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EFFECT OF TEMPERATURE ON THE ELECTRO-OXIDATION OF ETHANOL ON PLATINUM[#]

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We present in this work an experimental investigation of the effect of temperature (from 25 to 180 °C) in the electro-oxidation of ethanol on platinum in two different phosphoric acid concentrations. We observed that the onset potential for ethanol electro-oxidation shifts to lower values and the reaction rates increase as temperature is increased for both electrolytes. The results were rationalized in terms of the effect of temperature on the adsorption of reaction intermediates, poisons, and anions. The formation of oxygenated species at high potentials, mainly in the more diluted electrolyte, also contributes to increase the electro-oxidation reaction rate.

Keywords: ethanol; fuel cells; high temperature.

INTRODUCTION

One of the main challenges of this century is certainly concerned with the replacement of our current energy sources by renewable ones. In this sense, Brazil has an advantage in comparison to other countries due to the large potential of natural energy sources that can generate a range of clean energy models, including eolic, solar and biomass. The ethanol production is well consolidated in Brazil, a country that is well prepared for the fabrication and distribution of this fuel since 1975, when the "Programa Nacional do Álcool" (PróAlcool) was launched. Apart from the use as a conventional fuel in combustion engines, an attractive alternative to produce clean energy is the use of ethanol as a fuel in direct alcohol fuel cells. A proton exchange membrane fuel cell (PEMFC) operating with ethanol converts chemical energy into electric energy with high efficiency, since it is not limited by the Carnot cycle. Ethanol has several advantages when compared with methanol, namely the low toxicity and volatility, higher theoretical energy density (8.0 kWh kg^{-1}) and, mainly, the fact that it can be produced from renewable biomass. The complete ethanol oxidation to CO_2 involves 12 electrons per molecule but at low temperature the kinetics of ethanol electro-oxidation is slow and produces different intermediates such as acetaldehyde, acetic acid, and adsorbed carbon monoxide, reducing considerably the fuel cell efficiency in practical applications. Adsorbed carbon monoxide is a very strong contaminator, which blocks platinum sites reducing the catalyst activity. An alternative to enhance the ethanol electro-oxidation and lower the effects of poisons is to increase the operating temperature[1] (above 100 °C). At 130 °C, Pt based catalysts tolerate 1000 ppm CO_2,[2] while at 80 °C CO concentrations between 10-20 ppm are enough to cause a significant loss in the cell performance. Conventional Nafion® membranes do not allow operation at temperatures higher than 80 °C. The search for electrolytes that can be used at higher temperatures and also low relative humidity is an active area of investigation nowadays, and promising examples are the phosphoric acid doped PBI[3,4] or ABPBI[5,6] membranes. The proton conductivity of phosphoric acid in doped membranes increases with increasing temperature and acid concentration, and with relative humidity due to the interaction of water with excess acid. Therefore, an efficient use of ethanol in direct alcohol fuel cells at high temperatures requires a deep understanding of the kinetics of its electro-oxidation in phosphoric acid media.

This article is focused on the experimental investigation of the ethanol electro-oxidation reaction on polycrystalline platinum surfaces in phosphoric acid electrolyte at high temperatures. The study was carried out by means of conventional electrochemical techniques (cyclic voltammetry and chronoamperometry) and between 25 and 180 °C using two concentrations of phosphoric acid.

