

## CO and *trans*-cinnamaldehyde as corrosion inhibitors of I825, L80-13Cr and N80 alloys in concentrated HCl solutions at high pressure and temperature

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### Abstract

In this paper, corrosion inhibition by chemisorbed CO, at high pressure and temperature, on a high-Ni ferrous alloy (Incoloy 825) and two high-Fe alloys (13Cr-L80 (Uniloy-420) and N80 steels) in very aggressive conditions (15% w/w HCl solution) is described. CO was either directly dosed into the electrolyte, or produced by dehydration of formic acid. It is shown that CO is a very good corrosion inhibitor, the inhibiting effect being even higher at high pressure and temperature than at normal pressure and room temperature. The effect of combining CO with a common acid corrosion inhibitor, *trans*-cinnamaldehyde (TCA), at high pressure and temperature, was also studied. Under these conditions, the polymerization of TCA may be favored, leading to a thin film on the metal surface that appears to serve as a barrier to corrosion. It was found that, when CO is used in combination with TCA, the inhibiting effect of the latter is considerably intensified.

**Keywords:** Corrosion inhibition; CO; *trans*-cinnamaldehyde; concentrated HCl; oilfield industry

### 1. Introduction

Acidification, consisting in pumping downhole concentrated (commonly 15%) HCl, is currently one of the most, if not the most, commonly employed method for oil-well stimulation. It was introduced by Herman Frasch in 1895 [1, 2], although, due to extensive corrosion of the alloys employed for tubing, it was not massively used until the development of the first acid corrosion inhibitors [3].

*Trans*-cinnamaldehyde (TCA) was found to be a very effective and environment-friendly acid corrosion inhibitor by Hugel [4]. Since then, it has been extensively used in the oilfield industry, and many attempts have been made in order to elucidate its inhibiting mechanism [5-7]. It has been proposed that, under high pressure and temperature conditions, TCA polymerizes forming a protective film on the metal surface [5].

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Carbon monoxide was first identified as a corrosion inhibitor for stainless steel in dilute hydrochloric acid by Uhlig in 1940 [8], but, although he found it to decrease the alloy corrosion rate very efficiently, direct dosing of carbon monoxide has never been used as a corrosion inhibition procedure. Instead, formic acid is often used as an intensifier of other corrosion inhibitors in the oilfield industry. Intensifiers are usually added in the acidizing process to the HCl-based acid blend, which also contains the corrosion inhibitors, in order to enhance the performance properties of the latter [9]. As it is well known [10], dehydration of formic acid to CO is catalyzed by strong acids, like concentrated  $\text{H}_2\text{SO}_4$ . Although HCl is not acidic enough to catalyze this reaction at room temperature, it can be catalyzed by hot concentrated HCl [11]. Cassidy *et al.* [12] have recently shown that CO resulting from the dehydration of formic acid in concentrated HCl in the presence of iron-based alloys at high pressure and temperature is most likely responsible for the intensifying action of HCOOH.

Some time ago, we reported a study of the adsorption of CO on Fe [13], Co [14] and Ni [15, 16] in the pH range 3-14 (studies of CO adsorption on these metals remain, more than 10 years later, very scarce [17-24]). As a consequence of the strong bonding of CO to the surface of Fe, Co, and Ni, surface oxidation or dissolution of these metals is strongly impeded in CO-saturated solutions [13-16], and very recently, we have reported that CO can be used as an efficient inhibitor of the corrosion of Fe, Ni and their alloys in concentrated HCl solutions at room temperature and normal pressure [25]. In this paper, we describe the inhibiting effect of CO in 15% w/w HCl, under high pressure (6.9 MPa) and temperature (100-200°C) conditions, both when it is directly dosed and when it is generated from the formic acid dehydration reaction, and compare it with that of *trans*-cinnamaldehyde, a commonly used acid corrosion inhibitor.

## 2. Experimental Section

All the electrochemical measurements at high temperature and pressure were performed at the premises of Halliburton Energy Services, Inc. in Duncan (Oklahoma, USA), using a commercial autoclave (Cortest Inc.) with a volume of 4.4 L, and an EG&G Princeton Versastat II potentiostat. The typical working pressure was 6.9 MPa and the working temperature was between 100°C and 175°C. The pressure vessel itself was made of Hastelloy B, and it contained a thermocouple for the measurement and regulation of temperature, electrical heating coils, gas inlets, valves and a rupture disk. The autoclave heating system was controlled by an electronic control unit, which kept the temperature of the solution within the autoclave constant. The accuracy of the temperature was always within  $\pm 1^\circ\text{C}$ .

The working electrodes for the high pressure and temperature experiments were cut from seamless alloy tubing, and exposed an area of 15 cm<sup>2</sup> to the solution. The electrical connection to the working electrode was made through an Inconel wire that was insulated with polytetrafluoroethylene (PTFE) tubing. The auxiliary electrode was a Pt wire, and the reference electrode was a 0.1 M Ag/AgCl (KCl<sub>sat</sub>) external reference electrode (Cortest Inc.), valid for a range of temperatures between 25°C and 220°C. The external reference electrode operated at normal temperature and pressure, and communicated with the high pressure and temperature zone via a non-isothermal electrolyte bridge [26, 27]. Because of the temperature gradient along the electrolyte bridge, the potential measured had to be corrected for the corresponding thermal liquid-junction potential drop. This was done with the conversion table provided by the manufacturer, which lists the temperature-dependent correction factors necessary to convert the measured potentials into the Ag/AgCl (KCl<sub>sat</sub>) scale at room temperature and normal pressure.

The electrochemical measurements at normal pressure and temperature were performed with disks 12 mm in diameter cut from alloy foils supplied by Metal Samples Co. The disks were sanded with emery paper (600 grit), and sonicated for 2 min in acetone and then for 5 min in Milli-Q water, before each electrochemical measurement or gravimetric test. The chemical composition of the different alloys employed (wt. %) is given in Table 1. A Wenking analog potentiostat, in combination with a digital oscilloscope for signal recording, and a one-compartment three-electrode cell were used. The disk electrodes were set in a polypropylene holder with a Viton O-ring, with a brass screw pressed against the back of the disk for providing electrical contact. A Pt wire and a home-made Ag/AgCl (KCl<sub>sat</sub>) electrode were used as the counter and reference electrodes, respectively.

Blank measurements were performed in N<sub>2</sub>-purged electrolyte (N50, Air Liquide), because under down-hole conditions the presence of oxygen is not to be expected. Measurements in CO-saturated solutions were performed after bubbling CO (N47, aluminium alloy cylinders, Air Liquide) for at least 20 min, or using CO to pressurize the autoclave. Aqueous solutions containing 15% w/w HCl, prepared with analytical grade reagents and Milli-Q water, were used as electrolyte. The polarization resistance measurements were performed applying a potential sweep with an amplitude of ±10 mV around the  $E_{corr}$ , at a scan rate of 1 mV s<sup>-1</sup>.

