

An in situ SERS and FTIRAS study of salicylate interaction with copper electrode

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Abstract The salicylate anion (*ortho*-hydroxy-benzoate- $C_6H_4OHCOO^-$) interacts with common metals forming a semi-passivating layer on the surface. This semi-passivating layer allows the application of relatively high positive potentials without significant dissolution of the metal. It enables the electro-synthesis of conducting polymers (e.g. polyaniline, polypyrrole) directly on the metal surface, and such polymeric layers can act as anti-corrosion materials. Notwithstanding this characteristic, the behavior of salicylate on different metal surfaces is not yet well-understood. In the present work, the interaction of salicylate with copper (a metal of great interest in the industry) was studied. For this purpose, in situ surface enhanced raman scattering (SERS) and Fourier transform infrared absorption spectroscopy (FTIRAS) experiments were performed. The results show the formation of a copper(II) salicylate complex in the solution since low potentials (ca. 0 V vs Ag/AgCl). At higher potentials, salicylate decomposition is observed. FTIR spectra show the formation of CO_2 in solution, indicating salicylate decarboxylation. The SERS experiments indicate the breakage of the benzenic ring on the surface. It is suggested that at potentials above 0.6 V, a film of insaturated aliphatic chains linked by oxygen atoms is formed on the surface.

Keywords Spectroelectrochemistry · IR spectroscopy · Surface enhanced raman scattering · Passivation

Introduction

Recently, an increasing interest in the use of conducting polymers (polypyrrole, polyaniline, polythiophene) for corrosion protection has been observed [1, 2]. The main advantages of the use of these materials in this area are their non-toxicity and relatively low cost.

Nevertheless, the electro-synthesis of conducting polymers from their monomers requires the application of relatively high positive potentials, and at such potentials, the dissolution of active metals occurs. Thus, several different procedures have been proved to obtain better conditions for the electro-synthesis of conducting polymers directly on non-noble metals surfaces [3–10]. A semi-passivating layer has been observed on the metal surface if electrolytes containing anions such as oxalate [9], tartrate [5, 6], and salicylate [7, 9] are used. This semi-passivating layer inhibits the dissolution of the metal, but it does not preclude the monomers oxidation and the polymer formation. The medium containing salicylate has presented the best conditions for the electro-synthesis of polypyrrole on different metals (Zn/Co, Zn/Ni, Zn/Al, Al, Cu, and Sn) [11]. Although several studies have shown this favorable characteristic, there is a lack of studies that could better explain the electrochemical behavior of different metals in salicylate-containing solutions. Cascalheira and Abrantes [12] have studied the behavior of copper in sodium salicylate aqueous solution by cyclic voltammetry. The authors suggest the formation of a copper(II)-salicylate complex layer, which would be responsible for the inhibition of the metal dissolution. An ex situ surface

This paper is dedicated in memoriam to Prof. Francisco Carlos Nart.

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enhanced raman (SER) spectrum of a copper electrode pre-polarized at 0.4 V (vs SCE) in sodium salicylate was presented by Cascalheira et al. [7], and it was compared with the raman spectrum of copper salicylate complex. The result, according to the authors [7], confirms the presence of a film of the copper salicylate complex on the metal surface.

In the present work, an in situ vibrational study of the copper/salicylate system was performed. For this purpose, the surface enhanced raman scattering (SERS) and reflection/absorption infrared spectroscopy techniques were used. Both techniques allow to record the spectra of the polarized electrode, at different potentials. The behavior of adsorbed species was mainly monitored by SERS and the solution species by IR spectroscopy. In this way, it was possible to obtain more accurate informations about the process occurring at different potentials, and so, to delineate a better characterization of the system.

Experimental

All the solutions were prepared with Millipore® water and sodium salicylate (*Pro-Analysis* Merck).