EXPERIMENTAL

The electrochemical cell used in the experiments was especially designed to perform high temperature experiments. The body and cell external lid were made of stainless steel and connected by screws and threads. The cell internal part, where the working solution and the electrodes are located, were made of PTFE, the same material used in the internal lid (below the stainless steel lid), preventing the contact between the solution and the steel. At the top of the external lid, a manometer was fixed to monitor the cell internal pressure. The temperature of the working aqueous solution was changed using a hot plate and monitored by a thermocouple covered by a thin PTFE layer inside the solution. The working electrode was polycrystalline platinum (Mateck), the reference electrode was a dynamic hydrogen electrode (DHE)[7] consisting of two platinum foils with 2 cm^2 welded to a platinum wire. The electrodes were placed inside an H-shaped glass tube with a glass frit at the end of the tubes to provide electrolytic contact. The tubes were filled with the same solution of the cell. Between the two platinum foils, a current of nearly 1 $mAcm^{-2}$ was passed between the electrodes with the help of a 45 V battery with a 45 kΩ resistor in series. The supporting electrolyte was H_3PO_4 (Mallinckrodt, 85 wt.%) used as received and ethanol (J. T. Baker) was added to the acid solution to obtain a 1.0 mol L^{-1} concentration. The cyclic voltammetric and chronoamperometric experiments were carried out at different temperatures at 20 atm pressure. An Autolab potentiostat was used in all experiments.

RESULTS AND DISCUSSION

The experiments were performed under a defined pressure of 20 atm to prevent ethanol evaporation at high temperatures. To evaluate the pressure effect on the Pt / H_3PO_4 voltammograms profile, experiments were performed at different pressures. Figure 1 shows the voltammograms at 1 and 20 atm pressures. As observed, the voltammetric profile was hardly affected by the change in pressure. As described by Conway and Currie,[8] this is in line with thermodynamic considerations. On the

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[#] This paper is dedicated to Prof. Hans Viertler other hand, temperature plays a major role in the electrode potential. Therefore, in order to minimize this effect, all potentials showed here were corrected using the well established procedure.[8]

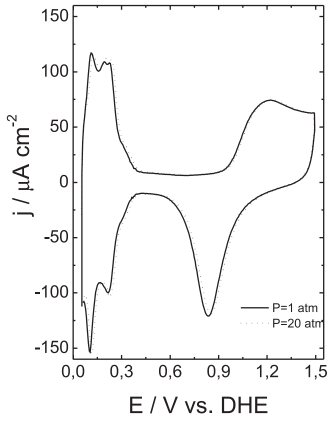

Figure 1. *Cyclic voltammograms of a polycrystalline Pt electrode in [H_3PO_4] = 14.6 mol L^{-1} under different pressures, P = 1 and 20 atm. Scan rate = 50 mV s^{-1} and T = 25 °C*

Figure 2 shows the cyclic voltammograms for our electrode in a 14.6 mol L^{-1} H_3PO_4 aqueous solution at different temperatures. As clearly seen, the temperature variation does not change the main features of the CVs. The hydrogen adsorption/desorption region and the oxide formation region also did not show significant variations. But it is important to note an increase in the oxide formation charge as the temperature increases. In addition, is observed in the cathodic scan that the oxide reduction peak becomes sharper as the temperature increases. This effect, already observed by Cohen *et al.,*[9] can be attributed to the improvement in attractive forces between the surface and the adsorbed oxide species and to the increased kinetics favored by the temperature increase. It is important to note also in Figure 2 the presence of an additional peak in the anodic sweep around 0.5 V that increases as the temperature is increased. It was observed experimentally that the peak appearance/disappearance occurs as temperature increase/decrease, respectively. The potential of this peak clearly changes to lower values for increasing temperatures. Studies on the Pt/H_3PO_4 interface showed the appearance of a peak in the anodic sweep as the temperature is increased, which was attributed to the formation of impurities from phosphoric acid.[10-12] The peak appears around 0.70 V, the same potential observed by Vogel and Barris.[10] Similar behavior was observed by Sugishima[13] for high temperatures. In order to remove the impurities, the H_3PO_4 was further purified, but the adopted treatment did change considerably this behavior. To compare the results, the currents were normalized by the platinum active area determined by the oxidation of a monolayer of adsorbed CO, considering a charge of 420 μC cm^{-2}.[14]

