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Mechanistic changes observed in heavy water for nitrate reduction reaction on palladium-modified Pt(hkl) electrodes

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Reduction of nitrate on palladium-modified platinum single-crystal electrodes has been investigated both voltammetrically and spectroscopically in acidic media (pH = 1). Results obtained in H2O and D2O solvents are compared for the three crystallographic orientations. FTIR and differential electrochemical mass spectrometry (DEMS) results clearly indicate that the isotopic substitution of the solvent has a large effect in the mechanism of the reaction, changing the nature of the detected products. For Pt(111)/Pd and Pt(100)/Pd, N2O is detected as the main product of nitrate reduction when D2O is used as solvent, while no N2O is detected when the reaction is performed in H2O. For Pt(110)/Pd, N2O is detected in both solvents, although the use of D2O clearly favours the preferential formation of this product. The magnitude of voltammetric currents is also affected by the nature of the solvent. This has been analysed considering, in addition to the different product distribution, the existence of different transport numbers and optical constants of the solvent.

Introduction

In spectroelectrochemical experiments it is common to use deuterated water to avoid interference from the bending vibrational mode of water, that appears around 1640 cm⁻¹.1 The substitution of hydrogen by deuterium in the solvent shifts this adsorption band to much lower wavenumber (1200 cm⁻¹)1 and enables the observation of signals coming from relevant reagents, products or adsorbates in this spectroscopic region. Adsorbed NO is one particular example having characteristic vibrations in the same frequency region than the O–H bending.2–7 In this case, D2O is frequently used to allow the observation of this region. The isotopic substitution of the solvent is also useful to discriminate vibrations from acidic groups in which labile hydrogen atoms suffer facile equilibration with deuterium atoms from the solvent, therefore changing their characteristic vibrational frequency.8,9 The difference in the atomic mass can help to track the origin of H atoms through a reaction, to understand the reaction mechanism,10 identify the nature of molecular adsorption11 or to determine the species by changing its mass.12 In all these cases, it is usually assumed that this substitution does not interfere with the reaction mechanism nor with its overall stoichiometry. Water, as solvent, provides the environment where the reaction takes place, participating in some steps, but it is usually accepted that its substitution for heavy water would not have the capacity of changing the final products. One particular example that showed that this assumption is not always valid was given by Krishnamoorthy et al. who observed that the Fischer–Tropsch synthesis on Co-based catalysts has an increased selectivity to C₅⁺ when D₂ is used instead of H₂.13 This example shows that the difference in the mass between isotopes can influence the reaction mechanism and, in some particular steps, a given pathway can be favored instead of another.

The objective of this work is to show that, in some particular cases and specific conditions, these effects can exist in an electrochemical environment. Nitrate electroreduction is known to have many pathways,14–18 with several final products (NO₂, HNO₂, NO, N₂O, N₂, NH₂OH and NH₃). Changes in nitrate concentration, pH, temperature, electrode material, etc., may favor a particular final product suggesting that different reaction paths have similar activation energies and small changes in the energy of intermediates are enough to modify the overall reaction. Voltammetric and FTIR results of nitrate reduction on palladium-modified platinum (hkl) electrodes, in H₂O and D₂O, are presented. They show that the isotopic substitution of the solvent can also have an important role on the pathway the reaction follows. These results are complemented with a differential electrochemical mass spectrometry (DEMS) study of the reaction.

Experimental

The platinum electrodes were prepared from small single crystal beads, by the method developed by Clavilier et al.19 Before each experiment the Pt electrodes were flame annealed, cooled to
room temperature under Ar + H₂ atmosphere, protected with a droplet of water saturated with these gases and then transferred to the electrochemical cell. The palladium adlayers were prepared electrochemically and characterized voltammetrically as previously described.⑨ The palladium atoms were deposited until the first Pd monolayer was almost completely covered.⑨ After palladium deposition, the modified electrode was rinsed with water and transferred to a cell with 0.1 M H₂SO₄ (0.1 M HClO₄) + 0.1 M KNO₃. The immersion potential was selected as 0.9 V, because at this potential nitrate is not reduced. In all cases, a platinum wire was used as counter electrode and a reversible hydrogen electrode (RHE) as reference electrode. No significant changes were observed for the blank voltamograms recorded in the absence of KNO₃ in H₂O and D₂O, for both electrolytes.

