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Temperature Effect on the Electrooxidation of Gamma Hydroxybutyric Acid (GHB) on Platinum Catalyst through Cyclic Voltammetry, Chronoamperometry, Impedance Spectroscopy and SERS Spectroelectrochemistry

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A study of the electro-oxidation of gamma hydroxybutyric acid (GHB) on platinum electrode in acidic media has been investigated by cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy in the temperature range between 5 and 30ºC. The variation of the j-E curves allows the determination of activation energy in a wide interval of potentials where three characteristic oxidation peaks appear. The j-t curves were registered at the more positive potentials corresponding with the A and B peaks. Stationary current intensity measurements allowed the determination of the activation energy in pure kinetic region conditions. Electrochemical impedance spectroscopy made also possible the study of the electrochemical behavior in the same potential region. Temperature dependence of the charge-transfer resistance (Rct) and the rate constant associated with the surface coverage by an adsorbed intermediate (τ^{-1}=Ro/L) during the GHB electro-oxidation process were evaluated and discussed. In all cases, the values of activation energy, below 30 kJ/mol, suggest that a complex mechanism takes place for the GHB electro-oxidation free of strong interactions with the platinum surface. In situ Surface Enhanced Raman Scattering (SERS) spectroelectrochemistry spectra corresponding to coadsorbed species, including intermediates of reaction, have been analyzed at several potentials.

Keywords: GHB, impedance spectroscopy, activation energy, platinum-catalysed, Surface-Enhanced Raman Spectroscopy (SERS) spectro-electrochemistry.

1. INTRODUCTION

Gamma-Hydroxybutyric Acid (GHB) is a simple molecule which simplicity contrasts with the complexity of its physiological activity, the difficulties to detect it in the body and the almost inexistent literature explaining its behavior from an electrochemical point of view.

GHB can be naturally found in the body in variable concentrations and also be present in alcoholic drinks and other foodstuff in small quantities [1]. In addition, this substance has become sadly famous by his frequent abuse as drug in clubs and pubs [2], and it is a drug associated with cases of sexual assaults [3,4]. This drug can produce euphoria, drowsiness, amnesia, visual impairment, unconsciousness and even the death in extreme case (from 500 mg/L). GHB has an average short life in the organism, which makes its detection difficult [5].

On the other hand, GHB is a C4 alcohol with a carboxylic group and can be used as a model compound in alcohols for electrocatalytic purposes. Recently, we have studied the electro-oxidation of GHB on a polycrystalline platinum electrode by cyclic voltammetry and chronoamperometry in acidic medium [6,7]. The electronic current density observed for the different peaks in different experimental conditions of GHB concentration, scan rate and pulse potential applied allowed inferring the alcohol group oxidation by a pathway where the corresponding carboxylic acid (succinic acid) is the main product. As a general remark, these results agree, to a great extent, with those of the bibliography for the electro-oxidation of aliphatic alcohols on platinum electrodes [8-13]. Moreover, *in situ* Surface Enhanced Raman Scattering (SERS) spectra corresponding to GHB intermediates and water adsorbed species being formed/consumed at the potential-dependent adsorption processes were obtained using spectro-electrochemistry [7,14]. Though the electro-oxidation of alcohols in platinum electrodes has been the aim of numerous publications in the last decades, as indicated before, few studies have focused their study in the relation with temperature dependence by means of chronoamperometry and electrochemical impedance spectroscopy. These mainly concentrated on the oxidation mechanisms of ethanol and other alcohols on platinum and modified electrodes [15-17].

In this paper, the study of temperature dependence in the GHB electro-oxidation in a wide the region of potentials by cyclic voltammetry as well as chronoamperometric and AC-impedance measurements on Pt electrode in acidic medium has been performed. Additional information has been obtained by *in situ* SERS spectro-electrochemistry. It is important to emphasize that the determination of the activation energy and other aspects related to the adsorption of some reaction intermediates is a powerful tool for the comprehension of the electrochemical processes associated to the electro-oxidation of GHB on a platinum electrode. For this reason, a greater understanding of the electroactivity of GHB on the Pt surface is compatible with the possibility of facilitate the design of future strategies for the use of this electrode as a sensor for the detection of GHB and similar substances with multipurpose interest.

2. EXPERIMENTAL

Gamma-hydroxy butyric lactone (GBL) was obtained from Aldrich (reagent, minimum 99% purity). GHB, sodium salt, was prepared and identified as is described in reference 6. Other products used in this work are of the same characteristics as in the above mentioned reference.

Cyclic Voltammetry (CV), Chronoamperometry and Electrochemical Impedance Spectroscopy analyses were performed with an Autolab (Ecochemie model Pgstat30) instrument with a frequency response analyzer (FRA) module attached to a PC with proper software (GPES and FRA) for the total control of the experiments and data acquisition. Electrochemical impedance measurements were performed in the frequency range 10 kHz to 100 mHz with using single sine AC mode. The amplitude of the AC potential was 5mV in root mean square (rms). The impedance data were converted into equivalent circuits using the software available with the potentiostat (FRA Version 4.9). The fitted impedance curves correspond to the solid lines in all the figures.

A three electrode configuration was used for the electrochemical measurements: platinum electrode acting as a working electrode, a Ag/AgCl used as a reference electrode and a platinum electrode acted as a counter electrode. The working electrode used for the different experiments was a 1.6 mm diameter platinum electrode from Bioanalytical Systems (Kenilworth, UK). The working electrode was polished with 0.05 µm Al_2O_3 slurry, rinsed and sonicated in 18 MΩ Milli-Q water (Millipore, Maryland, US) and dried before use.