Figure 3 shows the voltammetric profiles for the electro-oxidation of ethanol (1.0 mol L^{-1}) in aqueous solutions with [H_3PO_4] = 14.6 and 5.0 mol L^{-1}. Considerably high activities are observed for higher water content. As already observed by Camargo *et al.*[15] for the electro-oxidation of ethanol in phosphoric acid, when the water concentration is high, the anion concentration decreases and the oxide formation is facilitated. The electro-oxidation behavior is similar in both electrolytes. In the low potential region the hydrogen adsorption/desorption is inhibited by the ethanol adsorption. At more positive potentials, two oxidation waves appear and in the cathodic sweep a reactivation peak is seen. It is interesting to note that in the more diluted electrolyte with the same ethanol concentration at the same temperature, an increase in the current is observed at the same time that the onset potential of the oxidation peak shifts to lower values, reinforcing the role of water in the reaction rate.

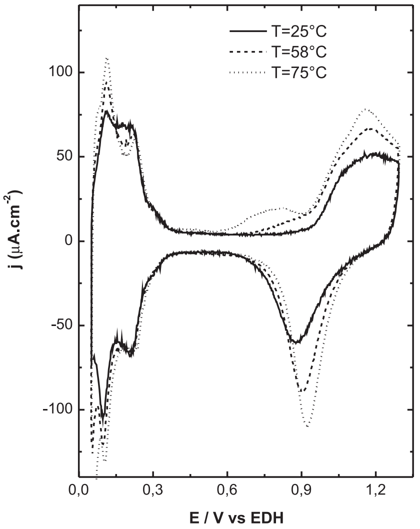

Figure 2. *Voltammetric profiles in [H_3PO_4] = 14.6 mol L^{-1} at different temperatures. Scan rate = 50 mV s^{-1}. The pressure changes as a function of temperature from 18 to 20 atm*

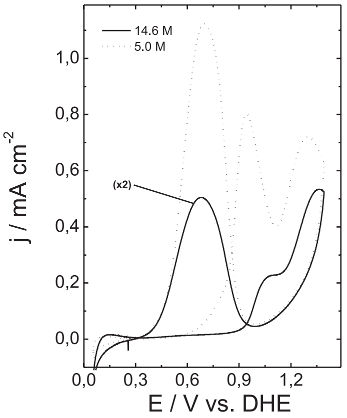

Figure 3. *Cyclic voltammograms in the presence of ethanol (1.0 molL^{-1}) in [H_3PO_4] = 14.6 mol L^{-1} and [H_3PO_4] = 5.0 mol L^{-1}. Scan rate = 50 mV s^{-1}, temperature = 25 °C and pressure = 1 atm*

Figure 4 shows the voltammetric features of the electro-oxidation of ethanol in two different electrolyte concentrations, 14.6 and 5.0 mol L^{-1} at different temperature. The first observation in this figure is the fact that the temperature increase causes an increase in current and the onset potential of ethanol oxidation decreases (Figure 4a-d), for both electrolyte concentrations. The CVs also show a typical hysteresis between the anodic and cathodic peaks, which diminishes as the temperature increases due to differences in the oxide formation/dissolution as the temperature changes. This hysteresis is very common in these systems and have been discussed by Varela and coworkers.[16] The cathodic peak showed higher current when compared with the anodic peaks for all temperatures. This can be attributed to the coupling between oxide reduction and the electro-oxidation of ethanol.[16] For the pure electrolyte, as the temperature increases, the onset potential for oxide dissolution changes to more positive values. When the alcohol is introduced in the electrolyte, the free Pt sites are occupied by ethanol, which adsorbs and oxidizes at more positive potentials. On the other hand, in the positive going sweep, the formation of intermediates and poisons, such as CO, adsorb on the electrode surface at low potentials, preventing ethanol adsorption and its subsequent oxidation. In addition, anions also adsorb on the electrode surface, preventing alcohol adsorption which results in a diminution of the peak current in the anodic sweep. On the other hand, in the negative going sweep this effect is less pronounced.

