used to prepare the aqueous solutions. A platinum wire was employed as the auxiliary electrode and an Ag/AgCl (KCl saturated) as the reference electrode.

Alcoholic extracts of *Mentha* plants were obtained from fresh herbs using a simple Soxhlet process with ethanol as the solvent. Only the first portion of the solvent extract was used in order to avoid thermal decomposition of the active compounds during multiple extractions. The solvent excess was then removed by distillation. During the corrosion inhibition experiments, one or two drops of these extracts were added directly into the aggressive medium in order to verify the corrosion inhibition effect of the active compounds present. The choice of this amount of *Mentha* extracts drops was necessary considering the concentration of the active species as well as the solubility of the extracts in the aggressive solutions. The chemical compositions of these extracts have been published elsewhere [33].

The weight loss experiments were carried out using a Sartorius analytical balance, model B210S, while the electrochemical tests were performed with an Autolab potentiostat, model PGSTAT30, coupled to a personal computer. All experiments were repeated at least three times in order to get a good reproducibility of the data.

Results and discussion

Weight loss experiments

Weight loss was measured using rectangular-shaped pieces of low-carbon steel ($1.5 \times 1.0 \times 0.1$ cm) totally immersed in 35 ml of aqueous sulfuric acid (0.20 mol L^{-1}), with and without the addition of two drops of each of the *Mentha*

extracts individually. The polishing and degreasing treatments described above were also applied to these metal pieces. The immersion time for these experiments was 2 h at room temperature. The weight loss values were used to calculate the protection efficiency as follows:

$$\eta\% = 100(1 - \Delta m / \Delta m^{\circ}) \tag{1}$$

where Δm and Δm° are the weight loss difference of steel samples with two drops of the alcoholic extract and without inhibitor, respectively.

Figure 1 shows the protection efficiency of two drops of *Mentha* extracts on the corrosion of low-carbon steel in sulfuric acid.

As observed in Fig. 1, the protection efficiency was almost 50% in the presence of two drops of *M. crispa* extract. Taking into account that the chemical composition of *M. crispa* extracts [33] reveals that carvone is the major compound (61% *w/w*), it is plausible to consider that this compound is largely responsible for the corrosion inhibition. As the average weight of one drop is 11.6 mg, the carvone concentration in this medium can be calculated as being 2.70×10^{-3} mol L^{-1}.

Since the inhibition efficiency of *M. crispa* was remarkably higher than that of the other extracts, the discussion in this paper will be based on the results obtained for this extract and, comparatively, for the *M. x gentiles* extract as a reference.

Cyclic voltammetry

Cyclic voltammetry experiments were performed in order to observe the electroreduction and electrooxidation of the
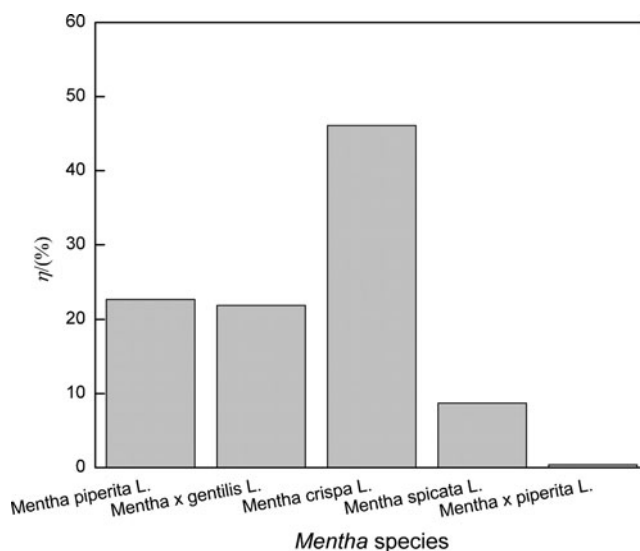

Fig. 1 Protection efficiency ($\eta\%$) of *Mentha* extracts in relation to the corrosion of low-carbon steel after 2 h of immersion in 35 ml of aqueous aerated sulfuric acid (0.20 mol L^{-1}) at room temperature

metal during the potential sweeps and to obtain the best conditions for the interaction between the organic extract and the electrode surface. Figure 2 shows the voltammograms of the low-carbon steel in 15 ml of aqueous sulfuric acid (0.20 mol L^{-1}) in the absence and in the presence of one drop of *M. crispa* extract (3.2 mmol L^{-1} of carvone).