Bard et al. [18] give the following correlations for the standard potential of the silver chloride electrode as a function of temperature (where t is temperature in °C): $E^0(V) = 0.23695 - 4.8564x10^{-4}t - 3.4205x10^{-6}t^2 - 5.869 \times 10^{-9}t^3$, for $0 < t < 95$ °C. Between 5 and 30 ºC, the temperature interval studied in this work, the potential of the reference electrode varied 15 mV. Therefore, it can be considered that the effect of the temperature on the position of the peaks in cyclic voltammetry and with respect to the applied potential in chronoamperometry and impedance spectroscopy is negligible.

The electroactive surface area of the working electrode was determined using the hydrogen adsorption/desorption voltammetric peaks of platinum electrode with a known charge density of 210 $\mu C/cm^2$ in 1.0 M H_2SO_4. A value of 0.036 cm^2 was found and used for normalise the current intensity in the cyclic voltammograms presented in this work. Nitrogen was bubbled in the electrochemical cell for 20 min before analysis. All the measurements realized in this work with GHB were carried out with a freshly prepared solution.

Surface Enhanced Raman Spectroscopic (SERS) measurements were performed with a HORIBA Jobin Yvon LabRaman spectrograph. The setup for the spectro-electrochemical measurement and the cell used in this experiments are described in reference 14.

3. RESULTS AND DISCUSSION

Recently we have carried out the study of GHB electro-oxidation on platinum electrodes in acidic medium by means of cyclic voltammetry, chronoamperommetry and spectro- electrochemistry [6, 7]. The j-E curves showed two peaks of oxidation, A and B, in the positive sweep direction in the zone of potentials of the double layer and region of platinum oxides, respectively. In the sweep towards negative potentials a peak assigned to the oxidation of GHB (peak C), and whose onset partially overlaps with the tail of the peak of reduction of the platinum oxide formed during the positive sweep, was obtained. The response observed for the current density of these peaks with the scan rate and the concentration suggested that the alcohol group is oxidized, so that the principal

product obtained is the corresponding carboxylic acid (succinic acid). It is necessary to emphasize that our results agree, to a great extent, with those reported in the literature on the electro-oxidation of aliphatic alcohols on platinum electrodes [8-13]. Combination of chronoamperommetry and in situ SERS spectro-electrochemistry allowed analysing the interaction of GHB on the platinum surface. In this respect, a step of surface diffusion or another diffusion path of GHB towards activated centres of oxidised platinum with a finite thickness of the diffusion layer cannot be ruled out. The observation of the co-adsorption of some GHB species, solvent and supporting electrolyte on the platinum surface supports this hypothesis [7].

3.1 Dependence with temperature

3.1.1. Cyclic Voltammetry

Figure 1 shows the j-E curves obtained for a 25mM GHB solution in aqueous media at pH 1.5 and with phosphoric acid acting as supporting electrolyte by cyclic voltammetry at scan rate 0.01 V/s in the temperature interval between 5 and 30ºC. The measurements at higher temperatures were rejected due to an increase of the rate conversion of the hydroxyacid molecule GHB into the cyclic lactone GBL.

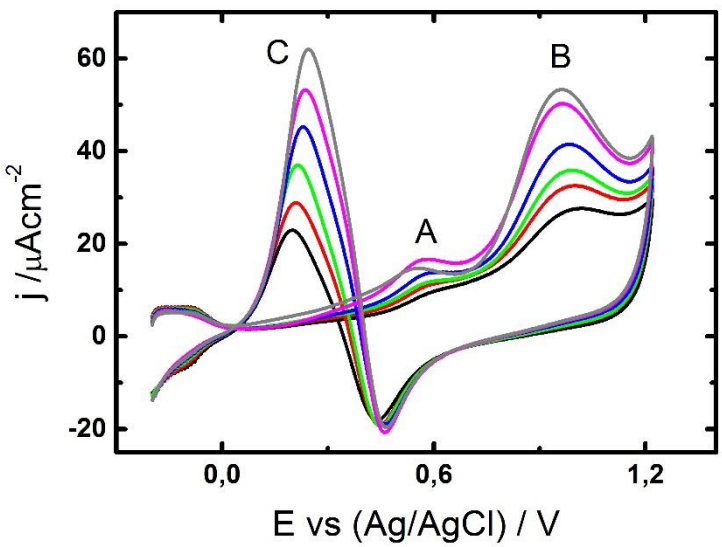


Figure 1. Cyclic voltammograms of 25 mM GHB in 0.1 M phosphoric acid pH 1.5 at several temperatures. (—) 5ºC, (—) 10ºC, (—) 15ºC, (—) 20ºC, (—) 25ºC, (—) 30ºC. Scan rate 0.01 V/s.

The current density of the peaks A, B and C simultaneously increases with the temperature. The plot of the log j vs 1/T at different potentials where GHB is electroactive was linear and allows obtaining the activation energy (E_a) for the electrochemical reaction. At potentials 0.7, 0.9 and 0.2 V

(corresponding to the peaks A, B y C) the values of E_a obtained were 17.4±0.5, 19.5±0.6 y 22.5±0.5 kJ/mol, respectively. In similar experimental conditions the behavior of the GHB [6] with the scan rate was studied and it was observed that the kinetic control is a mixture of diffusion and adsorption processes. In any case, the correction of the current density with the viscosity at different temperatures would lead to slightly lower values of activation energy.

