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## **The role of water in hydrogen electrocatalysis**

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### **3. Influence of water on the hydrogen evolution reaction on a gold electrode in acetonitrile solution**

**ABSTRACT**

Here we discuss the importance of water in the proton solvation for the hydrogen evolution on polycrystalline gold microelectrodes. We perform cyclic voltammetry in acetonitrile electrolyte, in presence and absence of added amounts of water, with the interfacial movement of water and ions monitored by means of in situ Fourier Transform InfraRed (FTIR) spectroscopy. Our results show that the small trace amounts of water accumulate at the gold-acetonitrile interface, and that in the absence of protons this water leaves the interface with more negative potential. On the other hand, in the presence of protons in solution, protons exhibit a preferential solvation by water and water accumulates at the electrode surface under conditions of hydrogen evolution. Tafel plot analysis shows that the hydrogen evolution on gold in acetonitrile presents the same rate-determining step as for polycrystalline platinum, implying that the first electron transfer to yield adsorbed hydrogen is the rate-determining step of the reaction.

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### 3.1. Introduction

Hydrogen evolution in non-aqueous solvents has been subject of study for many years, with a general focus on the dependence of the catalytic activity on the nature of the catalyst and the proton donor<sup>1</sup>. More recently, the influence of small or even trace amounts of water in acetonitrile solutions has been studied for a variety of electrochemical reduction or protonation reactions, such as hydrogen evolution, oxygen reduction, and carbon dioxide reduction<sup>2</sup>. In our previous work on hydrogen oxidation and proton reduction on the benchmark catalyst, i.e. platinum<sup>2c</sup>, we showed by in situ Fourier-Transform Infrared (FTIR) spectroscopic analysis that the hydrogen oxidation and evolution (HOR/HER) in acetonitrile is assisted by a preferential solvation of protons in water. The HOR/HER appears to be so sensitive to the presence of water that even trace amounts influence the process. It would be important to characterize the role of water for non-ideal catalytic behavior, as it is the case with polycrystalline gold electrodes, on which the HOR does not proceed. An older study on the HER on platinum and gold can be found in literature<sup>3</sup>, focusing on the solvation of two different acids (HCl and HPic) in acetonitrile. Their main findings pointed out the homoconjugation effect between the acid and the acetonitrile, due to incomplete dissociation of the acids, as well as the electrosorption of the solvent on the electrode surface, leading to irreversible behavior. However, the influence of water was not taken into account.

Here we present a spectroelectrochemical study, combining cyclic voltammetry and FTIR experiments, of the hydrogen evolution reaction in acetonitrile with 0.1 M tetrabutylammonium electrolyte, in presence and absence of 10 mM of perchloric acid as proton donor, under argon and hydrogen atmosphere. The experiments were also performed in presence of a small amount of added water (50 mM), in order to evaluate the importance of the water-proton and water-electrode interactions. The cyclic voltammetry and FTIR spectroscopy show that the hydrogen evolution on gold is mediated by the presence of water due to a preferential solvation of protons, in a similar fashion to what has been observed on

platinum electrodes. This behaviour appears to play an important role already at very low water concentrations.

### 3.2. Experimental Section

Prior to experiments, the glassware was rinsed with water (Milipore® MilliQ; resistivity >18.2 MΩ.cm), rinsed thoroughly with acetone (Sigma-Aldrich) and placed in the oven overnight at 120 °C. Acetonitrile (Anhydrous 99.8%, from Sigma-Aldrich) with tetrabutylammonium perchlorate (99.0% from Sigma-Aldrich) were used as received for preparing the electrolyte solutions. Ferrocenium hexafluorophosphate (97%, from Sigma-Aldrich) and ferrocene (99%, from Alfa Aesar) were used for preparing an equimolar solution in order to calibrate the equilibrium potential of the home-made Ag/AgClO<sub>4</sub> (97% from Sigma-Aldrich) reference electrode. The solutions were purged with argon (purity grade 6.0). For the experiments under hydrogen atmosphere we used a constant hydrogen flux (purity grade 5.6). All solutions used in this work are considered “wet”, since we did not treat the reactants to reduce their characteristic water content.