SERS spectra at 632.8 nm (He–Ne laser, Spectra Physics model 127) exciting wavelength were recorded using a Renishaw Raman Imaging Microscope (System 3000) with a CCD detector. The potential control was made with a potentiostat PAR model 173. The copper electrode was roughened by applying 15 potential cycles, at 0.1 V s^{-1} , between -1.0 and 0.4 V (vs Ag/AgCl) in a 1.0 M KCl

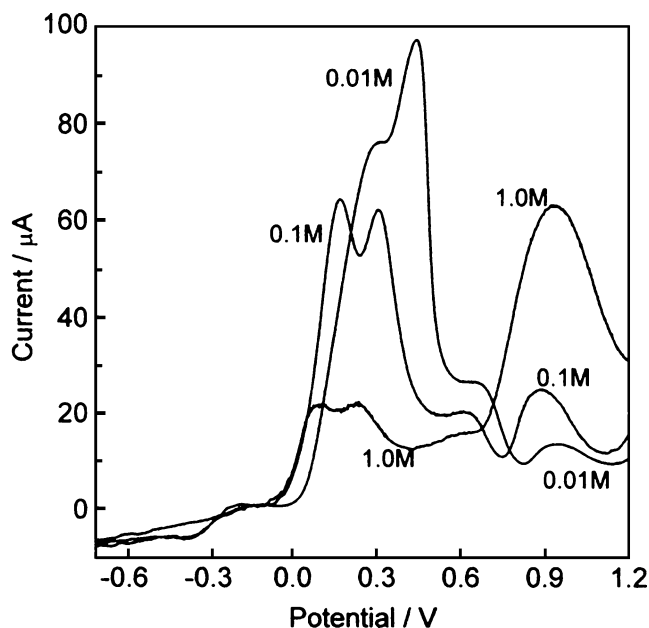
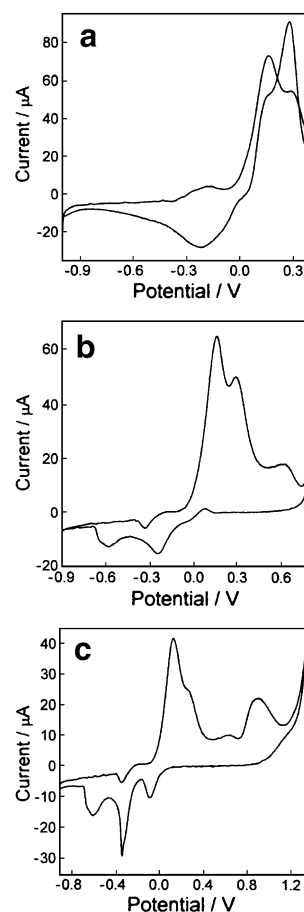


Fig. 1 Current–potential curves for a copper electrode in sodium salicylate solutions with different concentrations, as indicated. $v=5 \text{ mV s}^{-1}$

Fig. 2 Cyclic voltammograms of a copper electrode in 0.1 M sodium salicylate solution.

a First cycle, $-1.0 \rightarrow 0.4 \text{ V}$;
b second cycle, $-1.0 \rightarrow 0.8 \text{ V}$;
c third cycle, $-1.0 \rightarrow 1.3 \text{ V}$.
 $v=5 \text{ mV s}^{-1}$



solution. After activation, the electrode was washed with milli-Q water before contact with the sodium salicylate solution. The potential of -1.0 V was applied, and the spectra were collected after successive potential steps. The time required to record each spectrum was approximately 10 min.

Cyclic voltammetry measurements were performed in a potentiostat PAR model 163 with the copper electrode activated as explained above.

IR spectra were measured using a FTIR spectrometer Nicolet, Model Nexus 670, provided with a MCT detector. The electrochemical cell [13] was externally placed on the upper part of the IR sample chamber with the electrode in a horizontal position. A two mirror attachment was used to focus the IR beam on the electrode surface and on the detector. A prismatic CaF_2 window (60°) was used. The potential control was made by a potentiostat Wenking POS 73 and a function generator Prodis 1/161. In this case, the electrode (copper disc of 0.5 cm diameter) was polished to a mirror shine and washed with milli-Q water. After that, the electrode was put into the cell containing sodium salicylate solution and polarized at -1.0 V (vs Ag/AgCl); a reference spectrum was collected at this potential. Thus, successive potential steps were applied, and a spectrum (50 scans, approximately 30 s) was recorded at each potential.