ATR-SEIRA spectra were recorded using a Nicolet 6700 FTIR spectrometer, equipped with a liquid nitrogen-cooled MCT detector, using *p*-polarized light. Each spectrum consisted of 25 interferograms collected with a resolution of 4 cm<sup>-1</sup>. IR reflectance spectra of the TCA-derived film formed on the electrodes were recorded as follows: (i) A background spectrum was recorded by placing a TCA-free alloy disk on the reflection accessory of our spectrometer; (ii) the same disk was immersed in a 15% HCl solution containing 2% (v/v) TCA, and introduced in an autoclave, where it was left for 40 min at

121°C and 0.2 MPa; (iii) the disk was removed from the solution, rinsed with Milli-Q water, dried with  $N_2$ , and placed on the reflection accessory of the spectrometer, and the sample spectrum was recorded. All the spectra are shown in absorbance units, defined as  $A = -\log(R_{\text{sample}}/R_{\text{reference}})$  ( $A = -\log(I_{\text{sample}}/I_{\text{reference}})$  in the case of the transmission spectra), where  $R_{\text{reference}}$  ( $I_{\text{reference}}$ ) and  $R_{\text{sample}}$  ( $I_{\text{sample}}$ ) represent the intensities of the infrared radiation reflected from the electrode (transmitted through the solution) at the reference and the sample spectrum, respectively. With this convention, a negative band indicates that a species present in the reference spectrum has disappeared in the sample spectrum and, conversely, a positive band indicates that a new species, not present in the reference spectrum, has appeared in the sample spectrum.

### 3. Results and discussion

*3.1. Inhibition of corrosion by CO, TCA, and by a combination of both, at normal pressure and room temperature.* The open circuit potential in nitrogen-purged 15% HCl at normal pressure and temperature, i.e., the corrosion potential,  $E_{\text{corr}}$ , shows in all the cases values that are stable within an interval of  $\pm 5$  to  $\pm 30$  mV over a period longer than three days (Figure 1). In all the cases but U420,  $E_{\text{corr}}$  shifts to more positive values when the solutions are saturated with CO. In a previous work [25], we have shown using infrared spectroscopy that CO chemisorbs on the surface of the three alloys employed in this study. In general, as will be seen below, we observe that the larger the positive shift of  $E_{\text{corr}}$ , the higher the corrosion inhibition by chemisorbed CO.

In the case of I825 and U420 (Figures 1 A and B, respectively),  $E_{\text{corr}}$  in  $N_2$ -purged solutions shifts negatively during the very first seconds of the measurement. This may be due to dissolution of the native oxide film on the surface of the alloys. After these first seconds,  $E_{\text{corr}}$  shifts positively for ca. 20 hours, and then it reaches a roughly stationary value, that slowly drifts negatively. The shift of  $E_{\text{corr}}$  to positive values is usually related to adsorption processes on the electrode surface and, in this particular case, we associate it with the formation of a protective passive film. In the case of N80 (Figure 1 C) a roughly stationary value of  $E_{\text{corr}}$  is reached in the first hours after immersion, and  $E_{\text{corr}}$  also slowly shifts negatively over an extended period of time.

As shown in Figure 1 A, in the case of I825 no differences can be observed in the evolution of  $E_{\text{corr}}$  when TCA and CO are added together and when CO is added alone, suggesting that TCA does not interact strongly with the surface of I825. This is supported by the fact that, when TCA is added alone,  $E_{\text{corr}}$  is similar to that in the absence of any inhibitor in the solution.

The corrosion rate, at normal pressure and room temperature, of the different samples in  $N_2$ -purged 15% HCl, and in solutions containing TCA and/or saturated with CO, was evaluated with polarization resistance ( $R_p$ ) and gravimetric measurements. The results are shown in Figures 2 and 3,

respectively. As expected, the addition of a corrosion inhibitor (either TCA or CO) provokes an increase in  $R_p$  (Figure 2) (i.e., a decrease in the corrosion rate). CO is a clearly better corrosion inhibitor for I825, and for N80 at short times, than the commonly used TCA, which outperforms CO in the case of U420 and in the case of N80 at times longer than ca. 35 hours. In all the cases, and contrary to the case of  $E_{corr}$ , the corrosion rate oscillates considerably over time, and it never reaches a stationary value. The oscillations in  $R_p$  are larger in the presence of an inhibitor, and are particularly intense in the presence of CO, suggesting that the protecting film or adlayer formed by the corrosion inhibitor (TCA, CO, or both) is very sensitive to minimal perturbations in the experimental system, and is continuously being attacked and reformed.

Although I825 presents the highest dispersion in the values of  $R_p$  (with variations of more than one order of magnitude) in the presence of CO, under these conditions it shows the lowest average corrosion rate. Furthermore, when both TCA and CO are present in the solution, the average corrosion rate of I825 remains the same as in TCA-free and CO-saturated solutions, suggesting that, when CO is present, chemisorbed CO is solely responsible for the observed corrosion inhibition. On the contrary, in the case of U420 and N80, the corrosion rate is lower when CO and TCA are added together than when these inhibitors are used separately (Figure 2). In the case of N80, the inhibition achieved when TCA and CO are used together is roughly the sum of the individual effects of these inhibitors, but, interestingly, in the case of U420 a synergic effect is observed when TCA and CO are used together, the inhibition of corrosion being clearly larger than that expected from a simple sum of their individual effects.

Gravimetric test for I825, U420 and N80, shown in Figure 3, confirm the results obtained from the  $R_p$  measurements: CO acts as a corrosion inhibitor in all three cases, and is particularly effective in the case of I825. In the case of N80 and U420, the inhibiting effect is highest when CO and TCA are added together, while in the case of I825 combining TCA and CO does not improve the inhibiting effect of CO alone. Please note that the apparently lower mass loss at  $t > 2$  h, as compared with shorter times, in Figure 3B, is due to the accumulation of corrosion products on the sample surface, as evident from a simple visual inspection. These products remain on the surface even after sonication.

*3.2. Inhibition of corrosion by CO, TCA and a combination of both at high pressure and temperature.* Cyclic voltammograms at  $T > 100^\circ\text{C}$  and at  $P = 6.9$  MPa of I825, U420 and N80 in 15% HCl at  $1\text{ mV s}^{-1}$ , both in  $\text{N}_2$ -purged and in CO-saturated solutions, are shown in Figure 4. All the cyclic voltammograms were started at the negative potential limit (after a steady-state open circuit potential was established) in the positive direction.

As we have shown recently [25], and as was actually to be anticipated, chemisorbed CO is the species responsible for the inhibition of corrosion of I825, U420 and N80 in CO-saturated concentrated HCl solutions. Increasing the pressure and the temperature must have opposing effects on the CO adlayer. At higher pressure the activity of CO in solution will increase, increasing the rate of CO adsorption and favoring a higher steady-state CO coverage and a higher inhibiting effect. In contrast to higher pressure, higher temperature may increase the rate of CO desorption by providing the necessary desorption energy, in addition to decreasing the rate of CO adsorption due to the decrease of the activity of CO in solution (the CO solubility must decrease with increasing temperature), thus favoring a lower steady-state CO coverage (and, hence, a lower inhibition of corrosion) than at room temperature.

As can be seen in Figure 4, CO is an even better corrosion inhibitor at high pressure and temperature than at room temperature and normal pressure (compare with the results in reference [25]), suggesting that the increase in the solubility of CO at 6.9 MPa overwhelms the effect of increasing the temperature. This was actually to be expected, since the pressure has been multiplied by a factor of ca. 70, while the temperature has increased by 100-150°.