Using another concentration and similar scan rate (50 mM GHB and 0.02 V/s), Ea values obtained were 18.0±0.7, 23.1±0.6 y 21.0±0.3 kJ/mol, at 0.7, 0.9 y 0.2 V, respectively. These values are lower than the obtained ones by other authors by means of cyclic voltammetry for the ethanol electro-oxidation on different platinum surfaces [15], indicative of the important catalytic role of the platinum surface on GHB oxidation.

3.1.2. Chronoamperommetry

The electrochemical behaviour of GHB has been previously studied by chonoamperometry in our laboratory at several potentials and concentrations [7]. Figure 2 shows the j-t curves obtained keeping the potential at +0.9 V for a 50 mM GHB solution in phosphoric acid pH 1.5 at several temperatures.

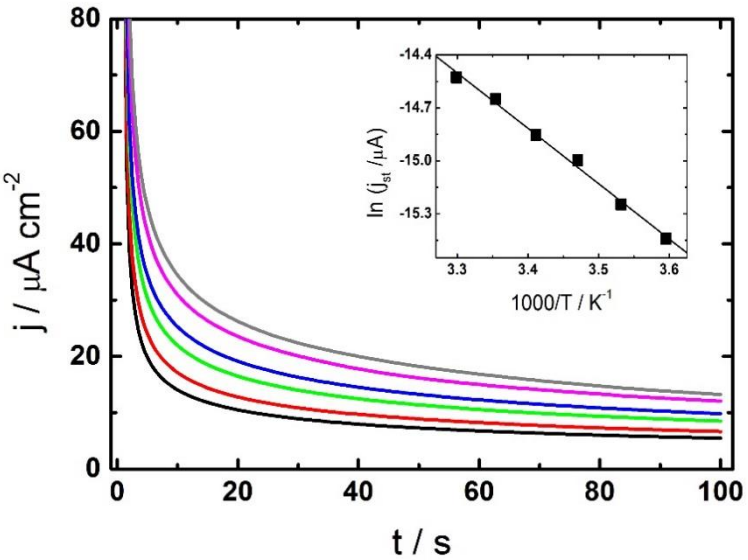


Figure 2. Chronoamperometric curves of 50 mM GHB in 0.1 M phosphoric acid pH 1.5 at several temperatures. (—) 5ºC, (—) 10ºC, (—) 15ºC, (—) 20ºC, (—) 25ºC, (—) 30ºC. Applied potential +0.9 V. Inset: Plot of ln j_{st} vs 1/T.

In all the cases can be observed that the curves describe a typical fall reaching a steady value of stationary current density at longer times. Likewise, we can see this behaviour as the stationary current density increases with the temperature. Similar behavior is observed at potentials of 0.7 and 0.8 V corresponding with the end of the wave corresponding to peak A and the start of peak B. The inset of the figure shows the representation of ln j_{st} vs 1/T. A linear variation is observed, and a value of energy

of activation, Ea, of 26.1±0.8 kJ/mol is obtained. Equally the activation energy values obtained at 0.7 and 0.8 V were 27.7±1.2 and 24.1±0.5 kJ/mol, respectively. In this case, the stationary current intensity measurement allowed the determination of the activation energy in pure kinetic region conditions. These values are of the same order of magnitude that those obtained by means of cyclic voltammetry.

3.1.3. Impedance spectroscopy.

There is little in the bibliography on the electrochemical characterization of the electro-oxidation of alcohols on platinum surfaces by means of impedance spectroscopy. In this respect, Gupta et al. [15] studied the electro-oxidation of ethanol using Pt and PtSn catalysts in different proportions. The spectra that they obtained presented Nyquist representations with a semi-circumference at high frequencies indicative of an electronic transfer in the electrochemical process and, equally, an inductive loop at low frequencies that reaches the next quadrant in the graphic representation suggesting the presence of an intermediate of reaction on the surface. Likewise, the characteristics of the spectra of impedance in the electro-oxidation of methanol and 2-propanol are similar, describing the electrochemistry process by means of equivalent circuits according to schemes of reaction that suggest the presence of some adsorbed intermediates [16, 17].

In Figure 3, the spectra of impedance (Nyquist plot) of a 50 mM GHB aqueous solution in phosphoric acid at pH 1.5 applying a constant DC potential of 0.8 V in the interval of temperatures studied can be observed.

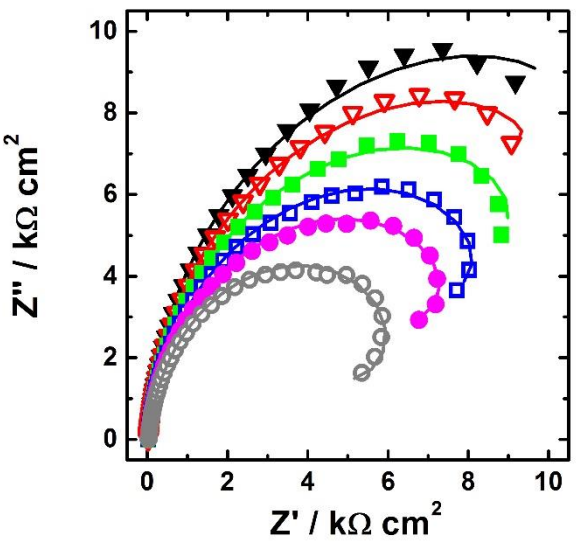
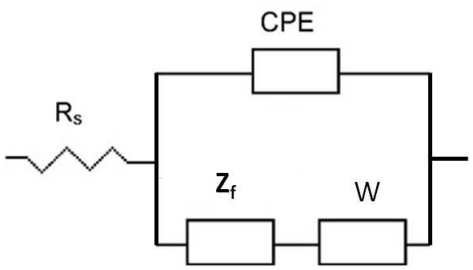