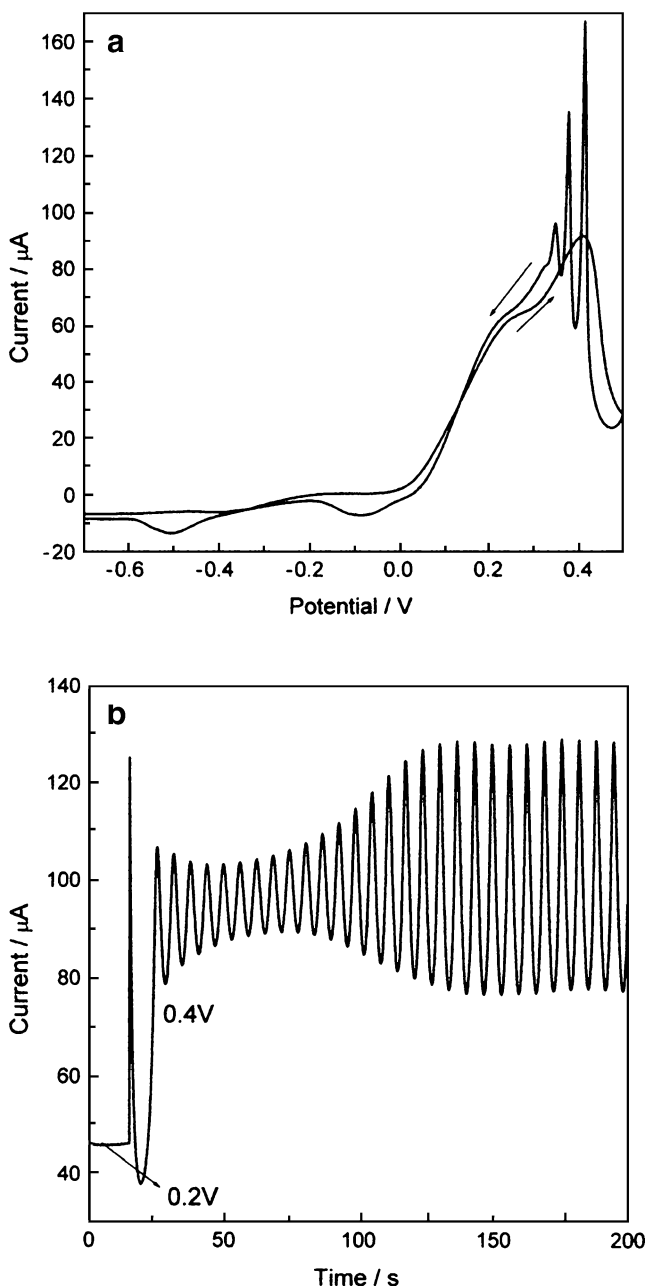


Fig. 3 **a** Cyclic voltammogram of a copper electrode in 0.01 M sodium salicylate solution; $\nu=5 \text{ mV s}^{-1}$. **b** Chronoamperometric curve for a copper electrode in 0.01 M sodium salicylate solution

For all experiments, Pt foils were used as counter electrodes. All the potentials are quoted vs Ag/AgCl electrode.

The copper(II) salicylate complex was prepared by mixing, under agitation, 1.0 M sodium salicylate and 1.0 M copper(II) chloride solutions in a proportion of 2:1. Immediately, a green precipitate was formed, which was filtered and dried under vacuum. The raman spectrum presented (632.8 nm exciting radiation) was collected with the pure solid compound and, for the FTIR spectrum collection, it was dissolved in KBr (FTIR Spectrometer Bomen, model MB-100).

Results and discussion

Electrochemical results

Positive sweeps of cyclic voltammograms of a copper electrode in sodium salicylate solutions with different concentrations (0.01, 0.1, and 1.0 M) are presented in Fig. 1. Completely distinct behaviors are observed in the region of low (<0.6 V) and high (>0.6 V) potentials. The current peaks below 0.6 V diminish significantly as the salicylate concentration increases. Instead, the peak at ca. 0.9 V increases with the salicylate concentration. Similar voltammetric behavior was observed by Cascalheira and Abrantes [12]. According to these authors, the current wave below 0 V is assigned to the formation of copper(I) species; the peaks between 0 and 0.4 V would be due to the formation of divalent copper species (first peak) and the formation of a copper salicylate complex [12]. The authors also suggested that the current peaks above 0.6 V are due to the salicylate ion oxidation. The small peak at ca. 0.6 V would represent an earlier oxidation of adsorbed species, further leading to the formation of a polymeric film [12, 14, 15].