On I825 and N80, and at a constant pressure of 6.9 MPa, the inhibiting effect of CO is higher at 120°C than at 175°C. This is actually what should be expected if the inhibition of corrosion is due to the molecular chemisorption of CO on the Ni and Fe atoms present at the surface of I825 and on the Fe atoms at the surface of N80, as found at normal pressure and temperature [25]. On the contrary, in the case of U420, the inhibition of corrosion is higher at 175°C than at 120°C. This may be due to the high amount of Cr present in U420, onto which CO can adsorb dissociatively [28]. If this were the case, and, consequently, the activation energy for the dissociation of CO is lower than the adsorption energy, chemisorbed CO could dissociate upon increasing the temperature, leaving a blocking carbon film or, alternatively, a carbide on the alloy surface.

We have also compared the inhibition effect of CO at high pressure and temperature with that of TCA, a common acid corrosion inhibitor, and have analyzed the effect of using CO in combination with TCA. With the only exception of U420 at 6.9 MPa and 120°C, CO is a more effective corrosion inhibitor than *trans*-cinnamaldehyde, and the highest inhibition effect is always observed when CO and TCA are used in combination (Figure 5), including the case of U420 at 120°C. It is worth noting that, although the inhibiting effect of TCA alone at 175°C is fairly small, if any, when used in combination with CO at that temperature the former considerably contributes to enhance the inhibiting effect of the latter.

*3.3. Formic acid as a precursor of CO at high temperature and pressure.* CO can be generated from the dehydration of formic acid, a reaction catalyzed by very strong acids, and that in concentrated HCl can occur at temperatures above 94°C. Using CO generated from the dehydration of formic acid as a corrosion inhibitor could be more practical than directly dosing CO. Actually, formic acid is often used as an intensifier of the action of common inhibitors like TCA, and it has been recently shown that the intensifying effect might be due to its dehydration to CO [12].

Figure 6 shows the cyclic voltammograms of I825, U420 and N80 in 15% HCl containing 4% (v/v) HCOOH, at 6.9 MPa. The cyclic voltammograms of I825 in the solutions containing formic acid (Figure 6 A) are very similar to those in CO-saturated solutions, suggesting that the observed inhibiting effect is actually due to the chemisorption of CO produced upon dehydration of formic acid. The inhibiting effect is larger in CO saturated solutions (Figure 4), certainly because directly dosing CO allows to reach a higher CO concentration in the solution and, hence, a higher CO coverage, but the inhibiting effect of CO generated from formic acid decomposition is significant, and improves at lower temperatures, as found when CO is dosed directly.

The addition of formic acid to the HCl solution has barely any effect on the cyclic voltammograms of U420, supporting our previous suggestion that, in this case, the effect observed in CO-saturated solutions is due to the dissociative chemisorption of CO.

In the case of N80 (Figure 6 C), a clear inhibiting effect is found when formic acid is used at 100°C. Under these conditions, a large inhibition of H<sub>2</sub> evolution is observed, an effect that is absent in CO-saturated solutions. This effect, that is not observed at room temperature and normal pressure, must be provoked by a formic acid residue, different to CO, that adsorbs on the surface strongly and blocks it.

*3.4. Spectroscopic study of the protecting film formed in the presence of TCA at high pressure and temperature.* The inhibition of corrosion at high pressure and temperature by TCA is usually attributed to the formation of a polymeric TCA-derived film on the metal surface [5, 7]. However, this idea is based exclusively on transmission spectra of the film, once extracted from the metal surface by dissolving it in CHCl<sub>3</sub>, and of the reaction products that remain in the solution.

A viscous layer, detectable with a simple visual inspection, forms on the metal after exposure to 2% (v/v) TCA in 15% HCl at high pressure and temperature (see conditions in the experimental section). We have performed experiments in which we have acquired reflectance infrared spectra of the film adhered to the alloy surface, in order to characterize the polymer composition, and to try to obtain some insight into the polymerization process. However in the laboratories at the Institute of Physical Chemistry "Rocasolano" the highest achievable pressure is 0.2 MPa, and we cannot, hence,

discard differences between our results and the situation at the more than one order of magnitude higher pressures downhole.

The external reflectance spectra of the TCA-derived films on I825, U420, and N80 after reaction in HCOOH-free and HCOOH-containing 15% HCl are shown in Figures 7 and 8, respectively. The periodic oscillations between 2800 and 1800  $\text{cm}^{-1}$  in the external reflectance IR spectra of U420 and N80 (Figures 7 and 8) are caused by interference of the IR beam reflected at the air/TCA film interface with the beam reflected at the TCA film/metal interface. When the reaction proceeded in the absence of formic acid in the solution, the main differences between the reflectance spectra of the resulting films (Figure 7) and the transmission spectrum of TCA at normal pressure and room temperature (Figure 9, red line) appear in the region between 1800 and 1400  $\text{cm}^{-1}$ . The band at 1629  $\text{cm}^{-1}$ , corresponding to  $\nu_{\text{C=C}}$ , appears wider due to the contribution of several species, and the band corresponding to the conjugated carbonyl ( $\nu_{\text{C=O}}$ ) at 1675  $\text{cm}^{-1}$  appears less intense than that observed in the transmission spectrum at normal pressure. The absorption frequency of C=O depends on several well-known environment variables, and if it can be determined with precision, provides valuable information related to that environment. When a C=C and a C=O bond are conjugated, the C=O stretching frequency decreases by ca. 30  $\text{cm}^{-1}$  with respect to that of an analogous non-conjugated carbonyl. The appearance of a band at 1715  $\text{cm}^{-1}$ , corresponding to an unconjugated carbonyl, confirms that part of the TCA polymerizes through the C=C bond on the alloy surface. The appearance of bands corresponding to non-polymerized TCA suggests that both polymerized and non-polymerized TCA molecules are present in the film. It has been suggested that non-polymerized TCA molecules, onto which the polymer film grows, adsorb directly on the metal and act as an adherent for the polymer film [6].

If the same experiment is carried out in the presence of 4% HCOOH (Figure 8), formation of a film on the surface of the alloys cannot be detected with a simple visual inspection. The external reflection IR spectrum shows that the film on I825 is mainly composed of non-polymerized TCA molecules. This might suggest that CO chemisorption on the alloy surface prevents the metal surface from catalyzing the polymerization reaction, or prevents the adsorption of the polymer film on the metal surface. In the case of N80, the spectrum is similar to that recorded in the absence of HCOOH, showing, again, the band at 1715  $\text{cm}^{-1}$  corresponding to unconjugated C=O. In the case of U420 no information can be obtained from the spectrum, because the sample was severely degraded after exposure to the solution.

After reaction in the autoclave at 121°C and 0.2 MPa for 40 min, the solution contained two phases: a slightly brown colored aqueous phase, and a dark-brown organic phase. The transmission spectra of the reaction products in the dark-brown organic phase of the solution after immersing the



different alloys in a 15% HCl solution containing 2% (v/v) TCA in an autoclave at 121°C and 0.2 MPa for 40 min, are shown in Figure 9. A blank experiment, in which no metal was immersed in the solution during the treatment at 121°C and 2 MPa is also shown for comparison. TCA is the main species in solution in all the cases, as deduced from the comparison with the transmission spectrum of TCA at room temperature and normal pressure. Only changes in the ratio between the intensities of the C=O and C=C bands appear. In the case of N80 there are no differences between the spectrum at 121°C and that at normal temperature (although the solution clearly changed its color after the reaction). In the cases of I825, U420, and of the solution that was submitted to the reaction conditions in the absence of any metal, the intensity of the band corresponding to the C=O vibration diminishes with respect to the intensity of the band corresponding to C=C, this effect being more pronounced in the case of I825. These results suggest that the polymerization reaction may be catalyzed by a metal, and that, hence, it is affected by the chemical composition of the alloy.