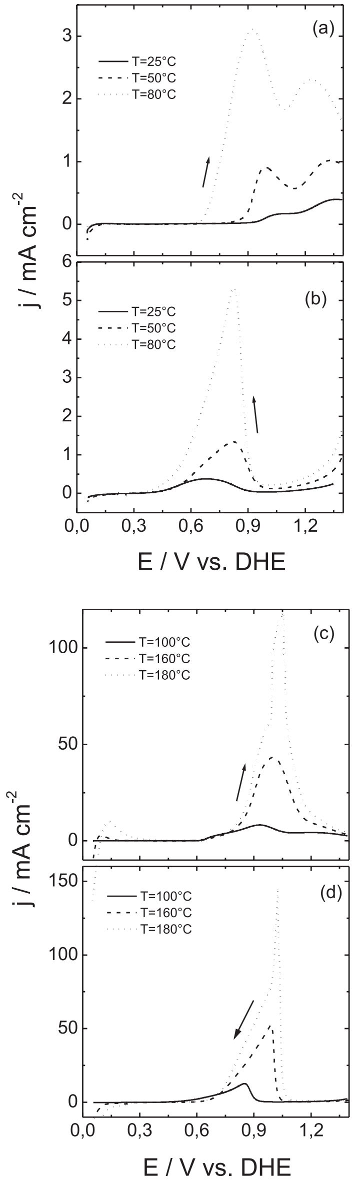

Figure 4. *Cyclic voltammograms of polycrystalline Pt in [H_3PO_4] = 14.6 and 1.0 mol L^{-1} ethanol for different temperatures. Scan rate = 10 mV s^{-1}. The pressure changes as a function of temperature from 18 to 20 atm*

For the more concentrated electrolyte (14.6 mol L^{-1}), the onset potential for ethanol oxidation changes to more negative values as the temperature increases (Figure 4a and c). A drastic potential change of about 330 mV is observed for a temperature increase from T = 25 to 80 °C, Figure 4a. The reason for this difference between 25 and 80 °C may be the decrease in the coverage of intermediates and poisons. Kardash *et al.*[17] investigated the effects of CO adsorption produced from methanol on polycrystalline Pt in 0.1 mol L^{-1} $HClO_4$, and concluded that in the temperature interval from 25 to 50 °C the CO surface coverage is not affected. However, at T = 75 °C, FTIR experiments showed that the CO adsorption is hindered and methanol adsorption/oxidation at more negative potentials. In the present case, we believe that the differences in the onset potential is due to the lower CO coverage on the electrode surface, which in turn allows higher rates of ethanol adsorption / oxidation at less positive potentials. Similar behavior is observed for ethanol electro-oxidation in less concentrated phosphoric, c.f. Figure 5, although the change in the onset potential from T=25 to 120 °C is lower, ~100 mV.

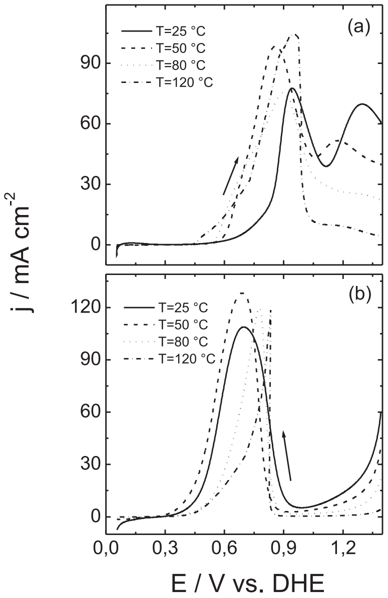

Figure 5. *Cyclic voltammograms of polycrystalline Pt in [H_3PO_4] = 5.0 and 1.0 mol L^{-1} ethanol at different temperatures. Scan rate = 10 mV s^{-1}. The pressure changes as a function of temperature from 18 to 20 atm*