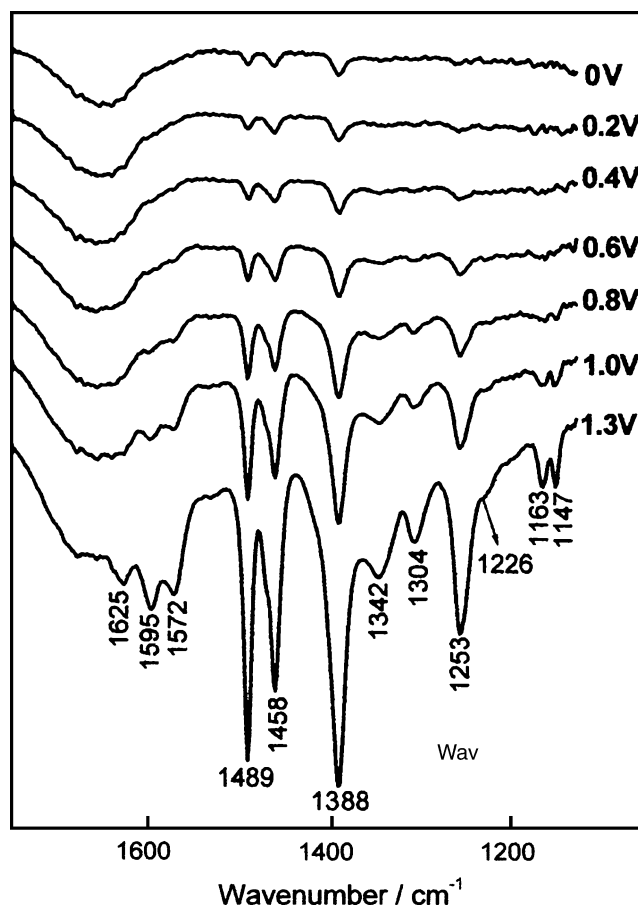


Fig. 4 FTIR spectra (50 scans) as a function of potential. Copper electrode in a 0.01 M sodium salicylate solution. Reference spectrum = -1.0 V

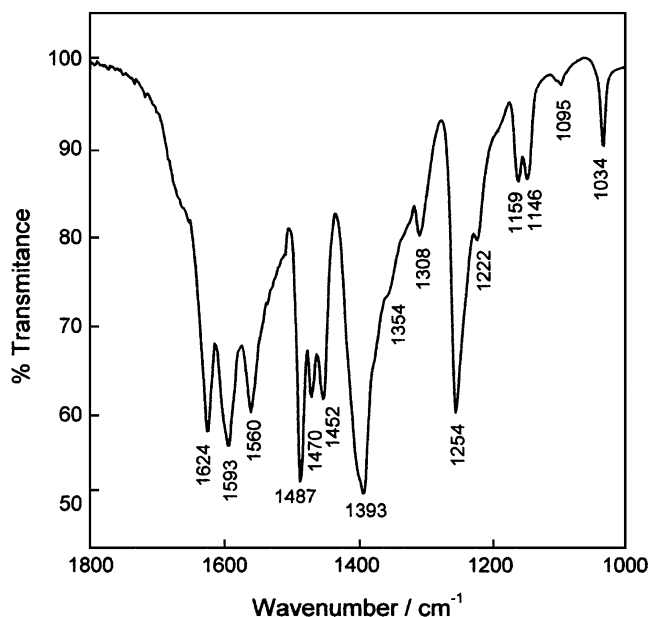


Fig. 5 FTIR spectrum of copper(II) salicylate complex in KBr

Apparently, the processes occurring at low potentials are inhibited by salicylate adsorption (current decreases as salicylate concentration increases). As potential becomes more positive, salicylate is more strongly adsorbed on the copper surface (probably recovered by a copper oxide layer), and it can be responsible for the decrease in current (peak at ca. 0.4–0.5 V). The adsorption process seems to be reversible, whereas, as can be seen in Fig. 2, an anodic peak is observed during the negative sweep if the limit potential of 0.4 V (Fig. 2a) is applied. However, if more positive potentials are applied, this peak is absent (Fig. 2b and c).

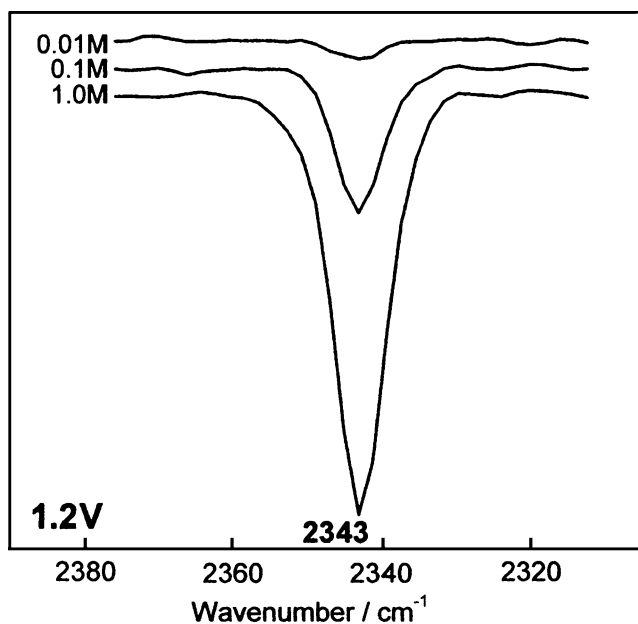


Fig. 6 IR band of CO_2 ($2,343\text{ cm}^{-1}$) at 1.2 V for different sodium salicylate concentrations, as indicated. Copper electrode, reference spectrum= -1.0 V , 50 scans. (CO_2 production starts at 0.8 V)

At higher potentials, salicylate is decomposed. It will be discussed in more details further with the spectroscopic results.

Another interesting result is that presented in Fig. 3. Using a 0.01 M sodium salicylate solution, current fluctuations between 0.4 and 0.3 V, during the negative sweep of the cyclic voltammogram (Fig. 3a), and also at a constant potential of 0.4 V can be observed (Fig. 3b). This result can be explained as follows: salicylate adsorbs and inhibits copper oxide formation (and copper dissolution); in the sequence, salicylate reacts forming a copper(II) salicylate complex, which is liberated to the solution, giving place again to copper oxide formation. The copper(II) salicylate complex was identified in the bulk solution by FTIR as will be shown below.

FTIRAS results

The IR spectra collected as a function of potential with a smooth copper electrode in a 0.01 M sodium salicylate solution are shown in Fig. 4. The reference spectrum was collected at -1.0 V . The usual thin layer configuration [13] was used.

The spectra obtained at high potentials is quite similar to the spectrum of the copper(II) salicylate complex (Fig. 5). The most intense bands appear since the potential of 0 V.

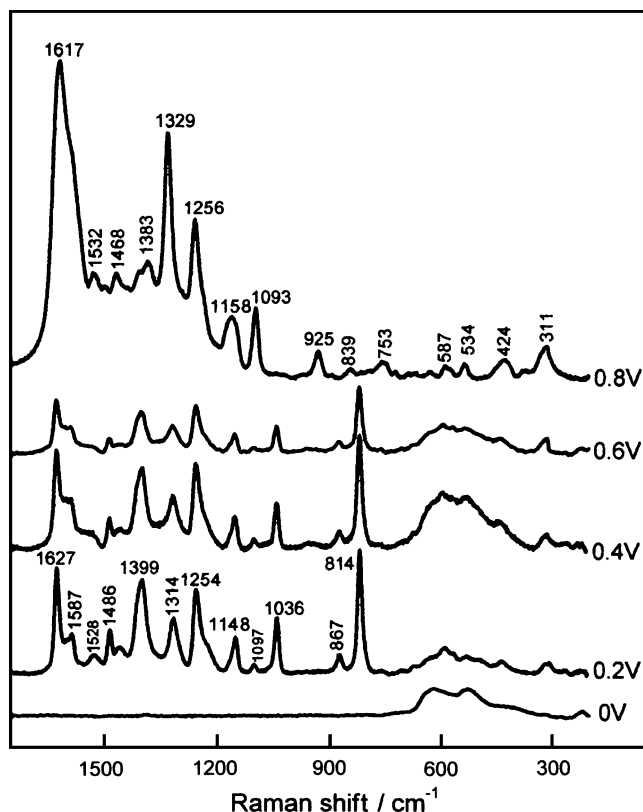


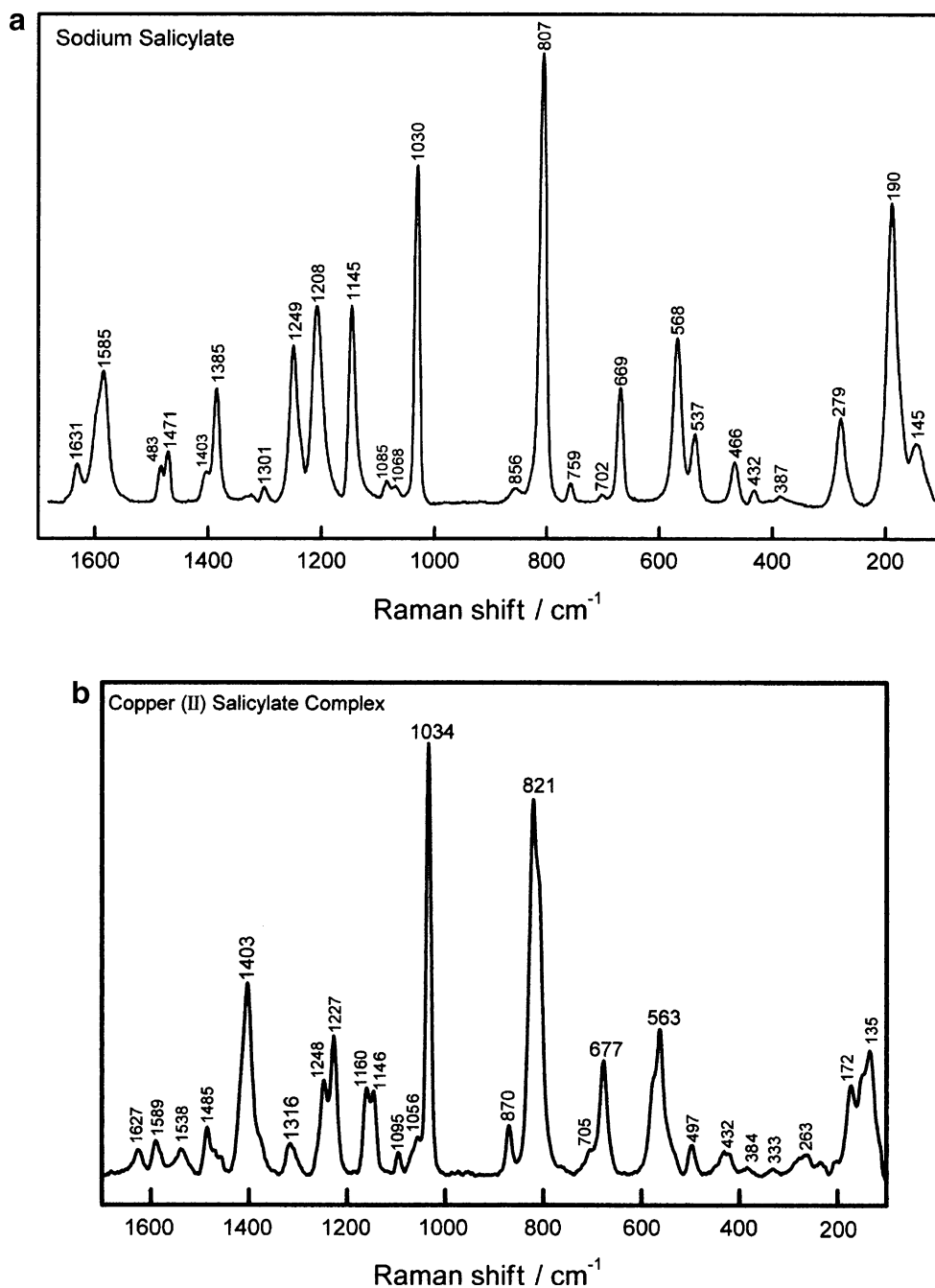
Fig. 7 SERS spectra collected as a function of potential. Copper electrode, 0.01 M sodium salicylate solution. (632.8 nm exciting radiation)

The bands increase in intensity with the potential, showing that the copper(II) salicylate complex is continuously produced. It is important to note that the higher intensity of the bands at high potentials, observed in Fig. 4, is not indicative that at these potentials the production of the complex is higher. It is not true because the experiments of FTIR in the thin layer configuration are cumulative, i.e., all the product remains in the thin layer and diffuses very slowly to the bulk of the solution.

At $2,343\text{ cm}^{-1}$, it is observed that a band starts to appear at the 0.8 V potential. This band is attributed to the production of CO_2 in the solution. The band presents a

clear dependence with the salicylate concentration. Figure 6 shows this region of the spectra in the 3 concentrations (0.01, 0.1, and 1.0 M), at the potential of 1.2 V. The CO_2 production increases significantly with the salicylate concentration. The produced CO_2 comes from the decarboxilation of the salicylate anion. In this way, the current peak at ca. 0.9 V, at the voltammograms (Fig. 1), which increases with the salicylate concentration, can be associated with the decomposition of the salicylate anion and consequent CO_2 production. This reaction involves the salicylate anion in the solution and is a diffusion-controlled reaction because it is greatly dependent on concentration.

Fig. 8 Raman spectra of sodium salicylate (a) and copper(II) salicylate complex (b). Pure solid compounds, 632.8 exciting radiation



SERS results

The SERS spectra collected as a function of potential with an activated copper electrode in a 0.01 M sodium salicylate solution are presented in Fig. 7.

The scattering cross-section of the solution species are too low and, hence, difficult to be detected. But, adsorbed species have their scattering cross-section enhanced, mainly due to two different SERS mechanisms: the great increase of the local electromagnetic field near the surface (electromagnetic effect—EM) [16] and the increase of the polarizability of the adsorbed species (charge transfer effect—CT) [17, 18].

In Fig. 7, it is seen that at 0 V, only copper oxides are present on the surface (bands at 400–600 cm^{-1}). After the potential step to 0.2 V, new adsorbed species are observed, as can be seen in the spectrum. For comparison, the spectra of sodium salicylate and copper(II) salicylate complex are presented in Fig. 8a and b, respectively. The vibrational spectrum of sodium salicylate was studied by Phillip et al. [19]. The bands at ca. 807, 1,030, 1,145, 1,208, and 1,585 cm^{-1} are due to the vibrations of the benzenic ring. The bands at 1,385–1,400 and 1,627–1,630 cm^{-1} are assigned to the carboxylate group, symmetric and anti-symmetric stretchings, respectively. The C–O stretching of the hydroxyl group appears at ca. 1,250 cm^{-1} [19].

The spectrum observed in Fig. 4, at 0.2 V, is something intermediate between the sodium salicylate (Fig. 8a) and the copper salicylate complex (Fig. 8b) spectra. It would be the adsorbed salicylate anion. In more concentrated solutions, quite similar spectra were observed even at negative potentials. A spectrum obtained at –0.7 V in a 1.0 M sodium salicylate solution is shown in Fig. 9. Some variations in frequencies and in band intensities for the adsorbed species in relation to the solution species are

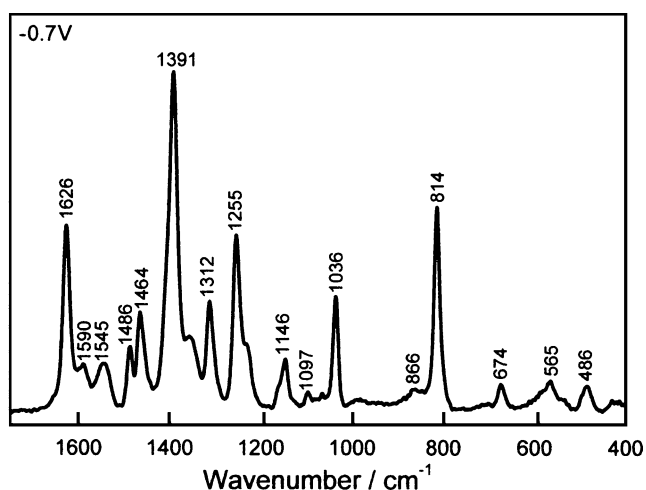


Fig. 9 SERS spectrum of a copper electrode in 1.0 M sodium salicylate solution, at –0.7 V

expected. The groups directly linked to the surface suffer a higher enhancement; besides, there are the ‘surface selection rules’ that favors vibrations modes with large polarizability tensor component normal to the surface [20]. The greater intensification is observed for the band at 1,627 cm^{-1} (anti-symmetric stretch of the carboxylate group), possibly indicating that the molecule interacts with the surface through the carboxylate group.

As can be seen in Fig. 7, in the potential region between 0.2 and 0.6 V, copper oxides and adsorbed salicylate are both present on the surface. The higher intensity for the copper oxide bands (ca. 400–600 cm^{-1}) is observed in the spectrum collected at the potential of 0.4 V. This potential value is approximately the maximum of the current peak observed in the voltammogram (Fig. 1, 0.01 M). It is an indication that the mentioned peak is related to copper oxides formation. According to the electrochemical results presented above, the salicylate is adsorbed and, in the sequence, liberated to the solution (as a copper salicylate complex). The presence of the copper salicylate complex in the bulk of the solution was confirmed with the FTIR results presented above (Fig. 4).

At 0.8 V, a profound modification in the SERS spectrum is observed (Fig. 7). The bands at 814 and 1,036 cm^{-1} disappeared completely. Because these bands are attributed to benzenic ring vibrations, their disappearance is an indication of ring breakage. This breakage is accompanied by the elimination of CO_2 to the solution, as shown in the IR results (Fig. 6). Thus, on the electrode surface, both decarboxilation and breakage of the ring occur. The product formed on the electrode presents a strong band at 1,617 cm^{-1} , which can be assigned to the stretch of double CC bonds. This assignment is reinforced by the observation of the bands at 1,329 and 1,256 cm^{-1} , which can be attributed to the in-plane CH bending observed in *trans*-dialkyl and *cis*-dialkyl ethylene derivatives, respectively [21]. The band at 1,256 cm^{-1} can also indicate that some hydroxyl groups of the salicylate anions remain linked to the insaturated aliphatic chains. But, the appearance of the bands at 925 and 1,093 cm^{-1} , which is a characteristic of the ether groups (symmetric and anti-symmetric COC stretchings, respectively), suggests that some OH bonds were broken and originated the ether groups.

In this way, it is suggested that at this potential, the decomposition of the salicylate anions occurs. The carboxylate group is liberated to the solution as CO_2 (see the “FTIRAS results” section). The benzenic ring is broken and the insaturated aliphatic CH chains are linked by the oxygen atom of the hydroxyl group. These insaturated chains form a polymeric film on the surface and the insaturations permits the conductivity through this layer.

The presence of this polymeric film on the surface inhibits the oxidation process occurring in the potential

region below 0.5 V, whereas, as can be seen in Fig. 2b, the anodic peak during the negative sweep is not present if the limit potential of 0.8 V is applied. In this way, copper dissolution, in the presence of this layer is also strongly inhibited.

It is possible that, even with the polymeric layer formed on the surface, suggested by the SERS results (Fig. 7), some copper dissolution remains occurring, liberating copper(II) species to the solution because the FTIR results (Fig. 4) show that the quantity of the copper(II) salicylate complex increases with the potential, even at potentials above the formation of the polymeric film on the surface.

Conclusions

The copper/salicylate interface was studied by electrochemical, SERS, and FTIRAS experiments.

The results showed that the salicylate anion adsorption inhibits copper oxides formation. A copper(II) salicylate complex is produced at low potentials (ca. 0 V vs Ag/AgCl). At ca. 0.8 V, salicylate decomposition starts. The FTIR spectra showed the production of CO₂, deriving from salicylate decarboxilation.

In the SERS experiments, it was initially observed that copper oxidizes on the surface only. At ca. 0.2 V, a new spectrum was obtained. This spectrum was interpreted as being the adsorbed salicylate. Salicylate adsorption is high when their concentration in the solution is high. In this way, copper oxides formations are more and more inhibited as salicylate concentration increases. At 0.8 V, a notable change in the spectrum was observed. The spectrum (at 0.8 V) was attributed to a polymeric film formed on the surface, prevent from the decomposition of the salicylate. Besides decarboxilation, the benzenic ring is broken and insaturated aliphatic chains are formed. The same are linked by the oxygen atom of the hydroxyl group.

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