Cyclic voltammetry was measured in a one-compartment, three-electrode cell connected to an Ivium potentiostat/galvanostat (IviumStat). The working electrode (WE) consisted of a gold wire, with a diameter of 120 μm and a real surface area of  $(4.2 \pm 0.2) \times 10^{-2} \text{ cm}^2$  (obtained by measuring the area of the reduction peak from the gold oxides in aqueous electrolyte), assembled into a glass stem. The gold microelectrode was flame-annealed and rinsed with water and acetone before each measurement. We used a gold spiral as the counter electrode (CE) and a Ag/AgClO<sub>4</sub> electrode in acetonitrile as the reference electrode (RE). A 10 μF capacitor was connected between the RE and a platinum wire immersed in the solution, as a noise filter. The equilibrium potential of the redox couple Fc<sup>0</sup>/Fc<sup>+</sup> was calculated as the half wave potential using cyclic voltammetry with a measured value of 0.038 V vs. Ag/AgClO<sub>4</sub>.

The Fourier Transform Infra-Red Spectroscopy measurements were performed in a three electrode cell coupled to a  $\text{CaF}_2$  prism slanted at 60 degrees, and connected to a Bruker Vertex80V IR spectrophotometer. A gold disk was mechanically polished with alumina of three different mesh (Alfa-Aesar), rinsed in an ultrasonic bath, flame-annealed and settled in the cell in a thin layer configuration, by pressing it against the prism. The CE was a gold wire and the RE was the  $\text{Ag}/\text{AgClO}_4$ . Hundred interferograms were averaged for each spectrum, with a resolution of  $8\text{ cm}^{-1}$ . The transmission spectra used for the elucidation of bands in “dry” electrolyte were reported previously<sup>2c</sup>, whereas the transmission spectra for the solutions containing electrolyte and added water were recorded using a SeZn window with an incident angle of  $60^\circ$ . One hundred scans were collected with a resolution of  $8\text{ cm}^{-1}$  using p-polarized light. The reference spectrum was acquired from pure acetonitrile. All spectra in this work are reported as absorbance spectra, according to the approximation  $A \approx \Delta R/R_0$  where  $R$  and  $R_0$  are the reflectance corresponding to the single spectra obtained for the sample potential and the reference potential at their respective potentials. The interpretation of the bands is as follows: bands pointing upwards correspond to the formation of species at the surface at the sample potential with respect to the reference potential, and are called positive bands, while bands pointing downwards indicate the depletion of species from the electrode surface and are called negative bands.

### 3.3. Results

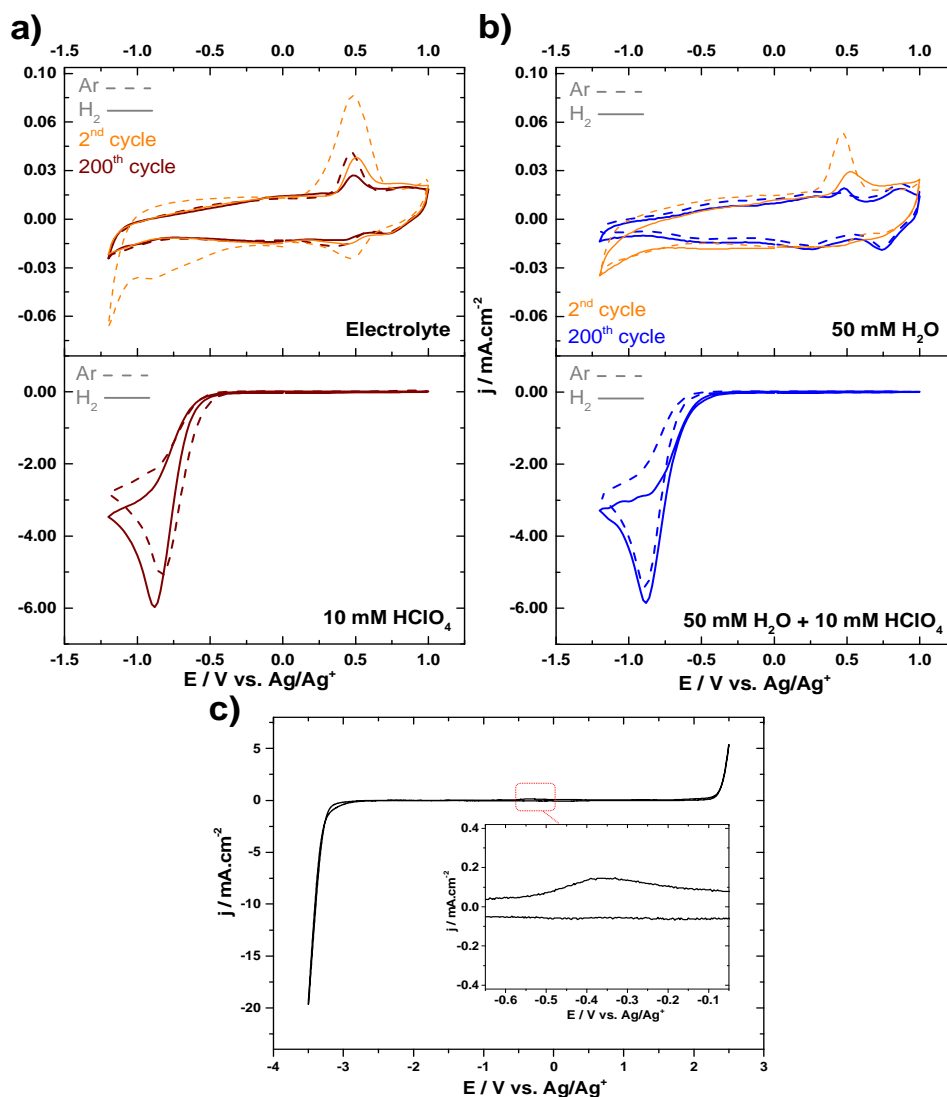
#### 3.3.1. Characterization of the hydrogen evolution on polycrystalline gold in acetonitrile by cyclic voltammetry

Figures 1a and 1b depict the voltammograms collected for a polycrystalline gold microelectrode in acetonitrile solutions, containing 0.1 M of tetrabutylammonium perchlorate (TBAP) used as received and in presence of 50

mM of water, respectively. We present the second and last scan out of 200 voltammograms, recorded at a scan rate of  $500 \text{ mV.s}^{-1}$ . The dashed lines correspond to electrolytes under Ar-saturated conditions, whereas the solid lines represent the voltammograms for the  $\text{H}_2$ -saturated solutions. For the electrolyte with argon (Fig. 1a) we observe a reduction current at ca.  $-0.8 \text{ V}_{\text{Ag}/\text{Ag}^+}$  and an adsorption/desorption process at ca.  $0.5 \text{ V}_{\text{Ag}/\text{Ag}^+}$ . These peaks decrease and stabilize after the sixth scan (not shown), reaching the size and shape presented in the 200<sup>th</sup> scan. In the same subfigure, it is shown that the main difference in the second and last scan for the electrolyte in presence of  $\text{H}_2$  is a smaller current corresponding to the peak at ca.  $0.5 \text{ V}_{\text{Ag}/\text{Ag}^+}$ , suggesting that this process is hindered under  $\text{H}_2$  saturation. This smaller current is probably due to a higher water availability at the electrode surface, as suggested by the blanks obtained in presence of added water, shown in Figure 1b, top panel, indicating that bubbling  $\text{H}_2$  brings (a small amount of) water into the cell. The second scans recorded in presence of argon or hydrogen also show the reduction peak at  $-0.8 \text{ V}_{\text{Ag}/\text{Ag}^+}$  as well as the oxidation-reduction peaks at ca.  $0.5 \text{ V}_{\text{Ag}/\text{Ag}^+}$ , but with a smaller current compared to the voltammograms observed in the electrolyte without added water. In the 200<sup>th</sup> scan for the water-containing acetonitrile, in presence of argon or hydrogen, we observe a redox peak at  $0.84 \text{ V}_{\text{Ag}/\text{Ag}^+}$ , presumably corresponding to the formation of gold (hydr)oxides<sup>4</sup>. These observations suggest that the gold-electrolyte interface is affected by the presence of water, and leads to oxide formation in the presence of considerable amounts of water. Our results also show that the hydrogen oxidation does not proceed on gold under the conditions studied.

In Figure 1a, bottom panel, we present the hydrogen evolution reaction (HER) current observed with the addition of 10 mM of  $\text{HClO}_4$ , in presence and absence of hydrogen. The two voltammograms are similar in current and shape, with an onset for proton reduction at ca.  $-0.50 \text{ V}_{\text{Ag}/\text{Ag}^+}$ . No significant differences are observed between the HER in presence and absence of hydrogen. We also present the same voltammograms after adding 50 mM of water in Figure 1b, bottom panel.