The only band observable in the transmission spectra of the aqueous phase of the products in the solution (not shown) is that corresponding to the  $\nu_{\text{C-C(O)H}}$  mode of TCA, and it presents a very low intensity. This suggests that, due to their hydrophobic nature, TCA and the reaction products remained in the organic phase, and only a few molecules of TCA are present in the aqueous phase.

### **Conclusions**

The main conclusion of this work is that carbon monoxide, when chemisorbed on the surface of the three alloys used, reduces the corrosion rate significantly, the inhibiting effect being even higher at high pressure and temperature than at normal pressure and room temperature. In the case of I825 and N80, the higher inhibition of corrosion by CO at high temperature and pressure, as compared to room temperature and normal pressure, is most likely due to the increase in the activity of CO in solution with increasing pressure, which will favor a higher steady-state CO coverage, and must overwhelm the opposing effect of increasing the temperature. The case of U420 is particularly interesting, because, although CO does not inhibit corrosion appreciably at normal pressure and room temperature [25], it provokes a great inhibition effect at 6.9 MPa and 175°C, most likely due to the dissociative chemisorption of CO, favored by the presence of Cr in the alloy and by the high temperature.

CO can be generated from formic acid at high pressure and temperature. The inhibiting effect, although significant, is smaller than in CO-saturated solutions, and, in the case of I825, it improves at lower temperatures, as found when CO is dosed directly. In the case of N80, a HCOOH-derived species different to CO is formed on the surface in the presence of formic acid at high temperature and pressure. This species, which we have not been able to identify, blocks the surface and might,

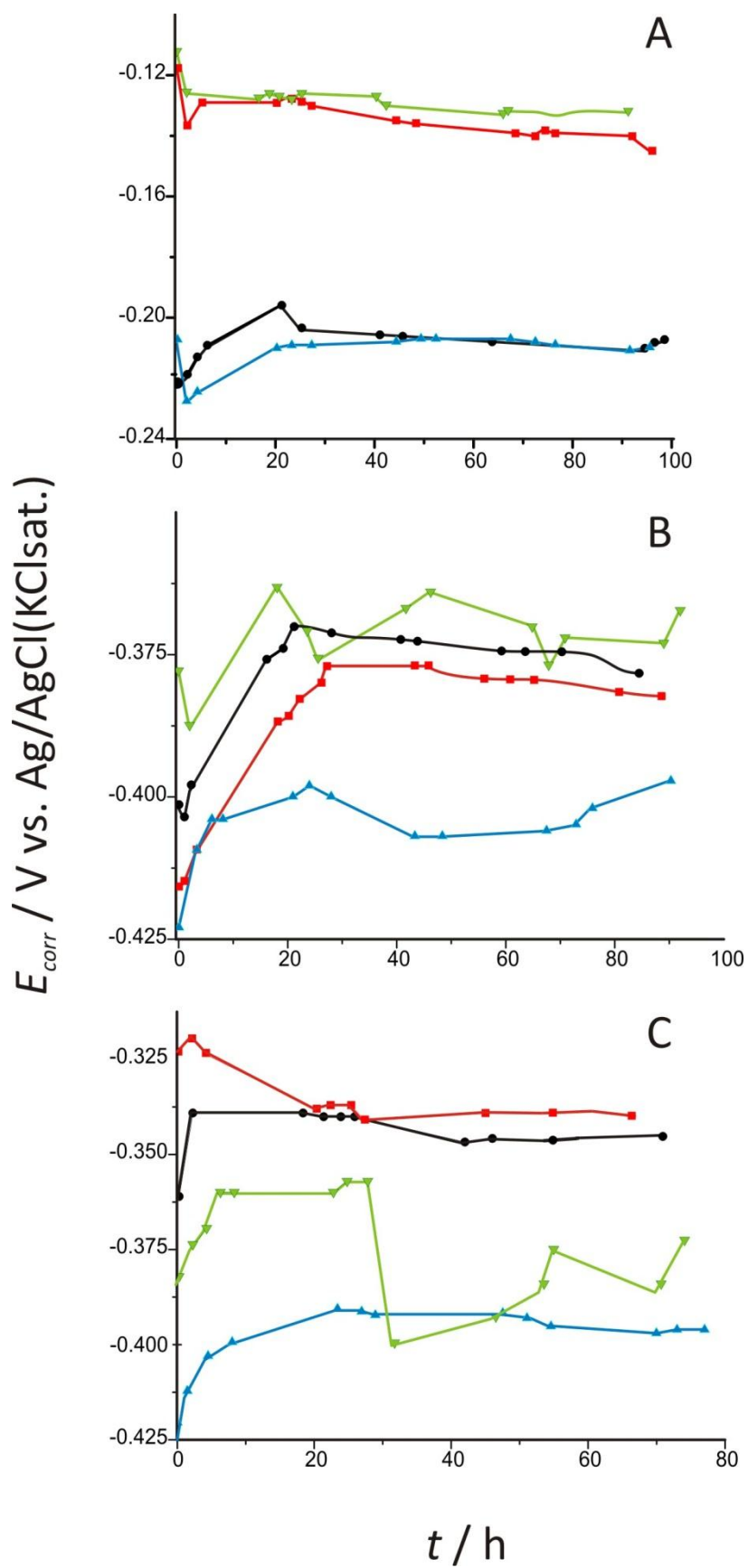
hence, act as a corrosion inhibitor. In the case U420, no significant inhibition of corrosion is observed when HCOOH is added to a 15% HCl solution at high pressure and temperature.

TCA has been used for many years as an inhibitor of steel corrosion in concentrated hydrochloric acid. TCA polymerization produces a thin blocking film [29], whose corrosion inhibiting effect is intensified when CO and TCA are used together. As we have shown recently using in situ FTIRS at room temperature and normal pressure [25], CO chemisorbs on Fe and Ni even when covered by a TCA thin film and contributes to reduce the rate of the corrosion process, intensifying the inhibiting effect of TCA.