Spectroelectrochemical experiments were performed as described elsewhere.⑨⑨ The spectroelectrochemical cell incorporates a prismatic CaF₂ window bevelled at 60°. After immersing the electrode at 0.9 V and creating a thin electrolyte layer by pressing the electrode against the spectroscopic window, immersing the electrode at 0.9 V and creating a thin electrolyte layer by pressing the electrode against the spectroscopic window, a single beam reference spectrum was collected at this potential. Then, the electrode potential was gradually stepped down at 50 mV intervals and a single beam spectrum collected at each potential down to 0.05 V. All spectra showed in this work are composed of 200 interferograms collected with a resolution of 4 cm⁻¹ and are presented as absorbances, according to \( A = -\log(R/R₀) \) where \( R \) and \( R₀ \) are the reflectance of the single beam spectra obtained at the sample and reference potentials, respectively. Thus, negative bands correspond to species with higher concentration at the reference potential while positive bands correspond to species that have been formed at the sample potential.

DEMS measurements were performed with a Balzers QMG 422 in which up to 64 different ion currents can be measured. The complete system has been described elsewhere.⑨ A conventional spectroelectrochemical cell connected through a PTFE membrane with the mass spectrometer was used to perform both electrochemical and mass spectrometry experiments. A PTFE membrane (Gore-Tex, 75 μm mean thickness and 0.02 μm mean pore size) was employed to avoid entrance of solution to the mass spectrometer. The electrode was immersed at 0.9 V and lightly pressed against the PTFE membrane. The first cycle, between 0.9 and 0.06 V, at 0.1 mVs⁻¹ was registered. For checking the formation of N₂, NO and N₂O, the \( m/z \) values chosen were: \( m/z \) = 28 (N₂), \( m/z \) = 30 (NO) and \( m/z \) = 44 (N₂O). Only for N₂O, fragmentation is appreciable: the relative abundance is 31.1% for NO⁺ (⑨⑨⑨) and 10.7% for N₂ (⑨⑨⑨) respectively. Thus, negative bands correspond to species with higher concentration at the reference potential while positive bands correspond to species that have been formed at the sample potential.

Results and discussion

The results for the FTIR experiments of nitrate reduction in 0.1 M HClO₄ on palladium-modified Pt(111) and Pt(100) electrodes are presented in Fig. 1. The results obtained in H₂O (see Fig. 1A) show the consumption of nitrate (band at 1370 cm⁻¹)⑨⑨ at potentials lower than 0.3 V and the simultaneous formation of N₂O (band at 2232 cm⁻¹)⑨⑨,⑨ with maximum intensity at 0.15 V. At lower potentials (0.1 and 0.05 V) it is possible to see a small band at 2750 cm⁻¹, that can be assigned to hydroxylamine.⑨ A small band at 1490 cm⁻¹ observed in the spectrum collected at 0.70 V can be attributed to adsorbed NO. Other bands due to NO and NH₄⁺ formation are obscured by a strong band due to water O–H bending that appears at 1640 cm⁻¹. To avoid this interference, the same experiment was repeated using D₂O as solvent (Fig. 1B). The peaks at 1700 and 1490 cm⁻¹ were attributed to NO.⑨⑨⑨ The band corresponding to N₂O formation is still observed at 2232 cm⁻¹ for potentials lower than 0.3 V. Conversely, the hydroxylamine band at 2750 cm⁻¹ is not present when D₂O is used as solvent while a new band emerges at 2060 cm⁻¹, that can be attributed to deuterated hydroxylamine, in agreement with Nightingale and Wagner.⑨⑨ This behavior reflects what is usually expected after changing the isotopic nature of the solvent: deuterated bonds change their vibrational frequency while non-deuterated groups remain unaffected. The final products are the same in both solvents, except for the isotopic substitution.