**Figure 1.** Cyclic voltammograms for a polycrystalline gold microelectrode in acetonitrile, containing 0.1 M TBAClO<sub>4</sub> as supporting electrolyte, with and without 10 mM of HClO<sub>4</sub>. a) Using acetonitrile and supporting electrolyte as received, scan rate: 500 mV/s; b) After adding 50 mM of water, scan rate: 500 mV/s; c) In a wider working window in presence of 50 mM of water and argon saturation, scan rate: 50 mV.s<sup>-1</sup>; insert: zoom in of the potential window -0.7 – -0.2 V<sub>Ag/Ag<sup>+</sup></sub>.

Still, no significant changes in current or features were observed when compared to the voltammograms obtained from the electrolytes without added water.

Finally, Figure 1c shows the last scan out of 50 voltammograms recorded in a much wider potential window at  $50 \text{ mV.s}^{-1}$ , for the electrolyte in presence of added water and argon, in order to ensure that no solvent decomposition is observed in the working window chosen for this work. No water reduction is observed; only solvent decomposition at ca.  $-2.9 \text{ V}_{\text{Ag}/\text{Ag}^+}$ . A small oxidation peak is observed at ca.  $-0.35 \text{ V}_{\text{Ag}/\text{Ag}^+}$ , probably related to the electrolyte adsorption at the electrode surface, as consequence of the lower scan rate used. This large potential window of (apparent) electrolyte stability is in agreement with what was previously reported by Gerischer and Wagner<sup>5</sup>.

### **3.3.2. Evaluation of the water effect on the hydrogen evolution on polycrystalline gold using Fourier-Transform InfraRed spectroscopy**

In order to study the interfacial processes occurring at the electrode interface, Fourier-Transform InfraRed (FTIR) spectroscopy was performed at a series of fixed potentials, for all the systems characterized in the previous section by cyclic voltammetry. The transmission spectra for these acetonitrile solutions have been discussed in our previous work<sup>2c</sup>; therefore, the interpretation of the main features shown in this work are based on the aforementioned study, in agreement with earlier reports from the literature<sup>6</sup>.

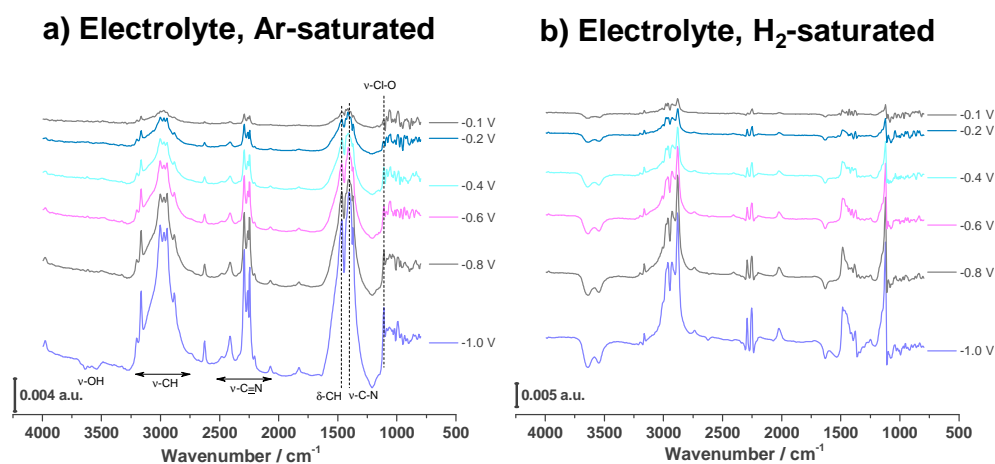
We will discuss the features which are sensitive to the presence or absence of added water and hydrogen; namely, the acetonitrile bands, the water bands and the bands attributed to the supporting electrolyte, TBAP, i.e.  $\text{TBA}^+$  cations and  $\text{ClO}_4^-$  anions. The C-N bending and stretching modes from acetonitrile are observed in the range  $2260\text{-}2340 \text{ cm}^{-1}$ , and the C-H modes in the range  $2900\text{-}3000$

$\text{cm}^{-1}$ . We note that the C-H modes are more intense in the presence of the electrolyte TBAP, due to the butyl chains present in the cation<sup>2c</sup>. The presence of water is characterized by bands in the O-H stretching region between 3100 and 3750  $\text{cm}^{-1}$ , and by the bending modes in the 1500-1650  $\text{cm}^{-1}$  range. Finally, the perchlorate ion presents a sharp band around 1130  $\text{cm}^{-1}$ , from the Cl-O stretching mode. This vibration of the perchlorate anion has been reported previously<sup>6a</sup> by Barthel *et al.* to be susceptible to the formation of ion pairs in acetonitrile solutions, as manifested by the presence of low- and/or high-frequency shoulders.

The spectra were acquired from positive toward negative potentials (top to bottom in each figure), and the reference spectrum was recorded at 0  $V_{\text{Ag}/\text{Ag}^+}$ . The positive bands are related to the formation or accumulation of species at or near the electrode surface, whereas the negative bands indicate the depletion of species out of the double layer region, respectively.

Figure 2 shows the spectra collected for a gold electrode in acetonitrile electrolyte without added water, under argon atmosphere and hydrogen atmosphere. The spectra corresponding to the Ar-saturated solution is shown in figure 2a, along with an indication for the characteristic bands in the FTIR measurements. Figure 2a shows clearly the positive bands corresponding to C-N modes from acetonitrile in the region 2260-2340  $\text{cm}^{-1}$ , as well as the C-H modes from  $\text{TBA}^+$  at 2900-3000  $\text{cm}^{-1}$ . The perchlorate band at 1133  $\text{cm}^{-1}$  is also positive in the whole potential range studied. No signs of residual water are registered until -1  $V_{\text{Ag}/\text{Ag}^+}$ , in contrast to the hydrogen-saturated solution, presented in Figure 2b. The spectra for these solutions show a potential-dependent band pointing downwards in the range 3400-3750  $\text{cm}^{-1}$ , with the corresponding bending tail at 1633  $\text{cm}^{-1}$ , indicating the depletion of water from the electrode surface with increasingly negative potential. All the other bands have a diminished intensity in presence of molecular hydrogen (Figure 2b). These observations appear to be related to the observations made in Figures 1a and 1b, where the presence of  $\text{H}_2$  brings water into the electrolyte. Figure 2 suggest that trace amounts of water accumulate at the

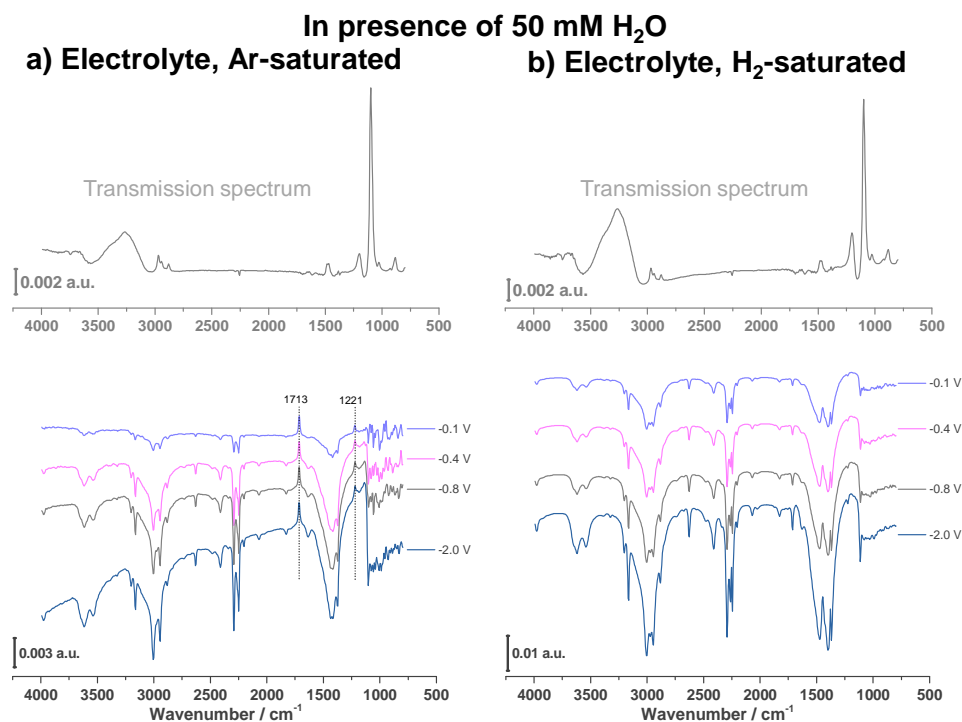
gold-electrolyte interface, with water depleting from the interface with more negative potential.



**Figure 2.** Potential-dependent absorbance spectra for a polycrystalline gold electrode in acetonitrile, containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. Reference spectrum recorded at 0 V<sub>Ag/Ag+</sub>.