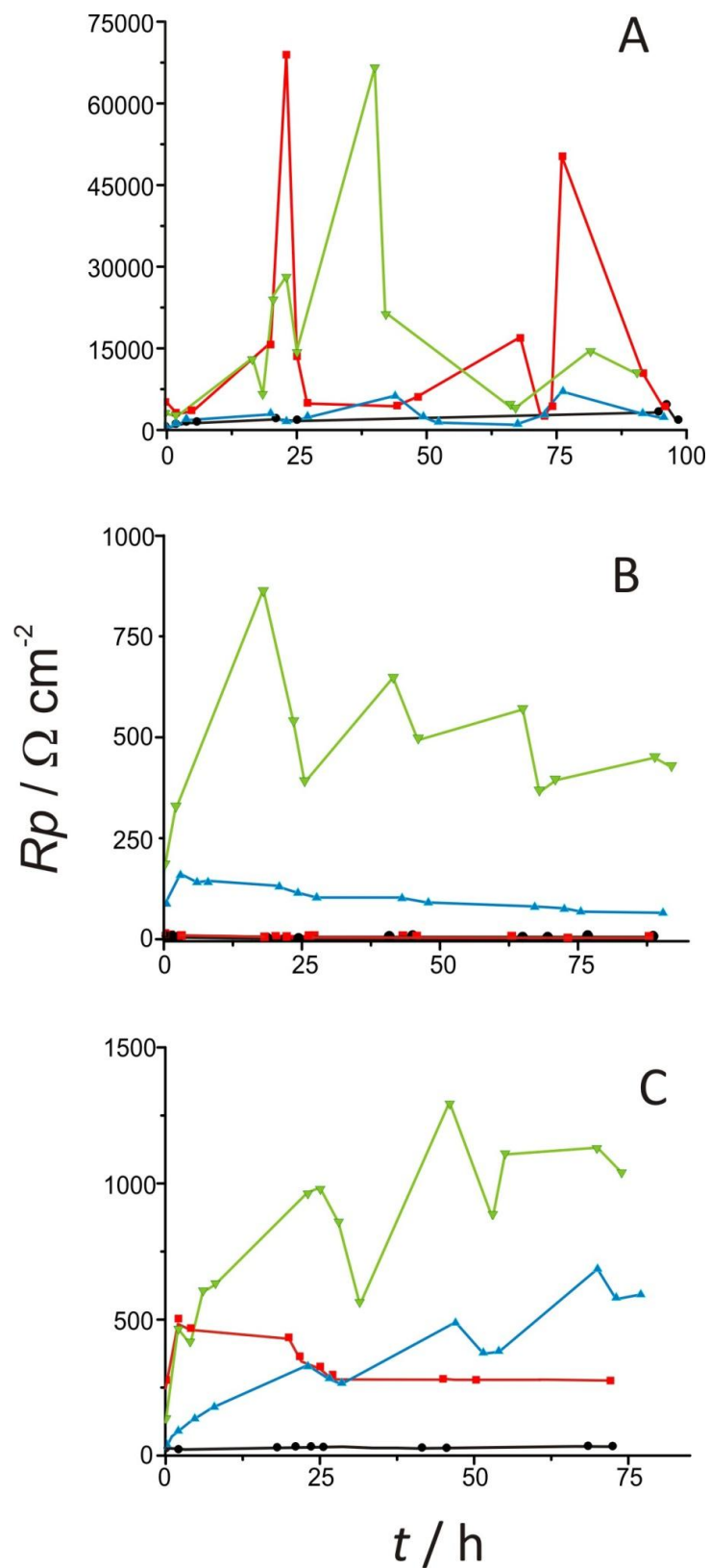
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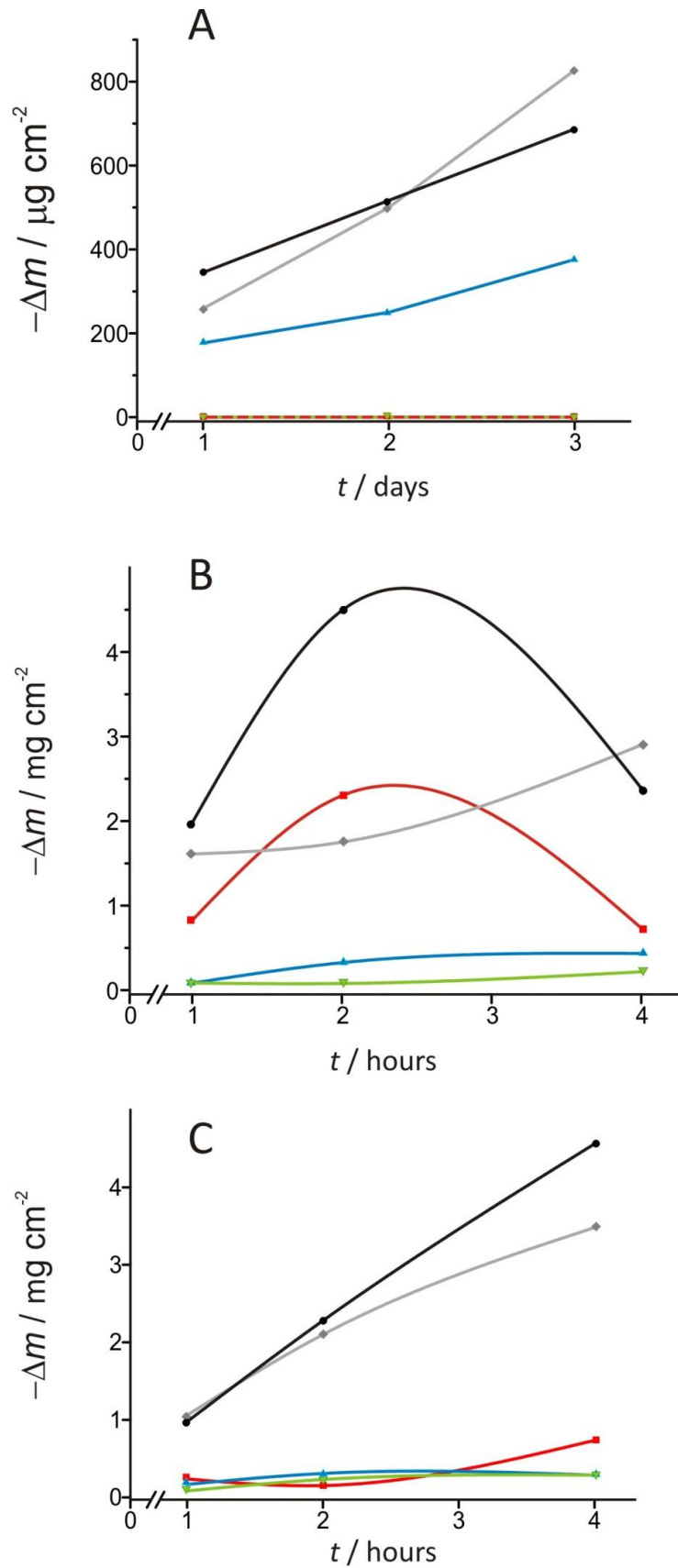
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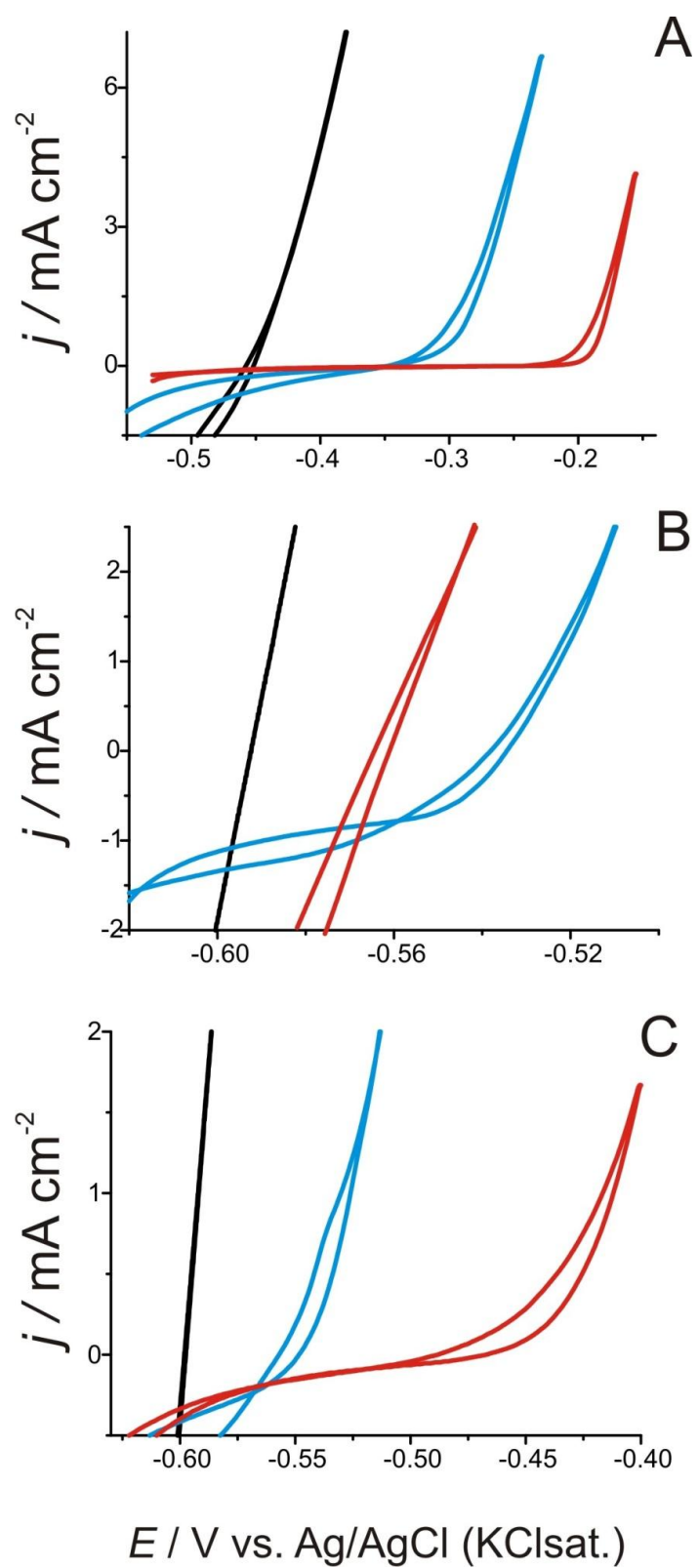
**Figure 1.**  $E_{corr}$  vs. time plots for I825 (A), U420 (B), and N80 (C) in 15% HCl at normal pressure and temperature. Black circles: N<sub>2</sub>-purged solution; Red squares: CO-saturated solution; Blue up-triangles: N<sub>2</sub>-purged, 5 mM TCA; Green down-triangles: CO-saturated, 5 mM TCA. The lines are a guide to the eye.