Figure 3. Nyquist plot of 50 mM GHB in 0.1 M phosphoric acid pH 1.5 at several temperatures. (▼) 5ºC, (▽) 10ºC, (■) 15ºC, (□) 20ºC, (●) 25ºC, (O) 30ºC. Potential +0.8 V.

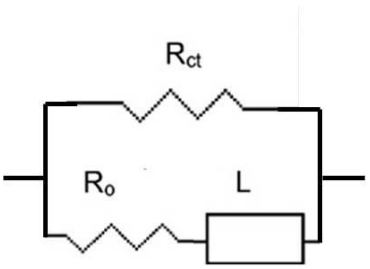
Globally, it is observed that the impedance increases as the temperature decreases. In all cases two typical semicircles are described. The first one at high frequencies presents the typical

characteristics of an electronic transfer process. The second one, at low frequencies, appears as an inductive loop that indicates the presence of some adsorbed intermediates. Nevertheless, it is remarkable that the values of Z" do not change sign as it would have been expected due to the presence of the inductive effect deduced from the profile obtained from the latter semicircle. The curve is located, in the studied interval of frequencies, in the same quadrant. This is an aspect that differentiates the electrochemical behavior of GHB, by means of measures of impedance, with respect to other alcohols that are described in the bibliography [15-17]. Similar Nyquist plots and their evolution with the temperature are observed at 0.7 and 0.9 V. The general characteristics of the electro-oxidation of GHB [6, 7] suggest the presence of a transport step of the electroactive species that is not negligible for the measures of impedance in view of the values of Z "and Z ' obtained at low frequencies (Warburg impedance). This way, the response by means of impedance spectroscopy can be represented through an equivalent circuit as the one that is indicated in the following graph (Scheme 1 and 2. Randless circuit type), and that is compatible with the scheme of electro-oxidation of GHB described before.



Scheme 1. Equivalent circuit for the electro-oxidation of GHB.

Z_f values are in agreement with the schemes that are suggested in the bibliography for the electrooxidation of alcohols [15-17]



Scheme 2. Elements combination corresponding to Z_f for the electro-oxidation of GHB.

3.2 Elements of the equivalent circuit.

3.2.1. Resistance of the solution and constant phase element.

According to the equivalent circuit shown in scheme 1 and the combination of elements corresponding to Z_f of the scheme 2, the curves of the best fit for the spectra of impedance were

produced and are shown in the figure 3 appearing as solid lines. This fit allows obtaining the values of the parameters associated with the elements of the circuit and their variation with temperature. In this respect, the resistance of the solution (R_s) diminishes with a rise in temperature indicating the increase of the conductivity of the water solution with this variable. The constant phase element (CPE) is described with two parameters Y_o and n according to the following expression:

$$Z_{CPE} = 1/(Y_o\omega)^n$$

For the spectra showed in figure 3, 'n' has an average value of 0.965±0.010 and the parameter Y_o slightly increases with the temperature from a value of $1.55x10^{-6}$ at 5ºC up to $2.24\cdot10^{-6}$ at 30ºC, with units $\Omega^{-1/n}s$. The set of CPE parameters obtained in function of the temperature and DC potential are summarized in the Table 1. The values for Y_o and n are similar to the reported Otomo et al. [17] and differ slightly to those obtained in a Pt-Sn surface by Gupta et al. [15].

Table 1. Parameter values of CPE of Pt electrode in function of the temperature for 50 mM GHB in 0.1 M phosphoric acid pH 1.5

E / V	**0.7**		**0.8**		**0.9**	
T / ºC	**$Y_o\cdot10^6$ / $\Omega^{-1/n}s$**	**n**	**$Y_o\cdot10^6$ / $\Omega^{-1/n}s$**	**n**	**$Y_o\cdot10^6$ / $\Omega^{-1/n}s$**	**n**
5	1.90	0.970	1.55	0.981	1.92	0.985
10	2.06	0.966	1.64	0.975	1.99	0.986
15	2.01	0.950	1.75	0.963	2.02	0.990
20	2.90	0.957	1.80	0.960	2.00	0.997
25	2.21	0.927	1.90	0.958	2.01	0.992
30	2.22	0.923	2.24	0.953	2.02	0.993