On the other hand, the electro-oxidation current for ethanol in H_3PO_4 5.0 mol L^{-1} is higher than for the more concentrated electrolyte (Figure 4). The difference in the alcohol electro-oxidation in the two different electrolyte concentrations can be explained as follows: the adsorption of anions and poisons can block the surface sites at which ethanol would adsorb. For ethanol to adsorb on these sites, it is necessary that the desorption of anions and intermediates and the adsorption alcohol occur at the same time. Analyzing the conditions of our experiments, one has to keep in mind that at [H_3PO_4] = 14.6 mol L^{-1} the presence of species such as molecular phosphoric acid and $H_5P_2O_8^-$ prevail, in contrast to $H_2PO_4^-$.[18,19] Therefore, H_3PO_4, $H_5P_2O_8^-$ and CO might compete for surface sites at low potentials and the number of sites occupied by the first two molecules may be high. Thus, only some sites are free for the adsorption of ethanol molecules. Molecular adsorbed species are probably laid down on the Pt sites with water molecules in between. FTIR experiments[19] showed that for an acid concentration of 6.6 x 10^{-3} mol L^{-1} the area occupied by each H_3PO_4 molecule is about 35Å^2 and the surface coverage nearly 0.42 at 800 mV vs. NHE. Thus, at low potentials, a competition between anions, molecular acid and EtOH intermediates for free Pt sites might be very high. A temperature increase displaces the anions and molecular acid from the Pt surface and makes the CO adlayer less resistant to oxidation, probably due to thermal effects, allowing at EtOH adsorption/oxidation at less positive potentials. This effect is clear in Figure 4a. For T ≥ 100 °C (Figure 4c) is not observed a significant onset potential variation for ethanol oxidation, staying around 600 mV from 100 to 180 °C. This can be due to the formation and adsorption of H_3PO_4 impurities at high temperatures that adsorb at low potentials preventing EtOH adsorption. As described above, the Pt/H_3PO_4 interface showed an oxidation peak in the CV as the temperature increases (Figure 2). Vogel and Bars[10] studied the Pt/hot phosphoric acid interface and found similar behavior. They attributed this peak to phosphine formation by direct reduction of H_3PO_4, or by a partial disproportionation of phosphorous with simultaneous formation of oxyacids, adsorbed at low potentials. It seems plausible that these impurities adsorbed at low potentials are very strongly adsorbed. As the potential reaches 600 mV, the impurities start to oxidize and leave the Pt surface, allowing the adsorption and further oxidation of alcohol molecules at c.a. 620 mV, as is observed in Figure 4c. On the other hand, Figure 4a, c, shows that the electro-oxidation current is higher and the CV profile changes with increasing temperature. The first and second oxidation peaks increase significantly from 25 to 80 °C and at 100 °C, the first peak overcomes the current value of the second oxidation peak, which is suppressed at high temperatures. It is also interesting to note a shift to more positive potentials of the first and the reactivation peaks as the temperature was increased. The shift in the potential of the first peak to more positive values is stronger for higher temperatures (Figure 4c) than for lower temperatures (Figure 4a). This is probably due to the adsorption of impurities from the acid that forces the displacement of ethanol adsorption/oxidation to more positive potentials, as discussed above. In addition, the consumption of oxygenate species increases as the temperature of the solution is increased, the surface oxide is consumed quickly due to the ethanol oxidation, contributing to the increase of the alcohol oxidation rate. In the case of the more diluted electrolyte, $[H_3PO_4] = 5.0$ mol L^{-1} (Figure 5), the CV indicates a similar behavior as for the more concentrated electrolyte, i.e., the onset potential shifts to more negative values when the temperature is increased, but it should be noted that the shorter potential interval between 25 and 120 °C, ~150 mV, is about 180 mV smaller than that for the more concentrated acid. This is caused to the difference between the onset potentials for ethanol oxidation at 25 °C for both electrolytes, 845 mV for $[H_3PO_4] = 14.6$ mol L^{-1} and 600 mV for $[H_3PO_4] = 5.0$ mol L^{-1}. For the more diluted acid, the oxidation starts at more negative potentials than for the concentrated one. In this case, the differences may be attributed to the presence of a larger water concentration and, consequently, to less anion adsorption on the electrode surface. Camargo *et al.*[15] showed that for $[H_2O] = 40$ mol L^{-1}, approximately the water concentration for $[H_3PO_4] = 5.0$ mol L^{-1}, the impact of water on the ethanol oxidation was found to be more pronounced from 600 to 900 mV. Estimated reaction orders[15] showed that the highest value occurs at 600 mV, which means that the effect of water bulk concentration is stronger at this potential. In addition, the temperature increase plays an important role in the anion and poisons adsorption. It has been observed that for Pt single crystals, specifically Pt (111) and Pt (110), the anion adsorption remains constant as the temperature increases,[20,21] but, in the case of Pt (100), the anion adsorption is strongly affected by temperature. In the case of the poisons adsorption (CO), the temperature increase diminishes the surface coverage, as already described.