Addition of 50 mM of water to the electrolyte in presence or absence of hydrogen leads to spectra shown in Figures 3a and 3b. In the transmission spectra we observe a small negative band around 2250 cm<sup>-1</sup> from the CN stretching modes, indicating the interaction of the electrolyte with the acetonitrile. We also observe a positive band in the range 3000 – 3500 cm<sup>-1</sup> from the water stretching mode and a displaced tail from the OH deformation at 1500 cm<sup>-1</sup>. The perchlorate band can be found around 1100 cm<sup>-1</sup>, next to the C-H modes from the TBAP (1250 cm<sup>-1</sup>). No significant differences were observed between the transmission spectra from the solution saturated with argon and the one saturated with hydrogen. From the Ar-saturated solution we recorded the potential-dependent spectra shown in Figure 3a, in which most water and electrolyte bands are negative, suggesting migration away from the electrode surface. However, the spectra show two small positive bands at 1221 and 1713 cm<sup>-1</sup>, presumably related to a C-N mode and a C-

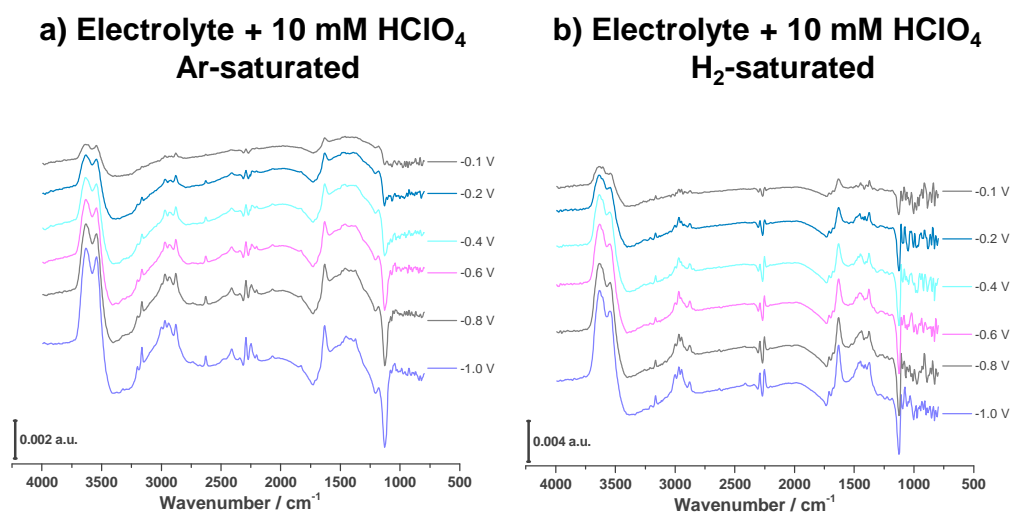
O stretching mode, respectively <sup>7</sup>, probably from the TBA<sup>+</sup> cation, since the acetonitrile does not decompose at these applied potentials. The spectra for the H<sub>2</sub>-saturated solution can be found in Figure 3b. All the bands from water and electrolyte are pointing downwards, suggesting the migration of species away from the electrode surface. The results presented in Figures 2 and 3 suggest that the electrolyte TBAP interacts more strongly with the electrode when water is not present. The potential-dependent behaviour of the electrolyte ions in Figures 2 and 3 is somewhat difficult to interpret, but one must bear in my mind these measurements were performed in a thin-layer configuration, which was sometimes difficult to stabilize. Also, since no current is flowing, one would not expect any significant movement of ions, other than those adsorbing or desorbing, or moving in and out of the double layer. When a small amount of water is present or added to the electrolyte, and no apparent hydrogen evolution is proceeding, water leaves the electrode surface when a cathodic potential is applied, and this behaviour is independent of the saturation gas.



**Figure 3.** Potential-dependent absorbance spectra for a polycrystalline gold electrode in acetonitrile, containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte and in presence of 50 mM of added water. Reference spectrum recorded at 0 V<sub>Ag/Ag<sup>+</sup></sub>.