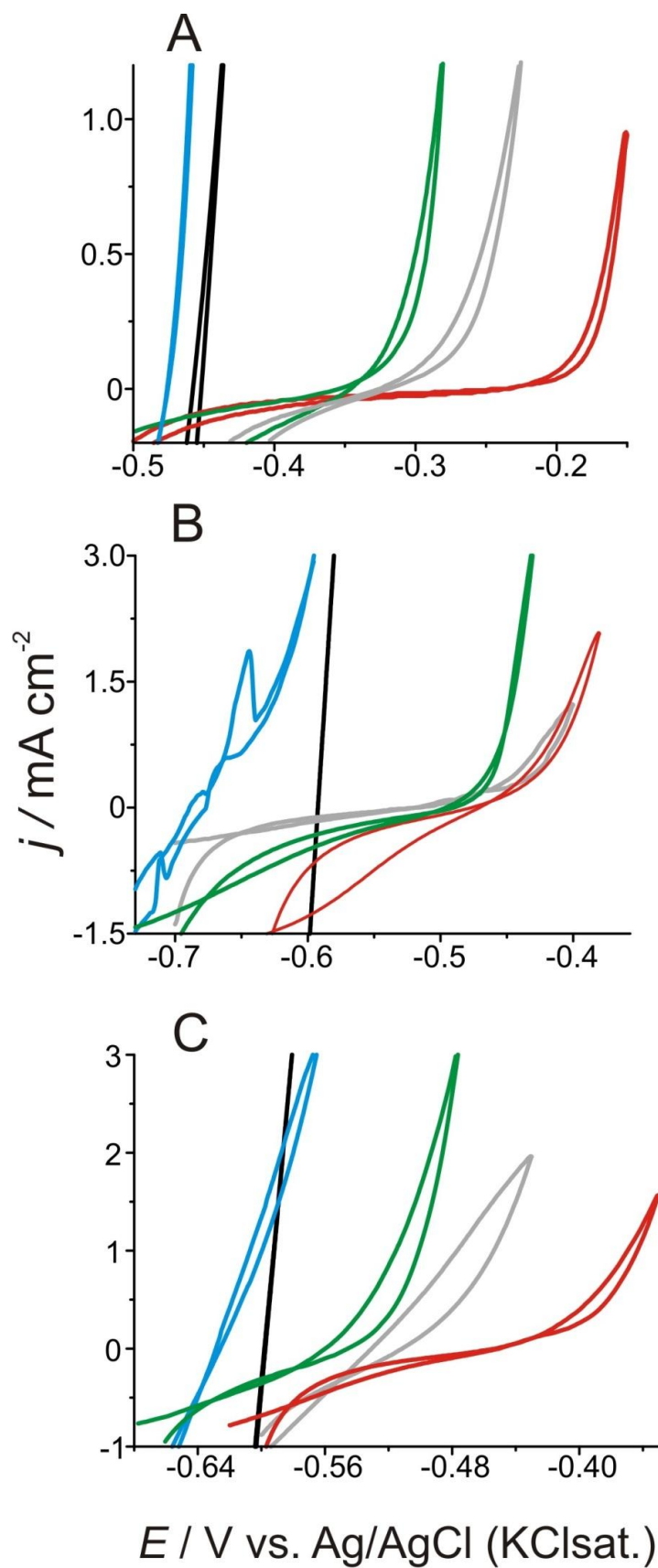
**Figure 2.** Polarization resistance,  $R_p$ , vs. time plots for I825 (A), U420 (B), and N80 (C) in 15% HCl at normal pressure and temperature. Black circles: N<sub>2</sub>-purged solution; Red squares: CO-saturated solution; Blue up-triangles: N<sub>2</sub>-purged, 5 mM TCA; Green down-triangles: CO-saturated, 5 mM TCA. The lines are a guide to the eye.



**Figure 3.** Gravimetric tests for I825 (A), U420 (B), and N80 (C) in 15% HCl at normal pressure and temperature. Grey: air-saturated solution; Black: N<sub>2</sub>-purged solution; Red: CO-saturated solution; Blue: N<sub>2</sub>-purged, 5 mM TCA; Green: CO-saturated, 5 mM TCA. The lines are a guide to the eye.