Following the main effects present in Figure 5, it was depicted that water plays an important role in the ethanol oxidation rate at low potentials and the temperature helps the surface become free from undesirable products. Thus, the small variation in the onset potential, when compared to the more concentrated electrolyte, may be attributed to the fact that the Pt sites, in the more diluted solution, are less susceptible to be blocked by adsorbed poisons or intermediated (CO, reactions intermediates, anion adsorption, and, maybe, H_3PO_4 impurities). Also, the higher water content helps the oxidation at lower potentials, 600 mV, than for the more concentrated electrolyte, 840 mV at 25 °C, resulting in a smaller variation when temperature is increased. At this point it is important to note that the formation of impurities originated from H_3PO_4 depends on its concentration. The electro-reduction of H_3PO_4 seems to be less aggressive for the temperature interval studied in the diluted electrolyte. This can be due to the lower molecular phosphoric acid concentration in the diluted electrolyte.

Figures 6 and 7 show the current transients under quasi-stationary conditions for $[H_3PO_4] = 14.6$ mol L^{-1} and $[H_3PO_4] = 5.0$ mol L^{-1} at 650 mV and with ethanol at 1.0 mol L^{-1}, at different temperatures. Apparent activation energies (E_{app}) were also obtained from the Arrhenius plots depicted in the lower plate for both figures. The calculated E_{app} value for $[H_3PO_4] = 14.6$ mol L^{-1} is 71.3 kJ mol^{-1} for the temperature interval from 160 to 180 °C. In the range between 50 and 160 °C,

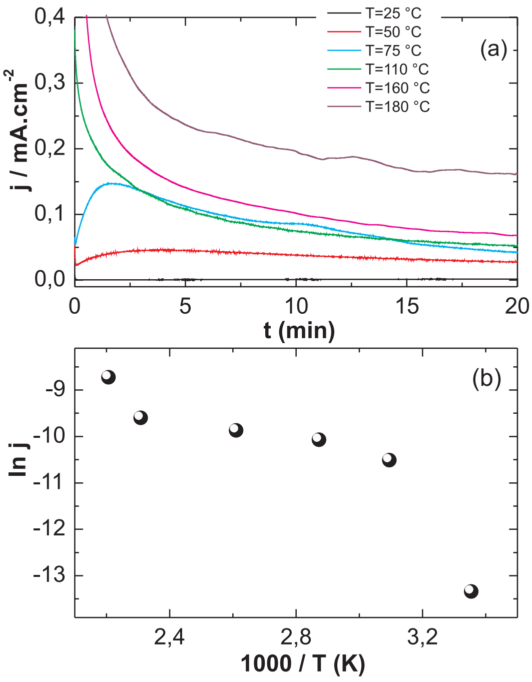

Figure 6. *Chronoamperometric profiles for E = 650 mV at 1200 s in different temperatures. $[H_3PO_4] = 14.6$ mol L^{-1} and [EtOH] = 1.0 mol L^{-1}*