The blank spectra presented in Figures 2 and 3 showed the conditions of the interface in the absence of proton reduction. Now we proceed to evaluate the hydrogen evolution in the acetonitrile electrolyte in presence of a proton donor in the absence and presence of added water, both under argon or hydrogen saturated regime. The spectra obtained for the HER in the acetonitrile electrolytes in the presence of argon or hydrogen are shown in Figures 4a and 4b. In Figure 4a the accumulation of water at the electrode surface is illustrated by the potential dependence of the double band near 3500 cm<sup>-1</sup> and the water bending mode at 1633 cm<sup>-1</sup>. We also observe the migration of the TBA<sup>+</sup> and the acetonitrile towards

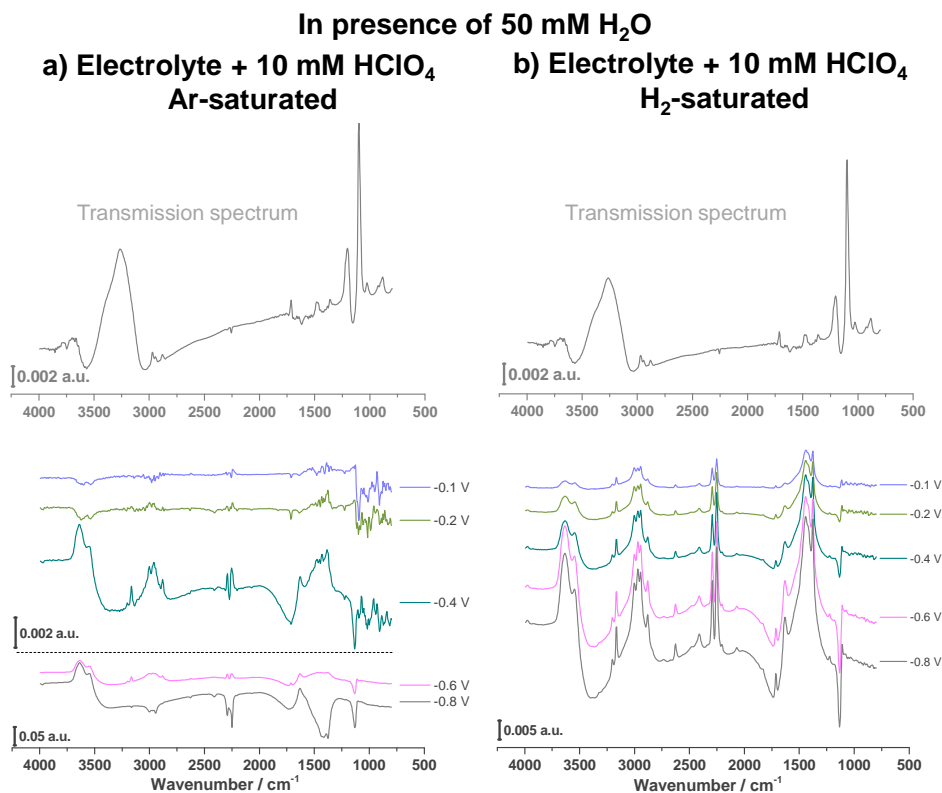
the electrode surface, described by the positive bands from the cation C-H at 2750 to 3250  $\text{cm}^{-1}$  and the C-N stretching modes at 2450  $\text{cm}^{-1}$ , respectively. On the other hand, the sharp perchlorate stretching mode at 1130  $\text{cm}^{-1}$  depletes with more negative potentials. Saturation with molecular hydrogen leads to similar observations as in Figure 4a, without significant changes from what is observed in the Ar-saturated solution in presence of proton donor. These observations suggest that water accumulates at the electrode surface in presence of protons, and that perchlorate anions deplete from the surface, in agreement with Faradaic current flow.



**Figure 4.** Potential-dependent absorbance spectra for the hydrogen evolution on a polycrystalline gold electrode in acetonitrile, containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte + 10 mM of  $\text{HClO}_4$ . Reference spectrum recorded at 0  $V_{\text{Ag}/\text{Ag}^+}$ .

In presence of added water and protons, the spectra from the Ar-saturated solution initially show a depletion of water from the interface until an inversion in the band orientation is observed at -0.4  $V_{\text{Ag}/\text{Ag}^+}$  at the onset of HER. At this potential, the water bands turn positive, indicating accumulation of water at the