The potentiodynamic curves were recorded after maintaining the electrode polarized for 5 s at the initial potential in order to increase the surface coverage with the adsorbed species formed. As observed in Fig. 2, the presence of one drop of *M. crispa* extract decreased both the anodic and cathodic current density values. Thus, even the addition of a small amount of this extract to the aggressive medium was effective in terms of the metal corrosion inhibition performance of the compounds. The decrease in the anodic current density values suggests that the anodic processes were inhibited in the presence of the extract. Despite this effect, however, the corrosion potential was not shifted in the presence of the *M. crispa* extract.

The best conditions for the interaction between the electrode surface and the compounds present in the extract were obtained when the electrode potential was kept at −0.75 V for 5 s, as observed in Fig. 3.

The strategy used in this figure was to plot the anodic current density value differences taken directly from the voltammograms at −0.32 V (Ag/AgCl), in the absence and in the presence of the *M. crispa* extract, against the initial potential (adsorption potential) of the potential program.

It was clear that the best conditions for the inhibitory effect were obtained after polarizing the electrode at −0.75 V (Ag/AgCl) for 5 s. By using these current density differences, the protection efficiency was calculated according to a
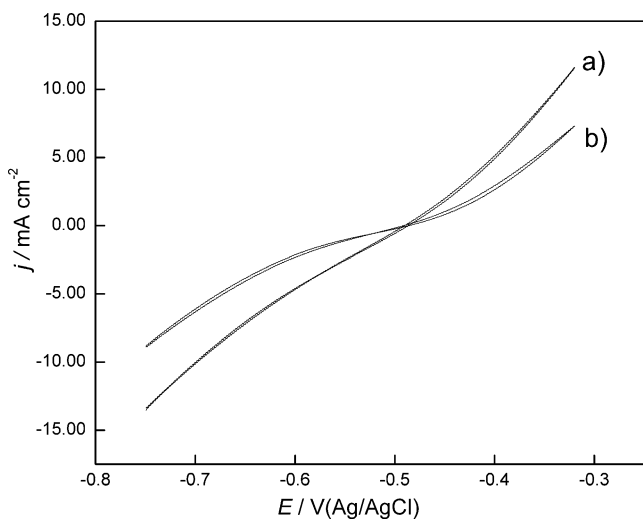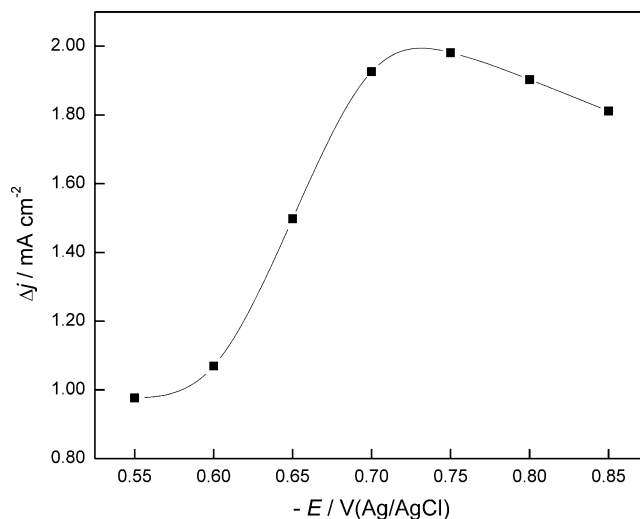

Fig. 3 Anodic current density differences obtained from the voltammograms at the most anodic potential (−0.32 V) in the absence and in the presence of one drop of *Mentha crispa* extract, in aerated sulfuric acid 0.20 mol L^{-1}, recorded at different adsorption potentials

previously published procedure [28]. The value was found to be around 40.0%, even with the addition of one drop of *Mentha* extract, that is, close to the result obtained in weight loss experiments.