Fig. 2 and 3 show the FTIR results for nitrate reduction in 0.1 M HClO₄ on palladium-modified Pt(111) and Pt(100) electrodes, respectively, when water and heavy water are used as solvent. It is possible to see the band corresponding to nitrate consumption at 1370 cm⁻¹, but no features associated to the products formed during nitrate reduction can be observed. To monitor the possible formation of NO, the experiments were repeated in D₂O. In addition to the NO bands in the region between 1700 and 1450 cm⁻¹, Fig. 2B and 3B show the formation of N₂O.
when heavy water is used, that was not observed in H2O solutions. Thus, the reaction follows a different pathway than in water. The experiment was repeated at least twice and the results shown here were consistently observed. Nitrate reduction has many possible reaction pathways, with NOads, NO, N2O, NH2OH and NH3 being some of the possible products. It has been proposed that nitrate is first reduced to NO that can be further reduced to NH2OH and NH3 or N2O and N2. From the fact that N2O could not be detected when the reaction takes place in water, but it is observed in D2O, it can be suggested that when H+ are replaced with D+, the reaction goes through a different path and N2O is produced. This different behavior is likely due to a different availability of H+ and D+. Deuterated water presents slightly different physical properties in comparison with ordinary water such as higher boiling and melting points and higher density. This indicates that D2O molecules are more strongly bonded to each other than H2O molecules, in agreement with the hydrogen-bond enthalpies ($\Delta H = 11.71$ kJ mol$^{-1}$ for deuterium and $10.88$ kJ mol$^{-1}$ for hydrogen). Since the cleavage of hydrogen bonds is the rate determining step for H+ mobility (Grotthuss mechanism), the difference in deuterium/hydrogen-bond enthalpies is also responsible for the isotopic effects in ionic conductivity ($\lambda_D = 249.9$ S cm$^{-1}$ mol$^{-1}$, while $\lambda_H = 349.65$ S cm$^{-2}$ mol$^{-1}$). In the same way, reactions involving D+ need a higher activation energy than reactions involving H+. In the case of competition between slow parallel reactions, like those involved in nitrate reduction, a small energy change can shift the mechanism to different final products.

It is assumed that nitrate first reacts to produce NO(ads) and this species reacts with another NO molecule to produce NH$_4^+$ or with protons to produce NH$_4^+$. This mechanism is described by reactions (1)–(3):

$$\text{NO}_3^- + 4\text{H}^+ + 3e^- \rightarrow \text{NO}_{\text{ads}} + 2\text{H}_2\text{O} \quad (1)$$

$$\text{NO}_{\text{ads}} + 6\text{H}^+ + 5e^- \rightarrow \text{NH}_4^+ + \text{H}_2\text{O} \quad (2)$$

$$\text{NO}_{\text{ads}} + \text{NO} + 2\text{H}^+ + 2e^- \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \quad (3)$$

According to the spectroscopic evidence given above, it can be proposed that in H2O, $k_2 > k_3$, and NO$_{\text{ads}}$ reacts to produce...
Table 1  Ratios of electrochemical charge and maximum integrated intensities for NO$_3^-$ and N$_2$O bands in D$_2$O/H$_2$O

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Electrolyte</th>
<th>$q(D_2O)/q(H_2O)$</th>
<th>NO$_3^-$ (D$_2$O)/NO$_3^-$ (H$_2$O)</th>
<th>N$_2$O(D$_2$O)/N$_2$O(H$_2$O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(110)/Pd</td>
<td>H$_2$SO$_4$</td>
<td>7.02</td>
<td>3.05</td>
<td>1.84</td>
</tr>
<tr>
<td></td>
<td>HClO$_4$</td>
<td>0.34</td>
<td>3.97</td>
<td>2.32</td>
</tr>
<tr>
<td>Pt(111)/Pd</td>
<td>H$_2$SO$_4$</td>
<td>3.48</td>
<td>4.97</td>
<td>2.49</td>
</tr>
<tr>
<td></td>
<td>HClO$_4$</td>
<td>1.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt(100)/Pd</td>
<td>H$_2$SO$_4$</td>
<td>3.21</td>
<td>2.92</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HClO$_4$</td>
<td>1.25</td>
<td>2.84</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5  Voltammetric profiles for nitrate reduction in (A, C, E) 0.1 M HClO$_4$ and (B, D, F) 0.1 M H$_2$SO$_4$ with 0.1 M of KNO$_3$ for (A, B) