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## Article

# Proving the Formation of Carbonic Acid Hemiesters Using Self-Assembled Monolayers and Electrochemistry

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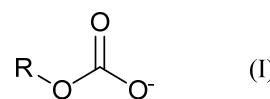
**Abstract:** This study demonstrates, for the first time, the formation of a hemiester of carbonic acid on self-assembled monolayers using voltammetric techniques and redox probes. A gold electrode (GE) was modified with 2-mercaptoethanol (ME) through self-assembly. With this modified electrode (GE-ME), a well-defined peak was observed by differential pulse voltammetry (DPV) for the negatively charged redox probe, ferricyanide/ferrocyanide,  $[\text{Fe}(\text{CN})_6]^{3-/4-}$ , in sodium acetate as electrolyte adjusted to pH 8.2. In the presence of dissolved  $\text{CO}_2$ , there is a decrease of the ferrocyanide peak current with time (~30% in 60 min), attributed to the formation of the hemiester 2-mercapto ethyl carbonate at the GE-ME/solution interface. Similarly, dissolved  $\text{CO}_2$  also affects the electrochemical impedance measurements by increasing the resistance to the charge transfer process with time (elevation of  $R_{\text{ct}}$  values), compatible with the formation of the hemiester. The addition of barium salt led to the displacement of the equilibrium towards  $\text{BaCO}_3$  precipitation and consequent dissociation of the hemiester, attested by the recovery of the initial ferricyanide DPV signal. With the positively charged redox probe  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  no decrease in the DPV peak was observed during the formation of the hemiester by reaction with bicarbonate. The repulsion of  $[\text{Fe}(\text{CN})_6]^{3-}$ , but not of  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  suggests that the formed species is the negatively charged 2-mercapto-ethyl carbonate, i.e., the hemiester with a dissociated proton. Due to the lack voltammetric signal from the hemiester itself, the formation of a self-assembled layer of thio-alcohol followed by the gradual formation of the corresponding carbonic acid hemiester allowed to reach an elegant way to demonstrate the electrochemical formation of these species.

**Keywords:** hemiester;  $\text{CO}_2$ ; alcohol; carbonic acid; self-assembled monolayer

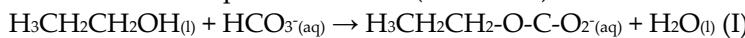
## 1. Introduction

Alcohols and carbon dioxide can form singly esterified compounds named hemiesters of carbonic acid (HECAs) [1], and their salts, monoalkyl carbonates (MACs) [2]. Although the formation of this species has been known for almost two centuries [3–6], the amount of information on the subject is still limited. This work aims to contribute to a better understanding of the processes involving the formation of HECAs.

These compounds or adducts are easily formed in aqueous media [2], and can be quite unstable and sensitive to changes in temperature and pH [7]. Their presence is generally not noticed, but they have been detected, e.g., in carbon capture processes [8–10] and in alcoholic beverages [11], and it is assumed that HECAs are present in the most different environments. These compounds have a general structure like bicarbonate:



One of the most common HECA is formed in small concentrations whenever ethanol and CO<sub>2</sub> or bicarbonate are in aqueous medium (Reaction I):

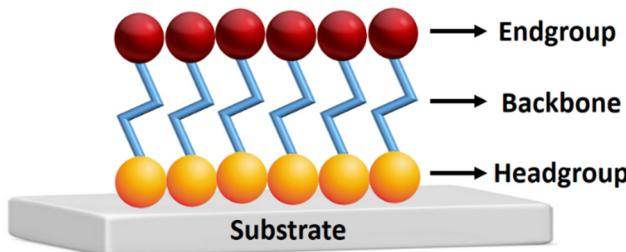


This ethyl carbonate anion is named more unambiguously as monoethyl carbonate (MEC), but it is also known as etabonate as an organic group in pharmacology. The protonated form has a pKa lower than 4, with an accurate value yet to be determined due to the fast decomposition of the conjugate acid-base pair in an acidic aqueous medium [11]. It has been called ethyl hydrogen carbonate (IUPAC preferred name), carbonic acid monoethyl ester, monoethyl carbonic acid, or etabonic acid.

It was only in the last decade that this and other hemiesters were studied by capillary electrophoresis (CE) [2,7,11], nuclear magnetic resonance (NMR) [7–9], and mass spectrometry (MS) [12], significantly improving the understanding of the formation and properties of HECA. Exploring the CE technique, do Lago and coworkers were able to determine some physicochemical parameters, such as formation and hydrolysis constants, and quantify MEC for the first time in beer and sparkling wine [11]. With NMR, it was possible to demonstrate the formation of HECA from sugars [7] and to detect these compounds in carbon capture processes by alkanolamines [8]. To achieve low LODs, an EC-MS system was used, making it possible to quantify MACs at concentrations of the order of  $\mu\text{M}$  [12].

This study shows for the first time the formation of a HECA on a self-assembled monolayer (SAM) using electrochemical techniques and two voltammetric redox probes: ferricyanide and ruthenium hexamine. SAMs are ordered molecular arrangements formed spontaneously on a variety of substrates [13] that are valuable to functionalize interfaces according to desired characteristics, e.g., with hydroxy groups to promote the formation of hemiesters. A typical SAM structure contains the three main parts depicted in Figure 1. The headgroup should strongly chemisorb on the (solid) surface and be responsible for molecular ordering; therefore, thiol, silane, or phosphonic acid groups are typically used, depending on the substrate. The backbone is formed by an aromatic oligomer or aliphatic chain. The terminal group (or end group), for example, methyl, amine, thiol, or hydroxy, defines the functionality of the SAM. It can be used for further functionalization, such as the immobilization of (bio)molecules [13–15].

In the present work, SAMs were used to modify the gold electrode to obtain a functionalized monolayer with –OH groups for hemiester formation. Hence, a thiol was used as the headgroup, given the high affinity of –SH and Au, Hg, Ag, or Cu, with the first being preferred as an electrode due to the wider potential window. 2-mercaptoethanol (HS-CH<sub>2</sub>-CH<sub>2</sub>-OH) was the thiol found suitable for the present application.



**Figure 1.** Representative figure of the structure of self-assembled monolayer.

## 2. Materials and Methods

### 2.1. Chemicals and Materials

Sodium acetate, ethanol, and hydrogen peroxide were obtained from Synth (São Paulo, Brazil). Potassium ferricyanide and barium nitrate were acquired from CAAL (São Paulo, Brazil). Mercaptoethanol and ethanol were obtained from Sigma-Aldrich, and sodium bicarbonate and sulfuric acid were purchased from Merck. All solutions were prepared daily by dissolving or diluting

appropriate amounts of the reagents in water or in a suitable supporting electrolyte, utilizing DI water from a Millipore Milli-Q system (resistivity  $\geq 18.2 \text{ M}\Omega \text{ cm}$ ).

### 2.2. Modification of the gold electrode with mercaptoethanol

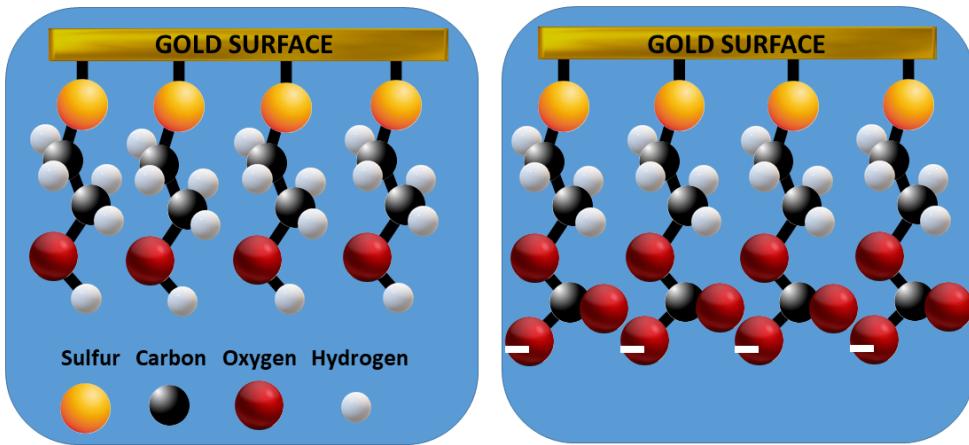
Before the modification, the gold electrode with a diameter of 3.0 mm was polished with 1  $\mu\text{m}$  alumina and washed with deionized water. In sequence, it was ultrasonicated in ethanol and then in deionized water (5 minutes each). After this initial cleaning step, the electrode was immersed in a piranha solution (7:3 mixture of concentrated sulfuric acid and 30% hydrogen peroxide), which was heated to 90 °C for 15 minutes to remove possible contaminants. In sequence, the electrode was cycled in a 1.0 M sulfuric acid solution in the potential range from 0 to 1.5 V at a 100 mV s<sup>-1</sup> scan rate until the characteristic voltammogram of clean polycrystalline gold in sulfuric acid was obtained (20 cycles). The electrode was washed copiously with DI water, dried, and then immersed in a 50 mg mL<sup>-1</sup> ethanolic mercaptoethanol solution for 2 hours. After this step, the electrode was again washed abundantly with DI water.

### 2.3. Electrochemical measurements

A conventional electrochemical cell, consisting of three electrodes (gold working electrode, platinum counter electrode, and Ag/AgCl reference electrode inserted through the holes in the lid of a 50 mL Metrohm titration vessel), was connected to a  $\mu$ AUTOLAB type III Metrohm potentiostat and used throughout this study. For the electrochemical characterization of the gold electrode - before and after modification - cyclic voltammograms (CVs) in sulfuric acid (0.5 mol L<sup>-1</sup>) were recorded using a scan rate of 50 mV s<sup>-1</sup> and steps of 2.44 mV. For the differential pulse voltammetry (DPV) measurements, the conditions were: potential step 5 mV, pulse amplitude 25 mV, modulation time 50 ms, and scan rate 10 mV s<sup>-1</sup>. For characterization with ferricyanide (redox probe), the measurements were performed in a 0.5 mol L<sup>-1</sup> sodium acetate electrolyte (pH adjusted to 8.2) and 0.5 mmol L<sup>-1</sup> of K<sub>3</sub>[Fe(CN)<sub>6</sub>]. A similar experiment was performed using hexaammineruthenium(II) chloride [Ru(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub> instead of ferricyanide as redox probe. In the study of the effect of pH, the conditions were the same, apart from the addition of small amounts of NaOH or Hac solution to the electrolyte. For the impedance experiments, an Autolab-PGSTAT302 N (Metrohm, Netherlands) equipped with Nova software (version 2.1) was used. These experiments were performed in 0.5 mol L<sup>-1</sup> sodium acetate as electrolyte (pH adjusted to 8.2) containing 0.5 mM of K<sub>3</sub>[Fe(CN)<sub>6</sub>].

## 3. Results

The direct electrochemical response of hemiesters proved to be unfeasible. Our preliminary studies confirmed that both the starting alcohols and the hemiesters formed (in small quantities) do not present characteristics to be detected by voltammetry (at least directly on conventional electrodes). After several attempts, a methodology was found that allowed demonstrating the formation of HECA using electrochemical techniques, using an alcohol that contains a thiol group at the opposite end of the molecule, e.g., 2-mercaptoproethanol adsorbed on a gold electrode. As mentioned in the Introduction, the thiol group strongly adsorbs on gold with the formation of a self-assembled film in which the hydroxy group is oriented outwards, i.e., the ratio of trans/gauche conformer is high [16]. Taking into account that when ethanol is exposed to a CO<sub>2</sub> source like bicarbonate in an aqueous solution, Reaction I takes place with the formation of the monoalkyl carbonate anion (predominant at pH higher than 4 [11]), as well as that at the solution/self-assembled ME interface the hydroxy group concentration is very high, the formation of 2-mercaptoproethyl monocarbonate is expected to occur as depicted in Figure 2:

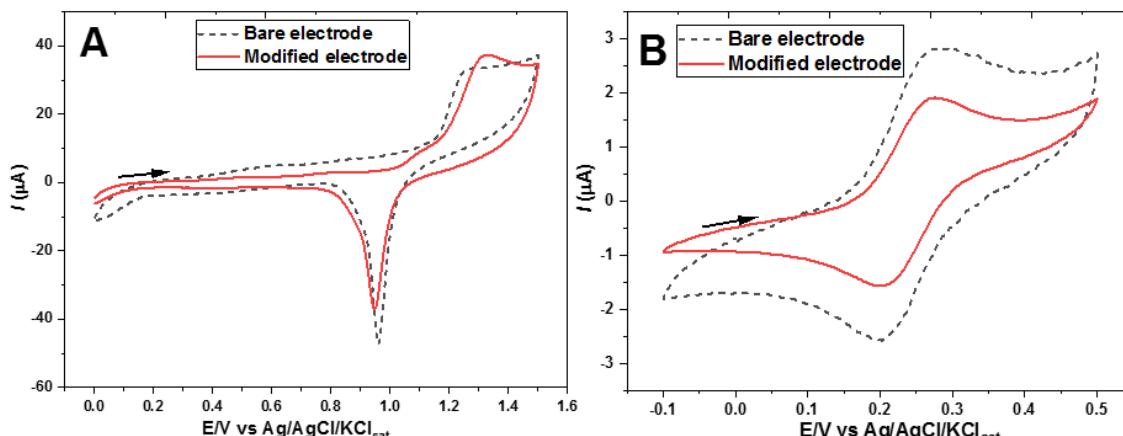


**Figure 2.** Representation of the GE-ME/solution interface (water molecules omitted) with the ME self-assembled as a trans conformer before (left) and after (right) exposure to  $\text{CO}_2$  with the formation of the dissociated hemiester, 2-mercaptoproethyl monocarbonate.

### 3.1. Electrochemical characterization of a gold electrode modified with 2-mercaptoproethanol

For electrochemical characterization purposes, CVs were recorded before and after the modification of the gold electrode with 2-mercaptoproethanol in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  alone and in  $0.5 \text{ mol L}^{-1}$  sodium acetate with the addition of  $0.5 \text{ mmol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]$ . Sulfuric acid is the typical electrolyte for the characterization of gold electrodes, while sodium acetate was chosen to adjust a slightly alkaline pH of 8.2, at which  $\text{CO}_2$  predominates in the form of bicarbonate in solution and HECA hydrolyze less than in acidic medium [11]. Since no oxidation or reduction processes attributable to HECA formation were identified in the CVs, it was sought to unveil its synthesis indirectly by adding  $0.5 \text{ mmol L}^{-1}$  of ferricyanide to allow the observation of the HECA effect on the voltammogram of this well-known (nearly) reversible redox process.

Figure 3A displays the voltammograms in the presence of  $\text{H}_2\text{SO}_4$  before and after the modification. The overall lower residual current, the increase in the  $\Delta E_p$  of the anodic signal of the oxidation of the gold electrode, and the attenuation of the gold oxide reduction peak are all good indications about the effective modification produced by the thiols bound to gold surface [17]. In Figure 3B, the voltammograms of the ferrocyanide redox probe recorded in sodium acetate medium also indicate electrode modification, since both the anodic and cathodic peak currents become proportionally smaller after the modification, while the peak potentials remain almost constant, presenting a  $\Delta E_p$  of about 80 mV. This signal decrease can be attributed to constrained access of  $[\text{Fe}(\text{CN})_6]^{3-}$  to the Au surface for electron transfer due to the presence of the 2-mercaptoproethanol monolayer.



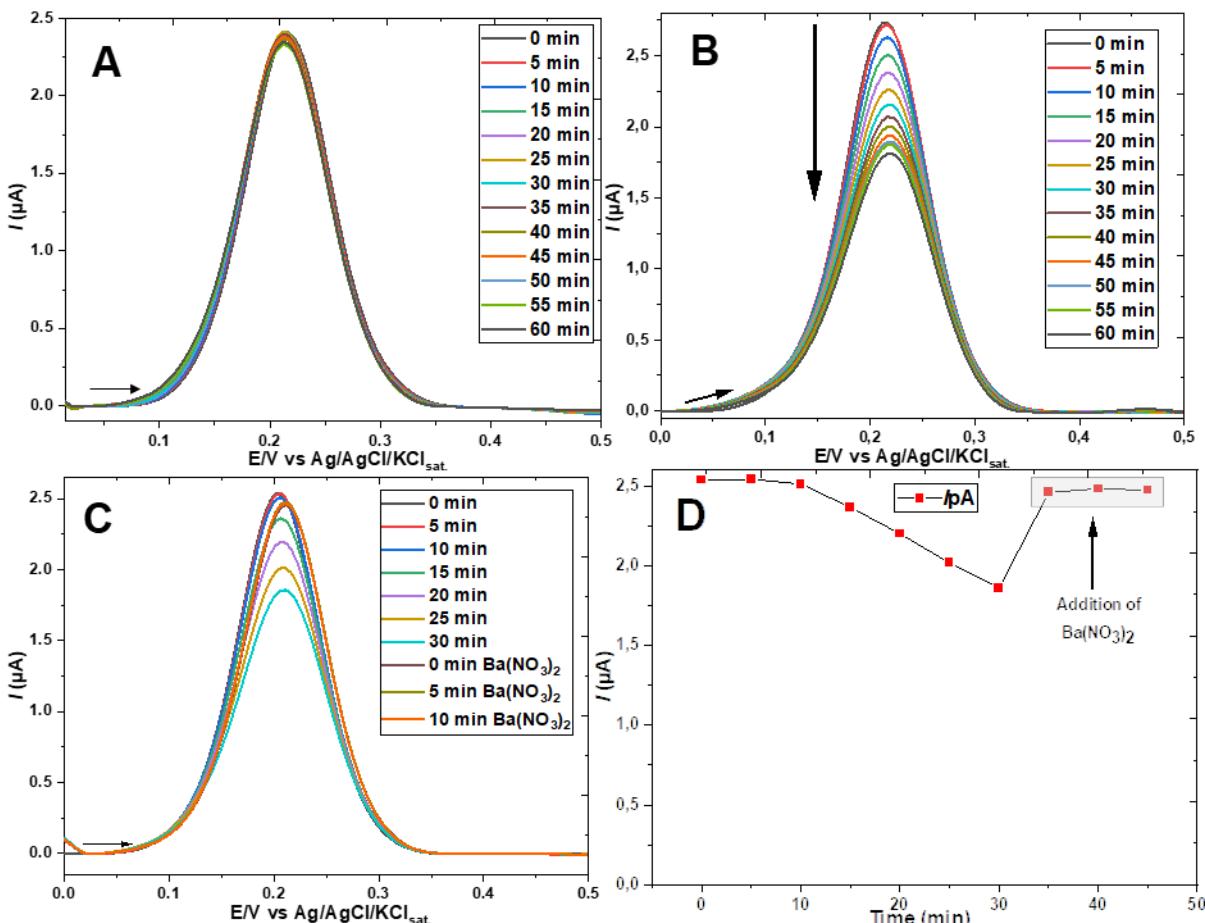
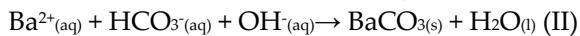
**Figure 3.** CVs of the gold electrode unmodified and modified with 2-mercaptoethanol recorded in (A) 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution, and (B) 0.5 M sodium acetate (pH 8.2) containing 0.5 mmol L<sup>-1</sup> K<sub>3</sub>[Fe(CN)<sub>6</sub>]. Scan rate: 50 mV s<sup>-1</sup>.

Differential pulse voltammograms (DPVs) better discriminate the faradaic current of the [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> redox couple from the residual capacitive current and, therefore, from now on they will be presented instead of CVs. DPVs of ferricyanide at the gold electrode, GE, without (Figure 4A) and with (Figure 4B) self-assembled 2-mercaptoethanol, GE-ME, were recorded short after immersion in sodium acetate electrolyte with the redox probe (0 min, in the figures) and after the addition of NaHCO<sub>3</sub> solution to the medium. After homogenization, a 5-minute equilibration time was respected before running the next DPV.

The first DPV of both figures presented similar shape, peak potential (0.214 V vs. Ag/AgCl), and half peak width (88 mV vs. 93 mV, respectively), while the peak height was slightly higher at the GE-ME (2.73  $\mu$ A vs. 2.41  $\mu$ A at the GE).

While the presence of bicarbonate causes no significant effect on the [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> process at the bare gold electrode (Figure 4A), at the GE-ME a remarkable peak height decrease occurs over time (Figure 4B), denoting changes in the film structure, e.g., the postulated formation of the hemiester.

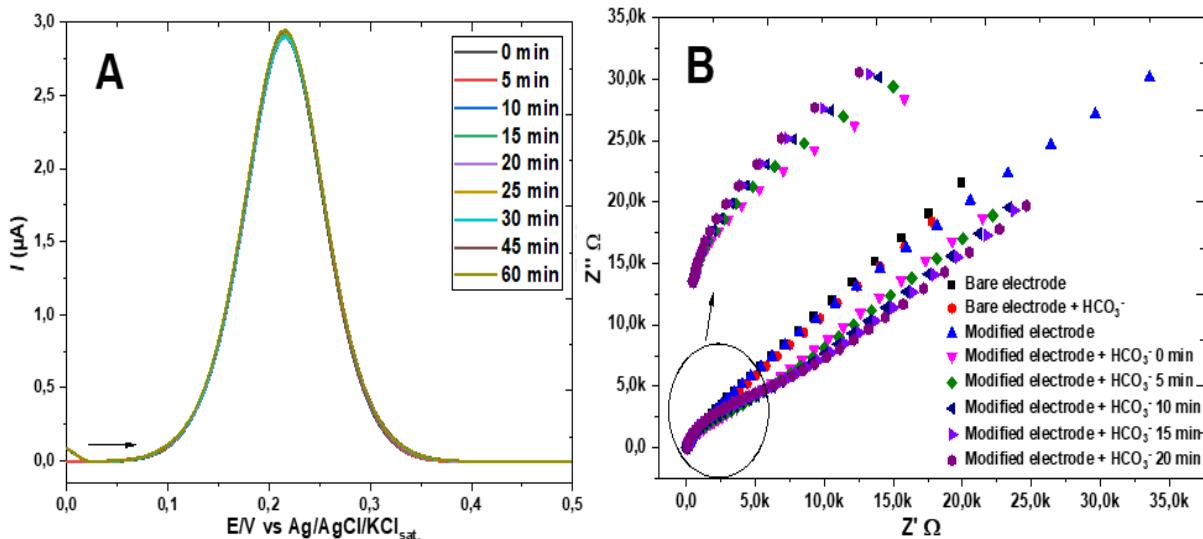
The current decay over time in the DPVs of Figure 4B,C were nearly identical for the first 30 minutes (even without adding bicarbonate in Figure 4C apart from sufficient CO<sub>2</sub> absorbed from the air). However, in the experiment of Figure 4C, after 30 min, 100 mg of Ba(NO<sub>3</sub>)<sub>2</sub> were added to the cell, under stirring, and just 5 min later the original peak current (time 0 before vs. time 0 after the addition of barium) was closely recovered and sustained afterwards, as better evidenced once plotted vs. time in Figure 4D. This fact denotes the decomposition of the hemiester that can be explained by the great affinity of the barium cation for the carbonate ion, as evidenced by the well-known formation of BaCO<sub>3</sub>, an insoluble salt (K<sub>s</sub> = 3 x 10<sup>-9</sup> mol<sup>2</sup> L<sup>-6</sup> [18]), according to the reaction (at pH 8.2):



**Figure 4.** DPVs of 0.5 mM potassium ferricyanide in 0.5 M sodium acetate electrolyte, pH 8.2, at (A) bare GE electrode, (B) GE-ME with addition of 1 mmol L<sup>-1</sup> bicarbonate, (C) GE-ME without addition of bicarbonate, and (D) ipA from (C) plotted against time. DPV settings: step 5 mV, modulation amplitude, 25 mV, modulation time, 50 ms, scan rate, 10 mV/s.

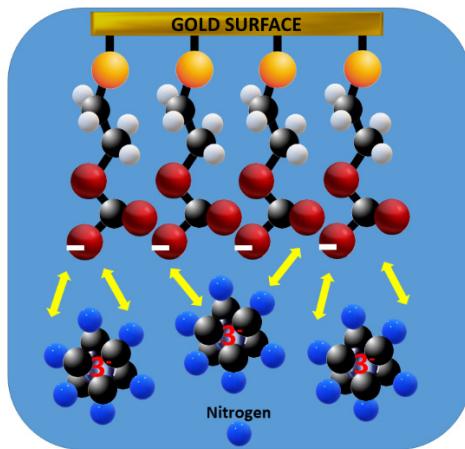
The observed effectiveness of barium ion addition in removing traces of bicarbonate was useful in an additional experiment. The peak current of the ferricyanide probe showed a decrease over time even without the addition of bicarbonate, as can be seen in Figure 4C. To confirm the hypothesis that this decline indicating the formation of hemiester is due to the presence of CO<sub>2</sub> absorbed from the air (in the open cell or previously in water, and electrolyte stock solution), barium salt was added before the immersion of the GE-ME followed by the recording of the first DPV. As can be seen in Figure 5A, the peak of the ferri-/ferrocyanide couple remained strictly constant throughout the experiment. The hemiester formation, signaled by the decrease of the peak over time, could, however, be triggered at any time by adding bicarbonate in excess of the stoichiometric concentration needed to precipitate the added barium ions. The elimination of dissolved CO<sub>2</sub> by such a procedure, although effective, unnecessarily complicates routine experiments. The elimination of dissolved gases from aqueous solutions by conventional techniques (inert gas bubbling, heat, vacuum, etc.) is also laborious and not very effective, especially in the case of CO<sub>2</sub> in a pH range where the equilibrium favors the formation of bicarbonate. In fact, the residual bicarbonate present in the electrolyte solution used throughout the work was estimated by calculating, with help of the software CurTiPot, the concentration of CO<sub>2</sub> (absorbed from the air) necessary to reduce the pH of the 0.5 mol L<sup>-1</sup> sodium acetate solution from the value expected in pure water, 9.09, to 8.20, that is, 0.13 mmol L<sup>-1</sup>.

To gain further evidence of the changes occurring on the film of the GE-ME, a set of experiments similar to that of the DPVs of Figure 4B was carried out, but measuring the changes in the electrochemical impedance spectrum. The gathered data is displayed in Figure 5B.



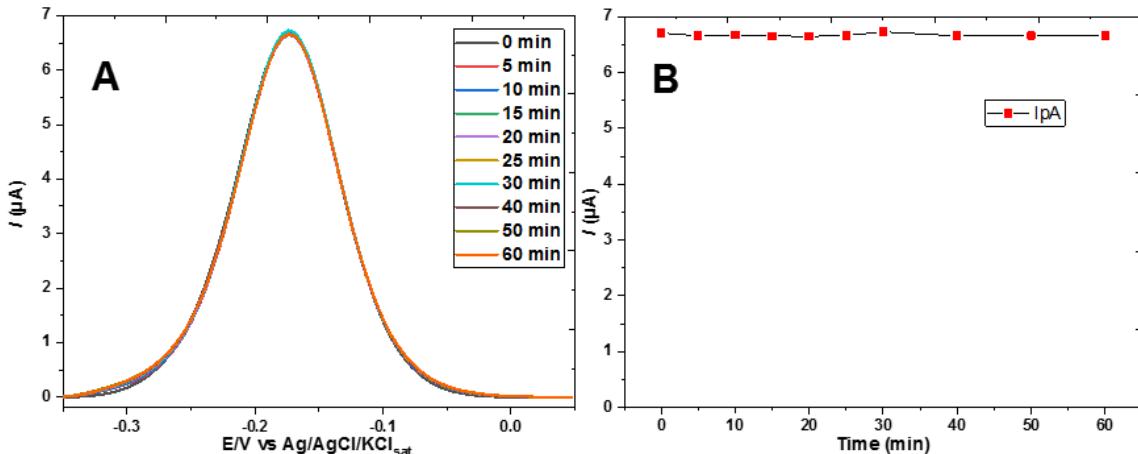
**Figure 5.** (A) DPV of the GE-ME in 0.5 mol L<sup>-1</sup> sodium acetate solution containing 0.5 mmol L<sup>-1</sup> K<sub>3</sub>[Fe(CN)<sub>6</sub>] + 100 mg (~16 mmol L<sup>-1</sup>) of barium nitrate; (B) Electrochemical impedance spectra in a solution of 0.5 mol L<sup>-1</sup> sodium acetate and 0.5 mmol L<sup>-1</sup> K<sub>3</sub>[Fe(CN)<sub>6</sub>] of the bare electrode before and after addition of HCO<sub>3</sub><sup>-</sup>, as well as of the GE-ME before and after addition of HCO<sub>3</sub><sup>-</sup>, after waiting 5, 10, 15 and 20 min.

The gradual decrease of the imaginary impedance, Z'', in relation to the real impedance, Z', at decreasing frequencies (higher Z), seen in Figure 5B after addition of HCO<sub>3</sub><sup>-</sup> indicates an increasing resistance to charge transfer, R<sub>ct</sub>, for the redox probe [19,20]. Both the decrease of the DPV peak current of the ferro-/ferricyanide couple and the increase of the EIS R<sub>ct</sub> are attributable to the hemiester formation on the ME- modified GE, resulting in a negatively charged interface that repels the also negatively charged ferricyanide ion, as schematized in Figure 6.



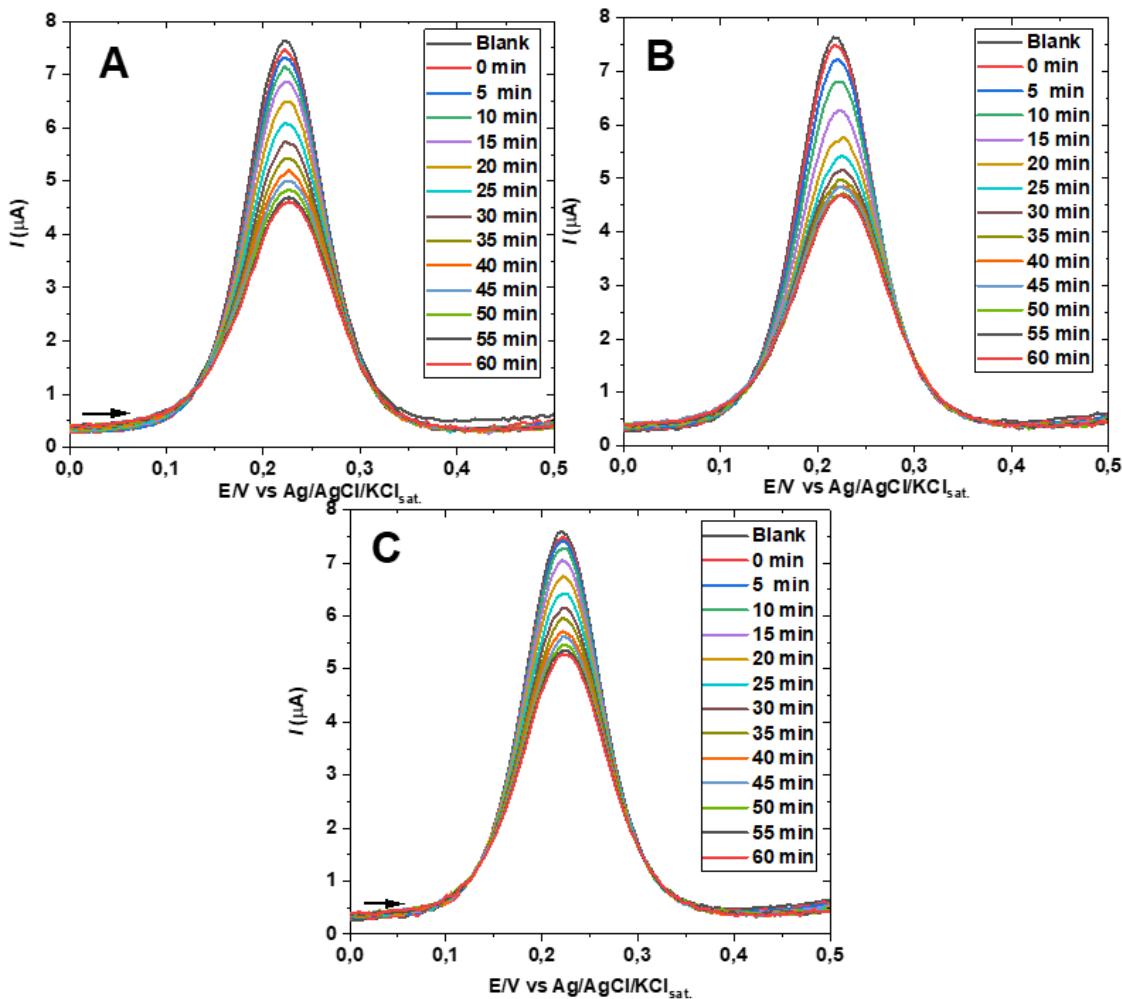
**Figure 6.** Electrostatic repulsion of ferricyanide by the dissociated hemiester group, 2-mercaptopethyl monocarbonate.

Further support to the scheme of Figure 6 was gained replacing ferricyanide by hexaammineruthenium(II) chloride,  $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_2$ , as the voltammetric redox probe. Unlike ferrocyanide, this complex ion is positively charged and therefore should not be subject to increasing repulsion by the gradual conversion of the alcohol to the hemiester anion. Experimental confirmation that the electrochemical signal of the ruthenium complex is not affected by the interfacial 2-mercaptopethyl monocarbonate anion formation due to gradual reaction with bicarbonate is presented in Figure 7A,B, to be contrasted with the decrease in signal, predominantly electrostatic, observed in Figure 4B, where ferricyanide was used as a probe.



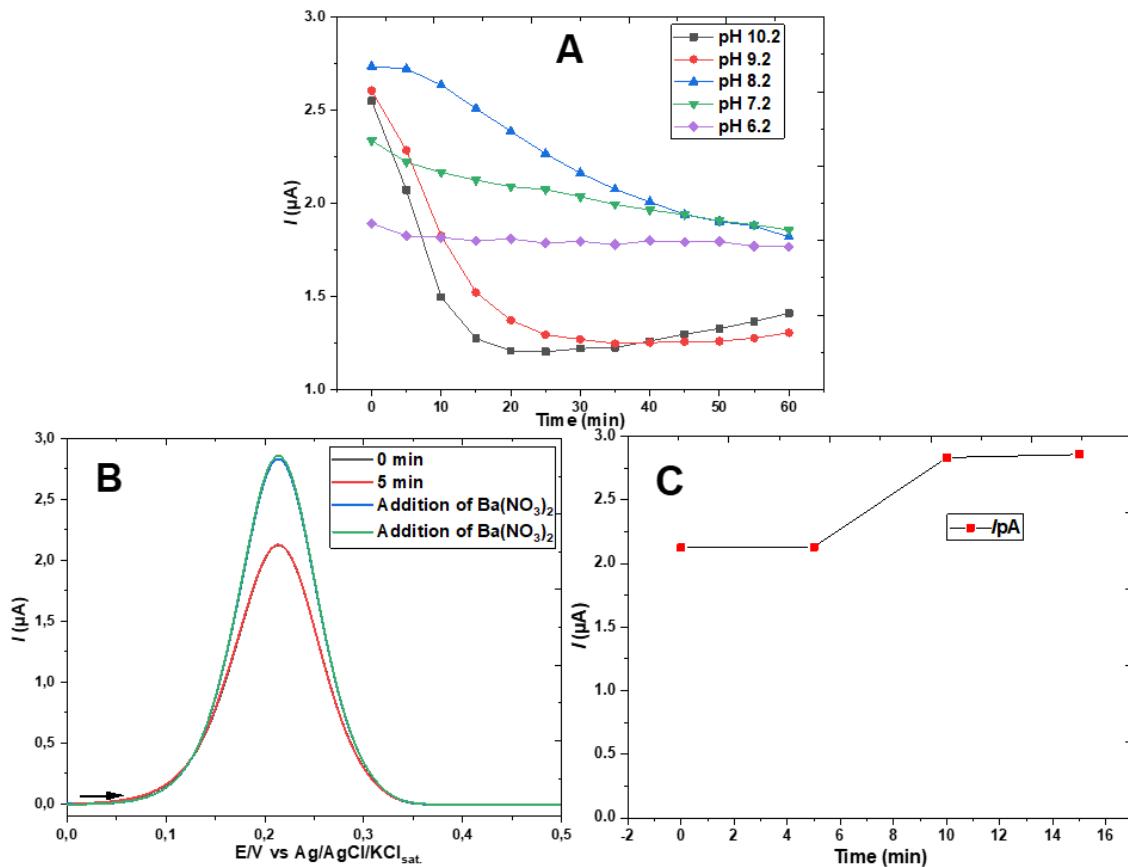
**Figure 7.** (A) Differential pulse voltammograms of 0.5 mM hexaammineruthenium (II) chloride in 0.5 M sodium acetate electrolyte, pH 8.2, with addition of 1 mM of bicarbonate, recorded using a gold electrode modified with 2-mercaptopethanol. (B) Anodic peak currents of DPVs in (A) plotted against time.

An estimation of the time until half of the equilibrium concentration of hemiester was formed on the SAM (supposing a linear relation hexacyanoferrate DPV peak current decay over time), as well as and indication of the repeatability of the experiments was obtained from the results shown in Figure 8A, B and C. The experiments were carried out at the same conditions (room temperature of  $24 \pm 2$  °C) using three new preparations of the GE-ME after polishing the electrode. The repeatability of the maximum and minimum peak current values was very good while the half formation time was of nearly 25 min in the experiments of Figure 8A,C, as well as Figure 4B, and about 17 min in Figure 8B, averaging  $22 \pm 5$  minutes.



**Figure 8.** Repeatability of the HECA formation for three successive modifications (A, B, and C) of the gold electrode with 2-mercaptoproethanol. Differential pulse voltammograms were recorded in the presence of 1.0 mM potassium ferricyanide and 1.0 mM sodium bicarbonate in a 0.5 M sodium acetate electrolyte at pH 8.2.

Another important parameter that affects the formation of the HECA is the pH of the medium. An increase of one or two units of the pH above 8.2 accelerates the HECA formation and accentuates the suppression of the  $[\text{Fe}(\text{CN})_6]^{3-}/4$  redox process peak current, as seen in Figure 9A. By reducing the pH, partial suppression of the redox couple peak was observed from the beginning on, being more pronounced at pH 6.2 than at pH 7.2. However, after 60 min the curves at pH 6.2, 7.2, and 8.2 converge to nearly the same peak current of about 1.8  $\mu\text{A}$ . To evaluate the hypothesis of rapid adduct formation prior to the recording of the first DPV, especially at pH 6.2, the experiment was repeated with the addition of  $\text{Ba}(\text{NO}_3)_2$  in excess after the second DPV. As can be seen in Figure 9B,C, the redox peak increased from 2.15  $\mu\text{A}$  to 2.83  $\mu\text{A}$ , i.e., the hemiester had already formed on the SAM surface at the time of the first DPV and was dissociated again by removing the bicarbonate from the solution as  $\text{BaCO}_3$ .



**Figure 9.** A DPV's anodic peak current as a function of time at different pH values. B DPVs at pH 6.2, before and after addition of  $\text{Ba}(\text{NO}_3)_2$ , and C respective anodic peak currents. All DPVs were recorded in the presence of 0.5 mM potassium ferricyanide and 1.0 mM sodium bicarbonate in 0.5 M sodium acetate/acetic acid electrolyte.

It is known that ferricyanide is nearly unprotonated from pH 1 up, while  $\text{Fe}(\text{CN})_6^{4-}$  predominates over  $\text{HFe}(\text{CN})_6^{3-}$  at pH 3 or higher, based on the dissociation constants at 0.5 mol  $\text{L}^{-1}$  ionic strength [21]. Therefore, the anionic charge of the hexacyanoferrate redox probe is unaffected by pH changes in the range of 6.2 to 10.2 pH. By taking into account that the equilibrium  $\text{CO}_2(\text{g}) \rightleftharpoons \text{HCO}_3^{-(\text{aq})} \rightleftharpoons \text{CO}_3^{2-}(\text{aq})$  presents  $\text{pK}_{\text{a}1}$  6.1 and  $\text{pK}_{\text{a}2}$  9.8 at 0.5 M ionic strength, i.e., bicarbonate is the predominant species in solution from pH 6.1 to 9.8, and that the  $\text{pK}_a$  of monoethyl carbonic acid is lower than 4 [11], as is probably the  $\text{pK}_a$  of 2-monomercaptoethyl carbonic acid (e.g., acetic acid is weaker than thioglycolic acid), future studies by other techniques may come to elucidate whether the pH dependence observed in Figure 9 has relation with the hemiester formation by preferential attack of  $\text{CO}_2$  molecules on the hydroxy group at lower pH and of bicarbonate or carbonate at higher pH values and/or if other factors are involved in the mechanism and kinetic of the reaction. Further research may also elucidate whether the incomplete and pH dependent suppression of the ferricyanide peak by electrostatic repulsion (Figure 9A) is a function of the molar fraction of interfacial hydroxy groups converted into the hemiester or a consequence of imperfections in the self-assemble monolayer (less likely, in view of the repeatability exhibited in Figure 8).

## 5. Conclusions

In this study, the formation of HECA bound to self-assembled monolayers was demonstrated for the first time by using, also for the first time, voltammetric techniques and the electroactive probes ferrocyanide and hexamine ruthenium. Quite interestingly, the observation that the formation of HECA affects the redox process of ferricyanide (an anionic species) but does not affect the redox process of hexammineruthenium (a positively charged species) was crucial to infer that the electrostatic effect is the preponderant to explain the decay of the voltammetric peak current of the

first probe but not of the second one. These results are in good agreement with the ones obtained by EIS measurements, which demonstrated that the formation of the adduct increased the Rct of the  $[\text{Fe}(\text{CN})_6]^{3-/-4}$  redox couple. A half formation time of about 22 min was determined at pH 8.2, while faster formation was observed at a pH one and two units higher or lower. Also, the presence of barium ions in solution prevents the formation of the HECA, while its addition to the already-formed HECA decomposes it rapidly. In conclusion, the present study expands knowledge by demonstrating that even the ubiquitous presence of dissolved  $\text{CO}_2$  in water exposed to the air suffices for the formation of a HECA-like mercaptoethyl carbonate at the interface of a SAM rich in hydroxy groups. This reinforces the hypothesis that the presence of HECA in solution and at interfaces is more widespread than supposed and that they are expected to be found in most diverse environments, including living organisms, maybe playing relevant roles yet to be discovered.

**Author Contributions:** **Berlane Santos** : Conceptualization, methodology, investigation, writing—original draft preparation, writing—review and editing. **Fernanda Carli** : Conceptualization, methodology, investigation. **Claudimir do Lago**: Conceptualization, investigation, writing—review and editing, supervision, project administration, funding acquisition. **Ivano Gutz** : Conceptualization, investigation, writing—review and editing, supervision. **Lúcio Angnes** : Conceptualization, investigation, writing—review and editing supervision, funding acquisition.

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**Conflicts of Interest:** The authors declare no conflicts of interest.

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