The same inhibitory effect was observed when these experiments were repeated with the *M. x gentilis* extract, as observed in Fig. 4.

The previous discussion on the interaction of the *M. crispa* extract with the electrode surface should also apply to the *M. x gentilis* extract. Both anodic and cathodic current densities decrease in the presence of one drop of *M.*
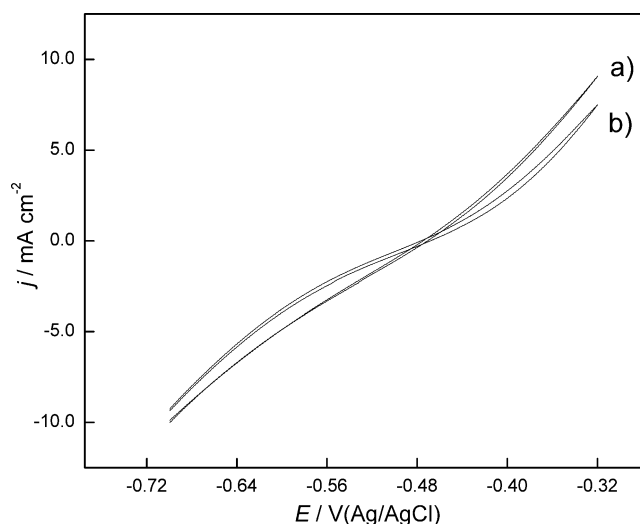

Fig. 2 Cyclic voltammograms of low-carbon steel in aerated sulfuric acid (0.20 mol L^{-1}), recorded at 50 mV s^{-1}, in the absence (*a*) and in the presence (*b*) of one drop of *Mentha crispa* extract (3.15 mmol L^{-1} of carvone)

Fig. 4 Cyclic voltammograms of low-carbon steel in aqueous sulfuric acid (0.20 mol L^{-1}), in the absence (*a*) and in the presence (*b*) of one drop of *Mentha x gentilis* extract, recorded at 50 mV s^{-1}

x gentilis. The protection efficiency for this extract, however, was calculated around 10.0%. In this extract, two major components were detected: linalyl acetate (45.59% *w/w*) and linalol (31.19% *w/w*). As observed from the results for the weight loss experiments, the inhibitory effect of the *M. x gentilis* extract was not as strong as that of the *M. crispa* extract. This was also observed when the experiment was repeated with the other *Mentha* extracts. This difference appears to be associated with the major components present in the *Mentha* extracts.

As suggested previously [34], the surface-active compound present in *Mentha* extracts may interact with the metal surface by adsorption mechanisms. This should involve the displacement of adsorbed water by a reaction described below:

$$M_{(H_2O)ads} + L_{(org)} \rightarrow M_{(L)ads} + H_2O \qquad (2)$$
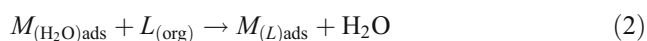
where L is the surface-active compound present in *Mentha* extracts.

Chronoamperometric studies

The chronoamperometric experiments were performed in order to verify the ability of the *Mentha* extracts to inhibit the anodic processes of the low-carbon steel, by polarizing anodically the electrode potential at −0.32 V (Ag/AgCl) for 600 s. The current density values associated with the electrooxidation of low-carbon steel were recorded in the absence and in the presence of one drop of *M. crispa* extract, as shown in Fig. 5.