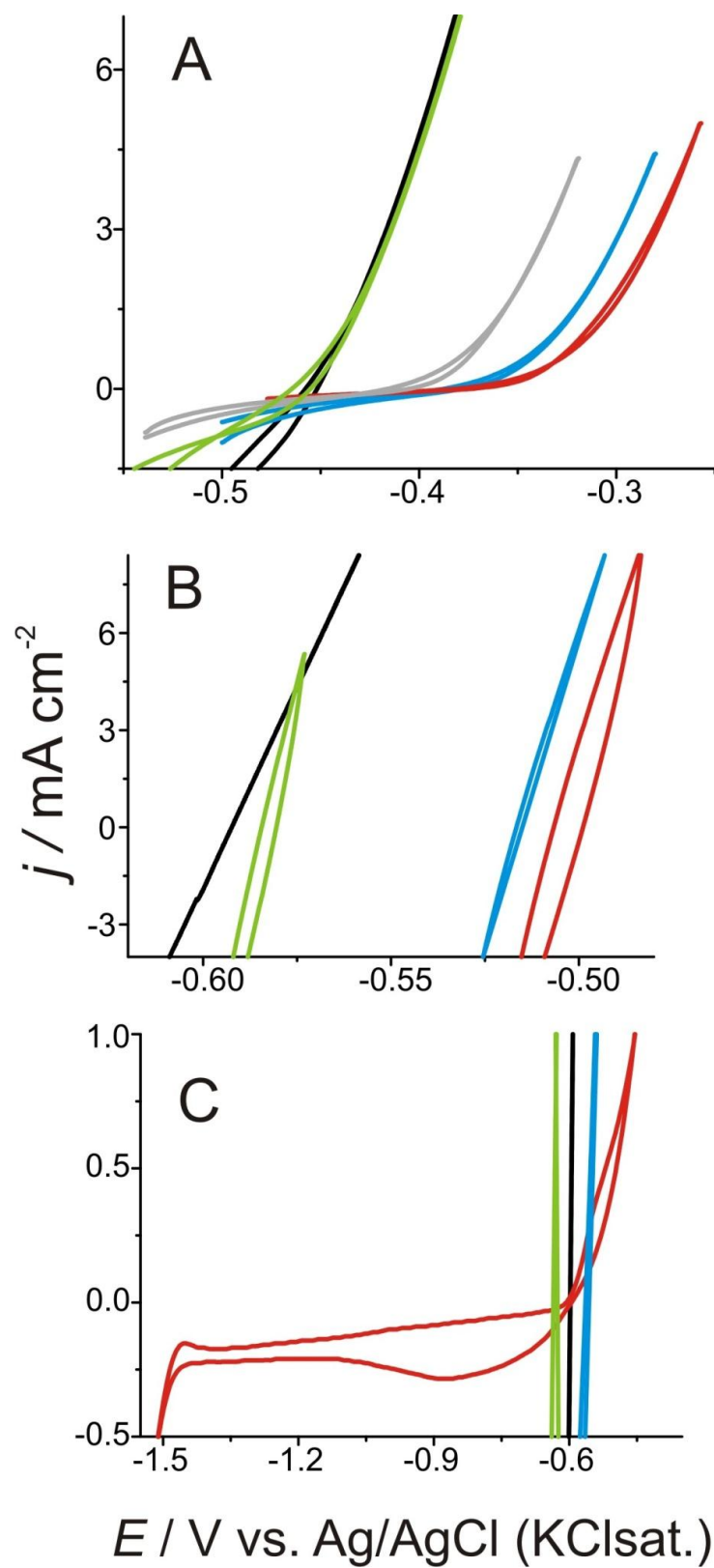


**Figure 4.** Cyclic voltammograms at  $1 \text{ mV s}^{-1}$  of I825 (A), U420 (B), and N80 (C) in 15% HCl.  $P = 6.9 \text{ MPa}$ . Black:  $\text{N}_2$ -purged solution,  $T = 175^\circ\text{C}$ ; Red: CO-saturated solution,  $T = 120^\circ\text{C}$ ; Blue: CO-saturated solution,  $T = 175^\circ\text{C}$ .

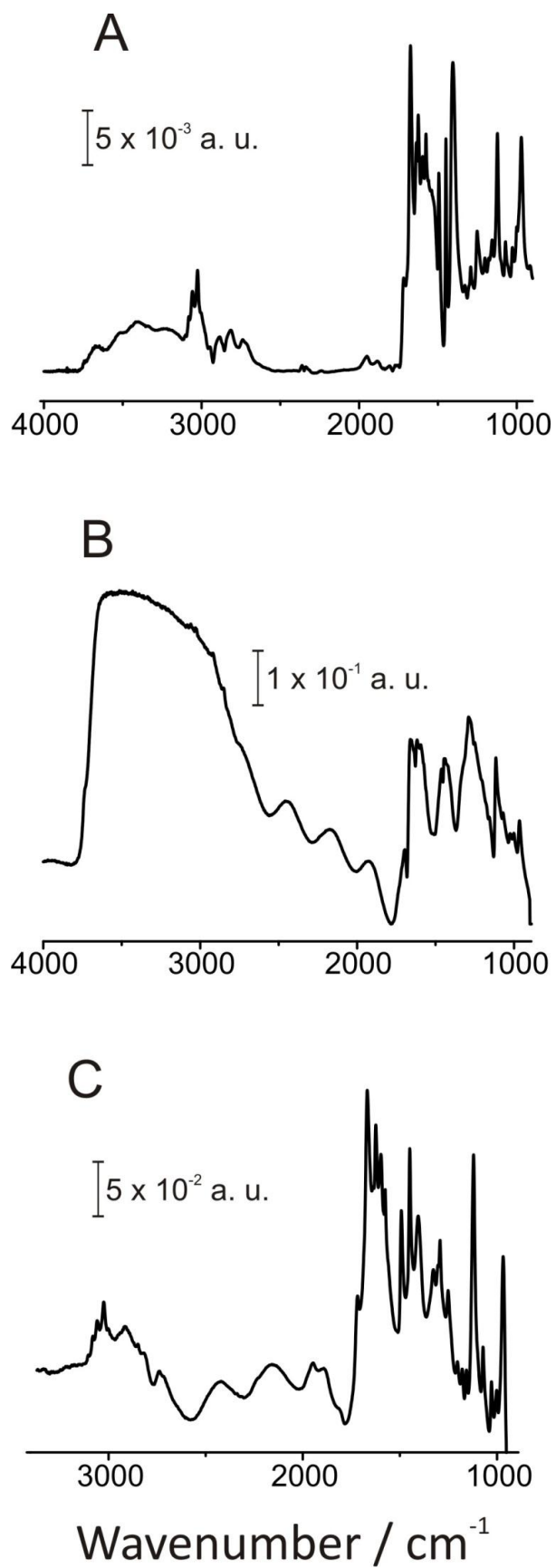


**Figure 5.** Cyclic voltammograms at  $1 \text{ mV s}^{-1}$  of I825 (A), U420 (B), and N80 (C) in 15% HCl,  $P = 6.9 \text{ MPa}$ . Black:  $\text{N}_2$ -purged solution,  $T = 175^\circ\text{C}$ ; Grey:  $\text{N}_2$ -purged, 2% (v/v) TCA,  $T = 120^\circ\text{C}$ ; Blue:  $\text{N}_2$ -purged, 2% (v/v) TCA,  $T = 175^\circ\text{C}$ ; Red: CO-saturated, 2% (v/v) TCA,  $T = 120^\circ\text{C}$ ; Green: CO-saturated, 2% (v/v) TCA,  $T = 175^\circ\text{C}$ .