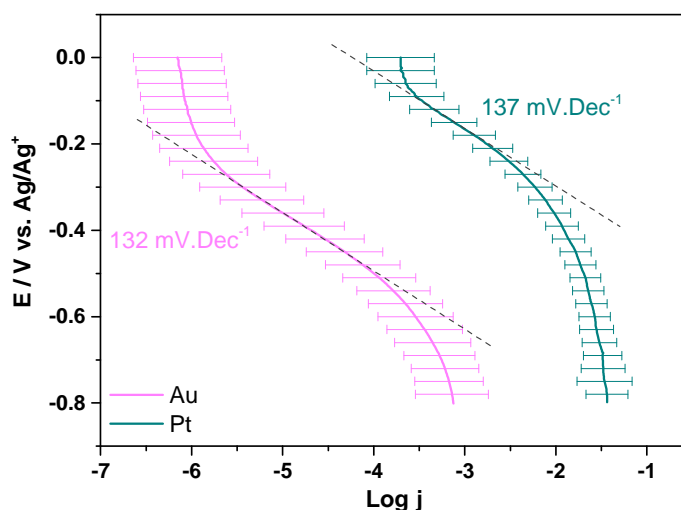
electrode surface. Acetonitrile and  $\text{TBA}^+$  are initially positive and then invert the configuration at  $-0.8 \text{ V}_{\text{Ag}/\text{Ag}^+}$ , indicating the migration of electrolyte-related species from the surface as we produce hydrogen, while water is present in the double layer. Under hydrogen-saturated conditions, Figure 5b shows all electrolyte-related bands and water migrating towards the electrode, except for the perchlorate, which leaves the surface. We also note that the C-N modes from  $\text{TBA}^+$  appear enhanced in this system.



**Figure 5.** Potential-dependent absorbance spectra for the hydrogen evolution on a polycrystalline gold electrode in acetonitrile, containing 50 mM of water and 0.1 M tetrabutylammonium perchlorate as supporting electrolyte + 10 mM of  $\text{HClO}_4$  as proton donor. Reference spectrum recorded at  $0 \text{ V}_{\text{Ag}/\text{Ag}^+}$ .



Finally, we compare the HER on gold and platinum electrodes in acetonitrile solutions containing supporting electrolyte and 10 mM of  $\text{HClO}_4$ . Figure 6 shows the Tafel plots obtained at a scan rate of  $10 \text{ mV.s}^{-1}$ . We subtracted the non-Faradaic contributions from the voltammograms in order to obtain polarization curves shown in this work. The measurements in Figure 6 show a Tafel slope value of  $132 \text{ mV.dec}^{-1}$  for a gold electrode and  $137 \text{ mV.dec}^{-1}$  for a platinum electrode. The Tafel slopes indicate that the hydrogen evolution on gold and platinum in acetonitrile proceed through the same rate-determining step, namely that the first electron transfer step is rate-determining for the hydrogen evolution in acetonitrile solutions on both metals. Interestingly, this mechanism resembles the mechanism for HER in alkaline aqueous solution<sup>8</sup> and may suggest an important role of solvent reorganization in the hydrogen adsorption step.



**Figure 6.** Tafel plots measured for gold and platinum microelectrodes in acetonitrile in presence of 0.1 M TBAP as supporting electrolyte and 10 mM  $\text{HClO}_4$  as proton donor. Argon atmosphere.

### 3.4. Discussion and conclusions

In this paper, we have illustrated how important small amounts of water may be in the proper description and understanding of the hydrogen evolution reaction at a gold electrode in acetonitrile. The FTIR studies presented in this work reveal that trace amounts of water accumulate at the gold-acetonitrile interface. Previous work has shown that the largest source water is the electrolyte salt, not the acetonitrile itself, but also the bubbling of hydrogen appears to bring water into the solution. In absence of protons and Faradaic current, the water migrates away from the surface into the bulk with more negative potentials. On the other hand, in presence of added protons, under hydrogen evolution conditions, water accumulates at the electrode surface with more negative potential, indicating that protons carry water to the surface during their migration as a consequence of preferential solvation. This conclusion is underlined by experiments with purposefully added water. A very similar observation has been made previously for hydrogen evolution on platinum electrodes in acetonitrile <sup>2c</sup>. Regarding the migration of anions and cations in the acetonitrile solutions, under conditions of Faradaic current, they behave in accordance with the applied potential, i.e. TBA<sup>+</sup> cations migrate towards the surface and perchlorate anions move away at applied cathodic potentials. In the absence of Faradaic current, the behavior of the motion of ions is not fully understood but it should be noted that the thin-layer configuration under which the FTIR measurements were performed may not be stable enough to draw clear conclusions.

From the Tafel plot analysis we conclude that the hydrogen evolution on gold and platinum proceeds via the same mechanism in the sense that the rate-determining step for the hydrogen evolution in (water-containing) acetonitrile is the first electron transfer, leading to the adsorption of atomic hydrogen.

### 3.5. Acknowledgements

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