The anodic current density values decreased significantly in the presence of only one drop of *M. crispa* extract. The
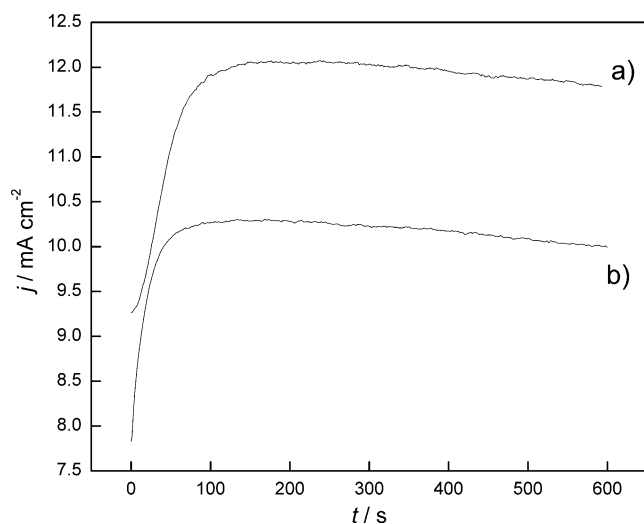
corrosion process was inhibited even using a low concentration of the *M.* extract. The protection efficiency was calculated around 15% and was determined taking in account the current density values in absence and in the presence of *M.* extract. This effect may be considered as remarkable given that the potential imposed at the working electrode was not ideal for the adsorption of the compounds present in the extract. The same effect was observed by repeating this experiment with the *M. x gentilis* extract, as shown in Fig. 6.

As mentioned above, the inhibition ability of the *M. x gentilis* extract is comparable with that observed for the other *M.* extracts (see Fig. 5), and consequently, the same comments apply. However, the protection efficiency was calculated around 12%, as expected lower than that observed with *M. crispa* extract.

Polarization measurements

These experiments were performed using the same procedure described for the cyclic voltammetry studies. Prior to the linear potential sweep, the electrode was polarized for 5 s at the adsorption potential. The potential range was then scanned at 1 mV s^{-1}, under static conditions.

The Tafel measurements were in a potential region very close to the corrosion potential (E^{corr}) as shown in Fig. 7, with the addition of one drop of the *M. crispa* or *M. x gentilis* extract.

Anodic dissolution of the metal was inhibited in the presence of only one drop of *Mentha* extract in 15 ml of aggressive acid solution. The anodic current density values decreased considerably in the presence of this small amount
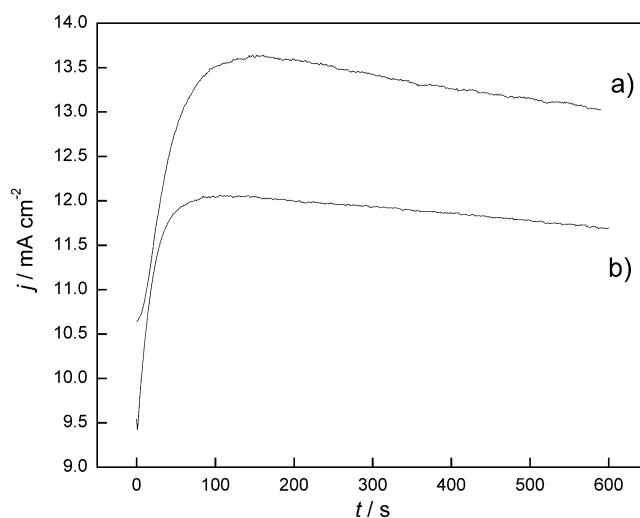

Fig. 5 Chronoamperometric curves of low-carbon steel in aqueous sulfuric acid (0.20 mol L^{-1}), recorded at −0.32 V (Ag/AgCl) in the absence (*a*) and in the presence (*b*) of one drop of *Mentha crispa* extract