3.2.2. Diffusion impedance

From the set of elements that characterize the spectra of impedance obtained for GHB on platinum it is important to draw attention to that associated with the transport of the electroactive species, the impedance W. Good fittings for this element at low frequencies is only possible by means of using W in the form associated with a process of finite diffusion, in particular with a T-type impedance that is a hyperbolic cotangent function following the expression:

$$Z_T = [1/Y_O (i\omega)^{1/2}]\coth[B(i\omega)^{1/2}]$$

with Yo and B being the Warburg impedance and time constant parameter, respectively. In the experimental conditions used in figure 3, Y_O slightly increases with the temperature from a value of $3.98\cdot10^{-4}$ at 5ºC up to $6.09\cdot10^{-4}$ $\Omega^{-1}s^{1/2}$ at 30ºC and can be related to an increase of the transport rate. On the other hand, B also increases with the temperature, what indicates that there must exist an increase of the thickness of the finite diffusion layer, since $B=l^2/D$, and being 'l' the thickness of the layer and D the coefficient of diffusion. The calculated values for the B parameter were 0.012 and 0.031s at 5ºC and 30ºC, respectively. This element is associated to the role that the PtOH nuclei formed on the electrode surface, and determinant in the conditions of transport of the electroactive

species (as previously reported by the authors by means of chronoamperommetry and in situ SERS spectroelectrochemistry [7]), exert on the general electrochemical behavior of the electro-oxidation of GHB. In this sense, it is suggested that GHB must follow a surface diffusion step towards the activated centres of oxidised platinum. At 0.7 and 0.9 V the evolution of these parameters is similar to those calculated before, and the average values obtained for Y_O and B are $6.70\pm0.42)\cdot10^{-4}$ $\Omega^{-1}s^{1/2}$ and 0.039±0.006 s, and $(4.22\pm0.023)\cdot10^{-3}$ $\Omega^{-1}s^{1/2}$ and 0.015±0.002 s, respectively.

At this point, it is possible to explain the fact that the values of current density obtained in the response j-E for CV are extremely low. If the electrochemical process for the oxidation of a primary alcohol to produce an aldehyde or a carboxylic acid is controlled by the diffusion of the electroactive substance towards the electrode surface, the current density should have values between 1 and 100 mA/cm^2 for GHB solutions in the range of concentrations and scan rates used in this study. The values obtained for the peaks A and B of GHB are very low (< 100 $\mu A/cm^2$), indicative that the oxidation of the molecule takes place by means of a superficial complex process that includes the diffusion step of the electroactive species. These low values for the intensity of current are a common fact found in numerous papers in the bibliography [19-24], in which the presence of superficial hydroxides of platinum formed at positive potentials play an important role.

3.2.3. Inductance y R_o

The values of R_o and L, elements that can be associated with the oxidation of some adsorbed intermediate, have also been obtained. Both decrease their values with increasing temperature, what is attributed to the fact that the oxidation rate increases at higher temperatures. The impedance, associated with L, for an electrochemical process with an adsorbed electroactive intermediate can be expressed as:

$$Z_L = i\omega L$$

being $L = \tau R_o$. This way, from R_o and L values, τ^{-1} can be obtained representing the first-order rate constant for the oxidative desorption of the above mentioned intermediate [17]. The results at 0.7, 0.8 and 0.9 V as DC potentials allows to describe the electrochemical behavior with the temperature in the zone of potentials of maximum electrocatalytic activity for the GHB oxidation on platinum. In figure 4a the values of τ^{-1} vs T at these three potentials are represented. An increase of τ^{-1} is observed with increasing temperature values in all cases. At potential 0.7 V, the obtained values are significantly lower than those achieved at potentials near to the maximum current density for peak B. These values are of the same order of magnitude than those observed for methanol and 2-propanol as reported by Otomo et al [17].

3.2.4. Charge transfer resistance, Rct

The values obtained for the curves Z"-Z' indicate that the R values decrease with increasing temperature values, in agreement with an increase of the electronic transfer rate. In figure 4b the plot

log1/Rct vs 1/T at three potentials is represented. The values of activation energy obtained were 17.5±1.8, 17.8±1.4 and 14.5±1.0 kJ/mol at 0.7, 0,8 and 0.9 V, respectively. It is important to draw attention that the lowest Rct values are obtained at 0.8 V for all temperatures. This corresponds to a zone of potentials close to peak B and where the platinum hydroxides are involved in the increase of the electronic transfer rate. In all cases the activation energy values are slightly lower than those found in other studies of alcohol on a platinum electrode [15,16].

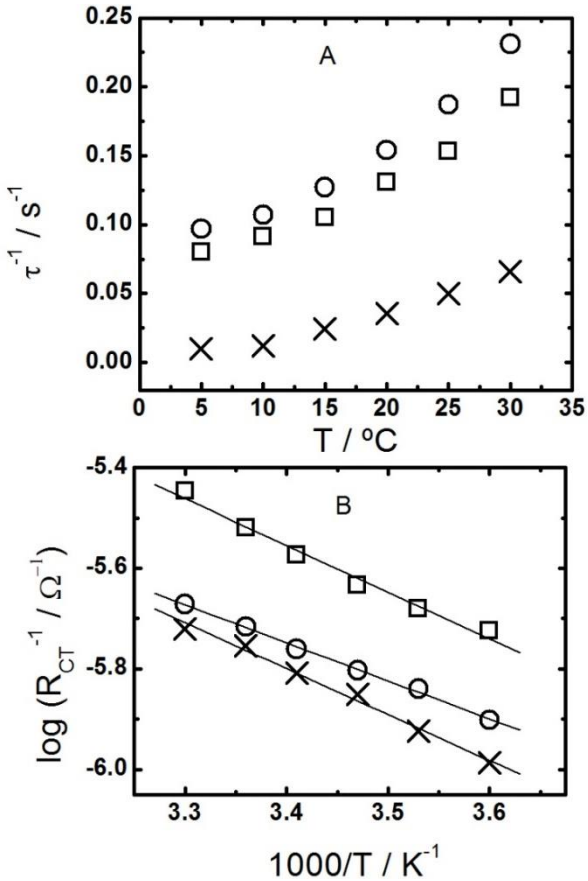


Figure 4. Impedance spectroscopy of 50 mM GHB in 0.1 M phosphoric acid pH 1.5. (A) Plot of τ^{-1} vs T, and (B) log R_{CT}^{-1} vs 1/T. Potentials (X) 0.7 V, (□) 0.8 V, (○) 0.9 V.

3.3. Measures of AC-impedance to higher concentrations

Measurements of impedance were carried out with 100 mM GHB solutions at potentials 0.7, 0.8 and 0.9 V vs Ag/AgCl using the same interval of temperatures. Also, measurements of 500 mM GHB at potentials 0.7, 0.8 and 0.9 V vs Ag/AgCl at 20ºC were carried out. Figure 5 shows the spectra of impedance for the specific case of 100 and 500 mM GHB at 0.8 V and 20ºC.

The characteristics of the spectra are similar to those previously observed, suggesting that GHB oxidation on platinum takes place in a similar way to that found in lower concentrations. Firstly, it can be observed in figure 5 that at these concentrations lower values of impedance are obtained with regards to the results achieved at 50 mM. The study with the temperature for 100 mM GHB yielded an activation energy of 17.8±0.5 kJ/mol, in the same magnitude order than those measurements performed

at lower concentrations. For 500 mM GHB some deviations were obtained in the behavior observed at the studied potentials. On the one hand the values obtained for the parameters that characterize the CPE element are summarized in the Table 2 being similar to those obtained previously (Table 1) with the exception of that at 0.7 V, where a clear decrease in both parameters is observed. This exception can be explained by the adsorption of phosphate ions on the platinum surface at potentials corresponding to the double layer formation, which is stronger under these experimental conditions before the formation of oxides on the metallic surface takes place [25].

Table 2. Parameters values of CPE of Pt electrode for 500 mM GHB in phosphoric acid pH 1.5

E / V	$Y_o \cdot 10^6$ / $\Omega^{-1/n}s$	n
0.7	1.09	0.870
0.8	2.06	0.961
0.9	2.27	0.985

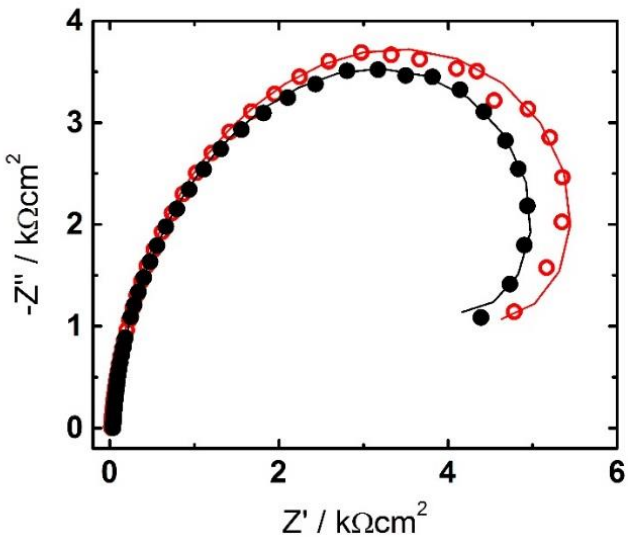


Figure 5. Nyquist plot of GHB in phosphoric acid pH 1.5 at 20ºC. (,) 100 mM, (–) 500 mM. Potential +0.8 V.

Studies of spectro-electrochemistry of GHB and compounds derived by means of SERS demonstrated the co-adsorption of phosphate anions, water and/or hydroxides on the platinum surface [14]. On the other hand the values of the charge transfer resistance Rct are generally lower, with the exception of that at 0.7 V where there is no variation with the concentration. The lowest value obtained was that for potentials at 0.8 V. Finally the values of the constant associated with the oxidative desorption, τ^{-1}, were 0.122, 0.239 and 0.229 s^{-1} at 0.7, 0.8 and 0.9 V, respectively. These values are slightly bigger than those found for 50 mM GHB, suggesting again an effect of phosphate adsorption and GHB interaction with the platinum surface during the process of electro-oxidation.

3.4. Intermediates of reaction. In situ Raman spectroelectrochemistry.

For the electro-oxidation of GHB a catalytic scheme that can be written as follows is generally accepted:

$Pt + H_2O = PtOH$ (or $PtOH_2$)

$Pt + GHB = PtGHB_{ads}$

$PtOH + PtGHB_{ads} = 2Pt + GHB_{OX}$

Some authors have suggested that the oxidation of alcohols occurs following a mechanism similar to that suggested by Langmuir-Hinshelwood [21].

In a previous paper the authors studied the behavior of GHB by *in situ* SERS spectro-electrochemistry and the conclusions were concordant with the above scheme [7, 14]. A close inspection of the potential dependence for the SERS spectra in the zone at low wavenumbers, between 100 and 600 cm^{-1}, showed an evolution of the band at 370 cm^{-1} corresponding to the interaction of the phosphoric electrolyte with the platinum surface at potentials lower than 0.5 V. Two bands at 480 and 420 cm^{-1}, overlapping with the phosphoric one, started gradually appearing at 0.5 V, most likely from the Pt-OH and Pt-Ox vibrations, respectively [26, 27]. The variation of the bands' position and Raman intensity with the potential suggest the competitive co-adsorption of phosphate and hydroxide groups on the Pt surface according to the catalytic activity of platinum, being the Pt-OH postulated as an intermediate of reaction as mentioned above [7]. The spectra obtained are consistent with Gaussian curves, which allow distinguishing the individual variation of the intensity of each band with the applied potential (Figure 6). The increase of the peak to 470 cm^{-1} resembles the j-E curves of the GHB voltammograms in parallel with the role of Pt-OH in the catalysis. At potentials higher than 0.5 V the peak at 420 cm^{-1} appears as an indication of the presence of a Pt-Ox bond.