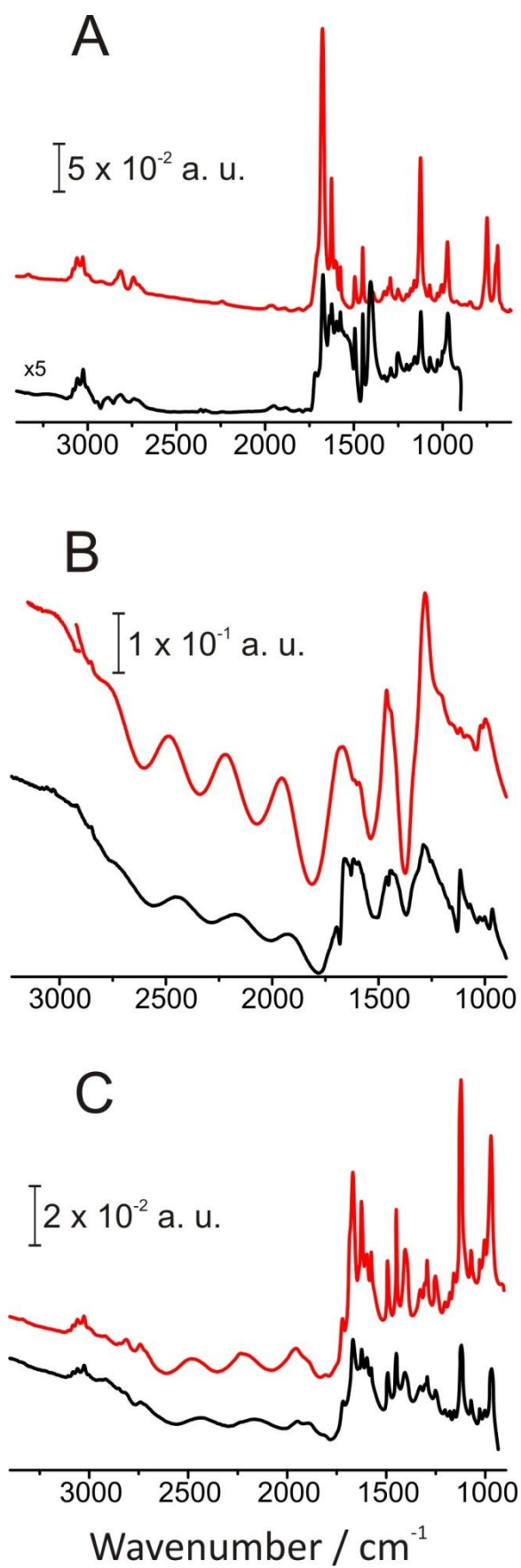




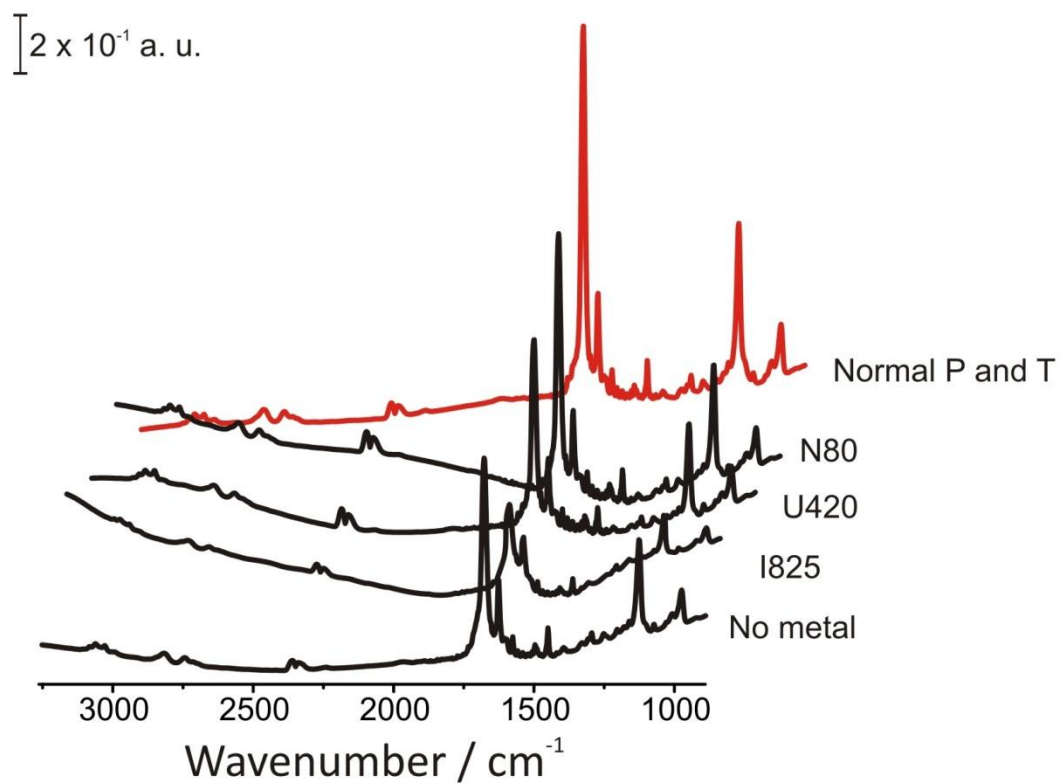
**Figure 6.** Cyclic voltammograms at  $1 \text{ mV s}^{-1}$  of I825 (A), U420 (B), and N80 (C), in 15% HCl.  $P = 6.9 \text{ MPa}$ . Black:  $\text{N}_2$ -purged solution,  $T = 175^\circ\text{C}$ ; Red:  $\text{N}_2$ -purged, 4% (v/v) HCOOH,  $T = 100^\circ\text{C}$ ; Blue:  $\text{N}_2$ -purged, 4% (v/v) HCOOH,  $T = 120^\circ\text{C}$ ; Grey:  $\text{N}_2$ -purged, 4% (v/v) HCOOH,  $T = 130^\circ\text{C}$ ; Green:  $\text{N}_2$ -purged, 4% (v/v) HCOOH,  $T = 175^\circ\text{C}$  (green).



**Figure 7.** IR external reflectance spectra of I825 (A), U420 (B), and N80 (C) after exposure for 40 min, at  $T = 121^\circ\text{C}$  and  $P = 0.2$  MPa to a 15% HCl solution containing 2% (v/v) TCA.



**Figure 8.** IR external reflectance spectra of I825 (A), U420 (B), and N80 (C) after exposure for 40 min, at  $T = 121^\circ\text{C}$  and  $P = 0.2$  MPa to a 15% HCl solution containing 2% TCA (black) and 2% TCA + 4% HCOOH (red).



**Figure 9.** IR transmission spectra of the oily phase of a 15% HCl + 2% TCA solution after 40 min at  $T = 121^\circ\text{C}$  and  $P = 0.2$  MPa. The transmission spectrum of pure liquid TCA at normal pressure and temperature is also shown (red line) for comparison. From bottom to top: in the absence of any metal; treated in the presence of I825; in the presence of U420; and in the presence of N80.