Fig. 6 Chronoamperometric curves of low-carbon steel in aqueous sulfuric acid (0.20 mol L^{-1}), recorded at −0.32 V (Ag/AgCl) in the absence (*a*) and in the presence (*b*) of one drop of *Mentha x gentilis* extract
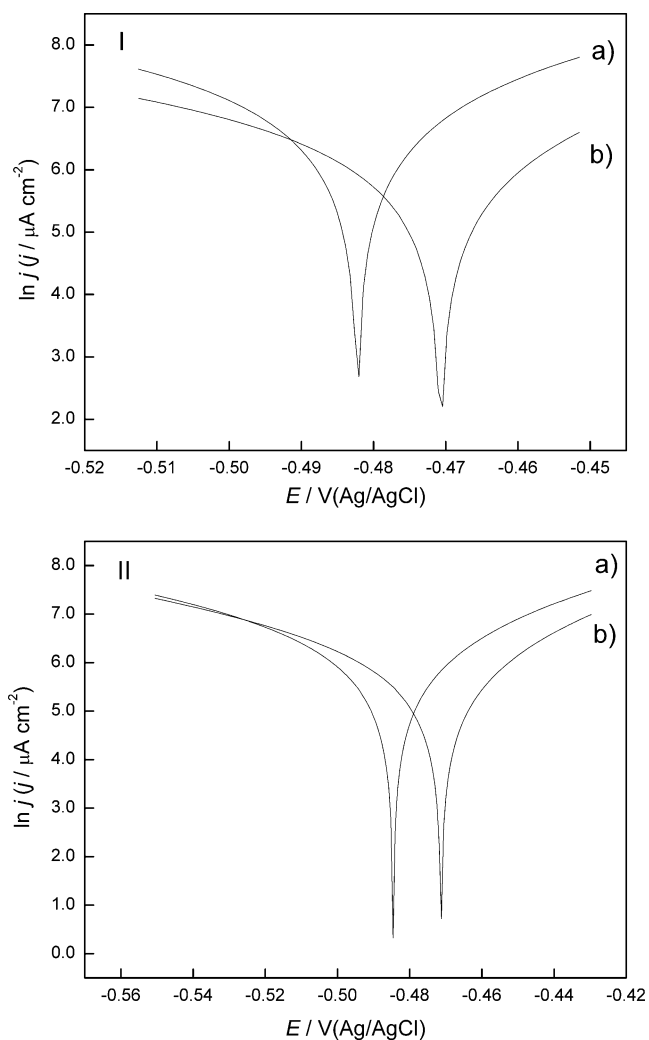
Fig. 7 Polarization behavior of low-carbon steel in aqueous sulfuric acid (0.20 mol L^{-1}), recorded in the absence (*a*) and in the presence (*b*) of one drop of (*I*) *Mentha crispa* and (*II*) *Mentha x gentilis* extracts

vof inhibitor. Using the anodic current values taken at −0.46 V (Ag/AgCl) in the absence and in the presence of M. extract, the protection efficiency was calculated around 75.6%. The cathodic processes were affected in the presence of the inhibitor mainly in the case of *M. crispa*. The corrosion potential (E^{corr}) was shifted to more anodic values. The inhibitive effect on both the anodic and cathodic processes suggests that the organic compounds present in the extracts may be considered as cathodic/anodic inhibitors. These effects are in agreement with those observed by cyclic voltammetry, including the lower corrosion inhibition ability of *M. x gentilis* (protection efficiency was calculated around 68.0%) compared with *M. crispa*.

AC impedance measurements

EIS was carried out at open-circuit potential, again applying the same procedure, that is, the electrode was polarized for

5 s at the adsorption potential prior to each EIS experiment. The sine wave voltage (10 mV), peak-to-peak, was applied to the electrode at frequencies between 100 kHz and 1 Hz. The impedance diagrams are given in the Nyquist representation in the absence and in the presence of one drop of *M. crispa* or *M. x gentilis* extract, as shown in Fig. 8.