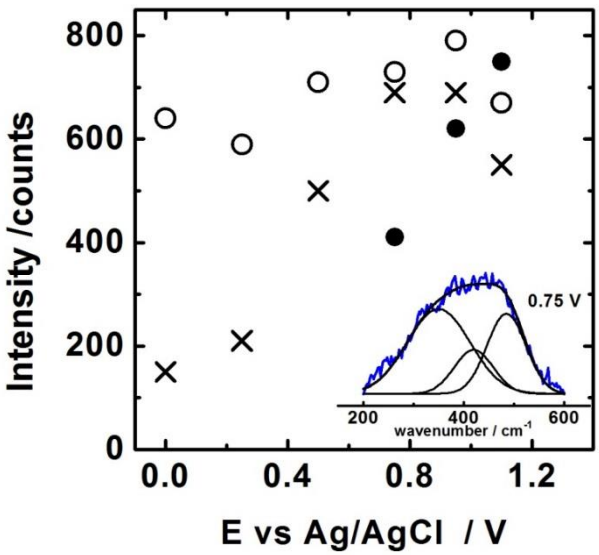


Figure 6. Intensity for the bands at wavenumber (cm^{-1}): 360 (O), 420 (●) and 480 (X). SERS spectra collected with a platinum surface electrodeposited on carbon electrode. Test solution: 0.5 M GHB + 0.5 M phosphoric acid. Bottom: Fitting of the spectra by contribution of gaussian curves at 360, 420 and 480 cm^{-1} (a negligible variation of half-width of each band fitted for different potential is found).

Details of the spectrum at 0.75 V makes it possible to visualize the contribution of the bands corresponding to the phosphoric electrolyte and those of the platinum hydroxide and platinum oxide to the global spectrum (see bottom of the figure 6).

On the other hand, figure 7 shows the spectrum of GHB in the wavenumber zone 600-1000 cm^{-1}. The peaks observed at 764, 830 (shoulder) and 957 cm^{-1} are assigned to the adsorbed phosphoric acid, the deformation scissoring mode of the carboxylic group and to the symmetric stretching of C-C bond, respectively [7, 28, 29]. The evolution with the potential suggests, in this case, the co-adsorption of GHB and oxidized derivatives with the phosphate group and, as previously mentioned, associated with the hydroxyl group linked to platinum surface. The global spectro-electrochemical behavior supports the previous scheme and it is in good agreement with the electrochemical results presented in this work.

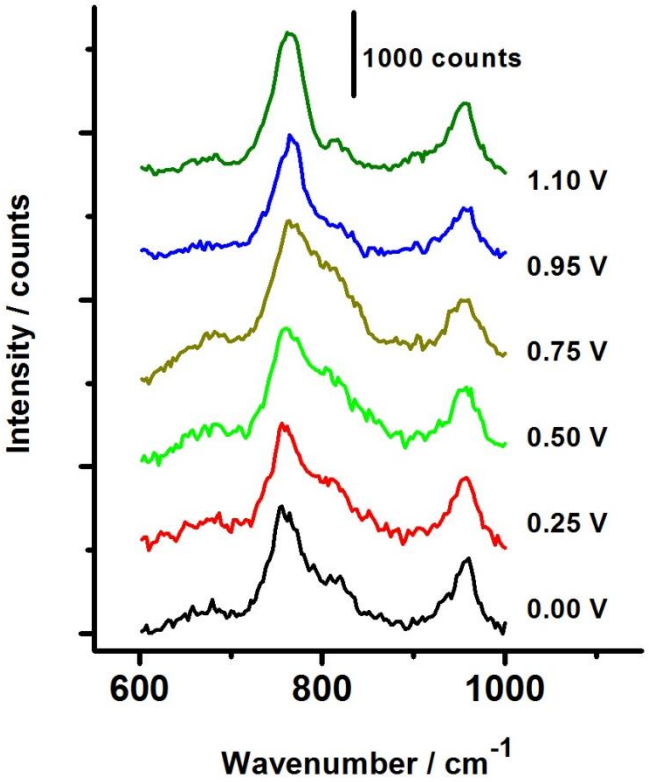


Figure 7. SERS spectrum collected with a platinum surface electrodeposited on carbon electrode. Applied potentials vs Ag/AgCl. Test solution: 0.5 M GHB + 0.5 M phosphoric acid. Two spectra collected with an acquisition time of 120 s were averaged.