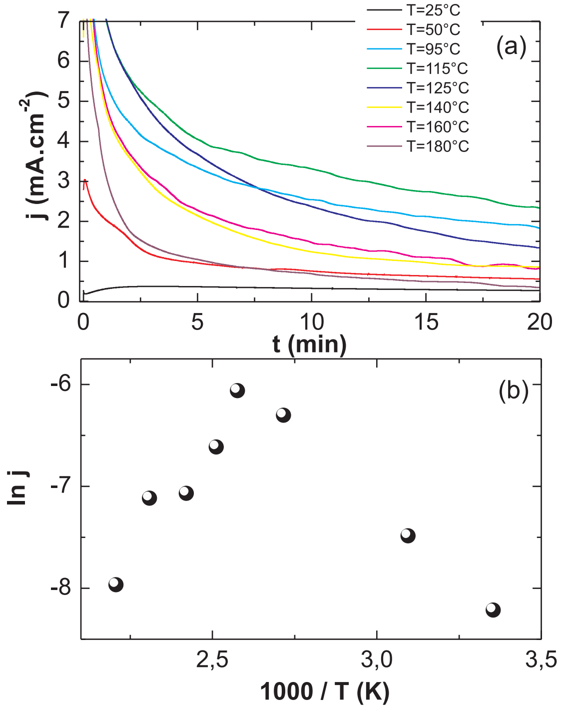

Figure 7. *Chronoamperometric profiles for E = 650 mV at 1200 s at different temperatures. $[H_3PO_4] = 5.0$ mol L^{-1} and [EtOH] = 1.0 mol L^{-1}*

the E_{app} value was 9.2 kJ mol^{-1}, and from 25 to 50 °C, E_{app} = 90.6 kJ mol^{-1}. The diluted acid concentration showed an E_{app} value of 23.7 kJ mol^{-1} from 25 to 125 °C. Estimating the apparent activation energies in such systems is a far from simple task.[9,22-26] Nevertheless, the results obtained here are well correlated with the role played by the increase of temperature and water content in facilitating the electrochemical oxidation of ethanol on platinum in phosphoric acid media. Moreover, the obtained values are in the range of that found for other comparable reaction and the changes with the electrolyte and the temperature range might well reflect the changes in the reaction mechanism. In addition, the considerable scattering observed at high temperatures in Figure 7b can be due to non-stationarity of our chronoamperometric curves. Indeed, in spite of the reliability of the apparent activation energies observed, one should be aware that longer current-time profiles could provide a more robust temperature dependence. The limiting factors for the, relatively short, time of our experiments were the stability of our set-up and also the formation of spurious products observed at high temperatures

CONCLUSIONS

The temperature influence on the electro-oxidation of ethanol on platinum and in phosphoric acid media was investigated in two different phosphoric acid concentrations and between 25 and 180 ºC. For higher acid concentration, the effect on the onset potential of the electro-oxidation reaction was more pronounced. The reason for this was attributed to the strong influence of intermediates, anions and the eventual adsorption of impurities of the acid. As the temperature increases, the desorption of this adsorbed products is favored, so that the electrode surface is freed from these contaminants. Decreasing the electrolyte concentration, it is also observed a shift in the onset potential with increasing temperature, but less intense that for more concentrated electrolyte. This difference in the potential interval between both electrolytes can be assigned to the lower presence of undesirable adsorbed products on the electrode surface. Also, the water bulk concentration is higher than for more concentrated water, and, consequently, the formation of oxygenate species is favored, which helps the oxidation process.

ACKNOWLEDGEMENTS

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