The impedance diagrams obtained have almost a semicircular appearance. This indicates that the corrosion of low-carbon steel in aqueous sulfuric acid is mainly controlled by a charge transfer process. With the addition of one drop of *Mentha* extract, the charge transfer resistance R^{ct} increased to a greater extent in the case of *M. crispa* than with *M. x gentilis*. This effect suggests an increase in the corrosion resistance, attributable to the compounds adsorbed on the electrode surface, in agreement with the results obtained from the weight loss and electrochemical measurements.
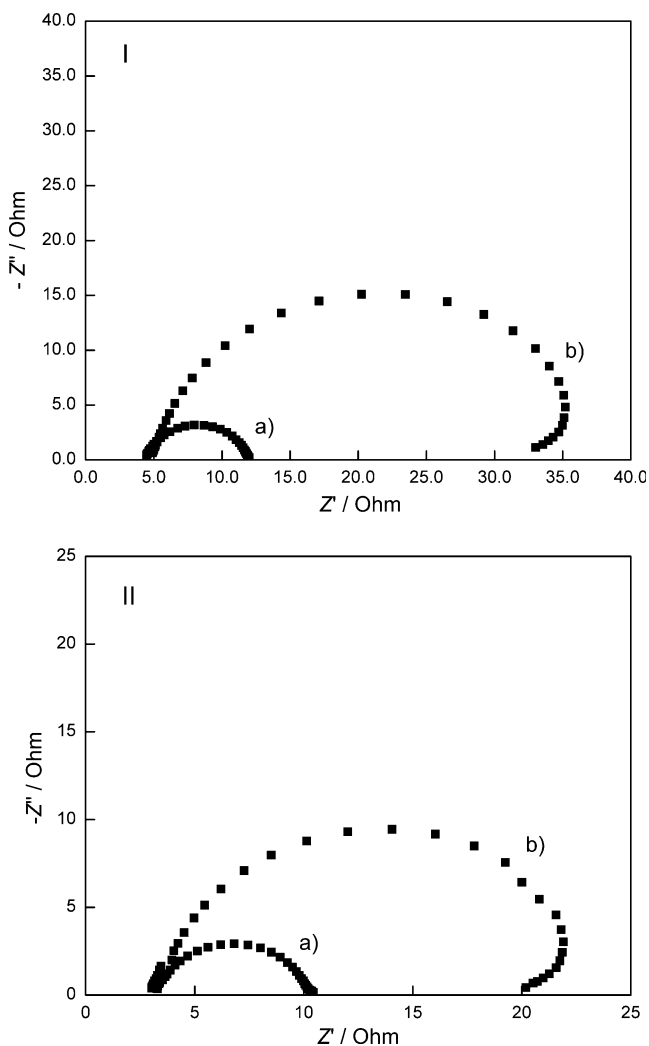

Fig. 8 Nyquist plots of low-carbon steel in aqueous sulfuric acid (0.20 mol L^{-1}), recorded in the absence (*a*) and in the presence (*b*) of one drop of (*I*) *Mentha crispa* and (*II*) *Mentha x gentilis* extracts

Conclusions

1. Weight loss experiments were conclusive regarding the ability of the *Mentha* extracts to inhibit the corrosion processes of low-carbon steel in aqueous sulfuric acid. It was unequivocal that *M. crispa* L. could decrease the weight loss of the metal by almost 50%.
2. Electrochemical experiments showed that the interaction between the metal surface and the active chemical compound present in the alcoholic *Mentha* extracts, leading to the protection effect, was dependent on the adsorption step.
3. The presence of the adsorbed species on the metal surface decreases the anodic current values suggesting an inhibitory effect on the electrochemical processes.
4. The presence of the alcoholic *Mentha* extracts decreases the anodic current as observed in the chronoamperometric experiments even in aqueous acid medium and under anodic potential polarization.

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