4. CONCLUSIONS

The set of results obtained in this work emphasizes the fact that the GHB electro-oxidation on platinum electrodes in acid media follows a pattern, in great extent, similar to that obtained for other alcohols under these experimental conditions. Nevertheless we have to highlight some particular aspects of their electrochemical behavior. First, the low values obtained for the activation energies, around 20 kJ/mol and often lower. This fact is indicative of the important catalytic role of the platinum

surface on GHB oxidation. The obtained values reject the presence of strong interactions with the surface of the electrode. Secondly, a step of diffusion at all the potentials where GHB electro-oxidation takes place is observed. Both aspects might take as a common denominator the role that the different groups present in the GHB molecule play in the interaction on the platinum surface. Co-adsorption of GHB and oxidized derivatives with the phosphate group and, platinum hydroxide at several potential suggested by *in situ* SERS spectroelectrochemistry is in a good correspondence with the electro-oxidation scheme of GHB deduced from the voltammetric, chronoamperometric an impedance spectroscopy measurements.

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References

1. W. Andrew, W. Rosen, Depressants. From Chocolate to Morphine, 2nd ed.,Houghton Mifflin Company, pp. 77 (1993), Boston/New York
2. P.M. Gahlinger, *Am. Fam. Physician* 69 (2004) 2619-2626
3. L.A. Ciolino, M.Z. Mesmer, R.D. Satzger, A.C.Machal, H.A.McCauley, A.S.Mohrhaus, *J. Forensic Sci.* 46 (2001) 1315-1323
4. S. Jickells, A. Negrusz, in: A.C. Moffat, M.D. Osselton, B. Widdop (Eds.), Clarke's Analytical Forensic Toxicology, Pharmaceutical Press (2008).
5. P. Palatini, L. Tedeschi, G. Frison, R. Padrini, R. Zordan, R. Orlando, L. Gallimberti,G.L. Gessa, S.D. Ferrara, *Eur. J. Clin. Pharmacol*. 45 (1993) 353-356
6. R. Jiménez-Pérez, J.M. Sevilla, T. Pineda, M. Blázquez, J. González-Rodriguez, *Electrochimica Acta*, 111 (2013) 601-607
7. R. Jiménez-Pérez, J.M. Sevilla, T. Pineda, M. Blázquez, J. González-Rodriguez, *J. Electroanal. Chem*., 766 (2016) 141-146
8. C. Lamy, E.M. Belgsir, J.-M. Leger, *J. Appl. Electrochem*., **31**, 799-809 (2001)
9. V. del Colle, A. Berna, G. Tremiliosi, E. Herrero, J.M. Feliu, *Phys. Chem. Chem. Phys*. 10 (2008) 3766-3773
10. T.H.M. Housmans, A.H. Wonders, M.T.M. Koper, *J. Phys. Chem*. B, 110 (2006) 10021-10031
11. G.A. Camara, T. Iwasita, *J. Electroanal. Chem*., 578 (2005) 315-321
12. R.M. Souto, J.L. Rodriguez, E. Pastor, *Chem. Eur. J*., 11 (2005) 3309-3317
13. R.J. Nichols, Adsorption of Molecules at Metal Electrodes (J. Lipkowski, P.N. Ross, Eds.), VCH, Publishers, Inc., Chap.7, (1992)
14. R. Jiménez-Pérez, J.M. Sevilla, T. Pineda, M. Blázquez, J. González-Rodriguez, *Electrochim. Acta*, 193 (2016) 154-159
15. S. Sen Gupta, S. Singh, J. Datta, *Mat. Chem. and Phys*., 120 (2010) 682-690
16. S. Shanmugam, B. Viswanathan, T.K. Varadarajan, *J. Mol. Catal. A: Chemical*, 241 (2005) 52-58
17. J. Otomo, X. Li, T. Kobayashi, Ch. Wen, H. Nagamoto, H. Takahashi, *J. Electroanal. Chem*., 573 (2004) 99-109
18. A.J. Bard, R. Parson, J. Jordan, "Standard Potentials in Aqueous Solution", Marcel Dekker, Inc., 1985, Chapter 11

19. H. Hitmi, E.M. Belgsir, J.M. Léger, C. Lamy, R.O. Lezna, *Electrochim. Acta*, 39 (1994) 407-415
20. M.G. Dimos, G.J. Blanchard, *J. Phys. Chem.* C , 115 (2011) 11247-11256
21. A.P.M. Camargo, B.A.F. Previdello, H. Varela, E.R. González, *Electrochem. Commun.*, 12 (2010) 140-143
22. S.C.S. Lai, S.E.F. Kleijn, F.T.Z. Öztürk, V.C. van Rees Vellinga, J. Koning, P.Rodriguez, M.T.M. Koper, *Catal. Today*., 154 (2010) 92-104
23. M. Heinen, Z. Jusys, R.J. Behm, *J. Phys. Chem.* C., 114 (2010) 9850-9864
24. Y. Ma, Y. Du, W. Ye, B. Su, M. Yang, C. Wang, *Int. J. Electrochem. Sci.*, 7 (2012) 2654-1679
25. F.H. Nart, T. Iwasita, *Electrochim. Acta*, 37 (1992) 385-392
26. B. Xu, I.S. Park, Y. Li, D.J. Chen, Y.J. Tong, *J. Electroanal. Chem*. 662 (2011) 52-56
27. J. R. McBride, G. W. Graham, C. R. Peters, and W. H. Weber, *J. Appl. Phys*. 69 (1991) 1596-1604
28. J.M. Delgado, R. Blanco, J.M. Orts, J.M. Pérez, A. Rodes, *Electrochim. Acta*, 55 (2010) 2055-2064
29. J.P. Schulte, S. Grass, L. Treuel, J. Raman *Spectrosc.*, 44 (2013) 247-254

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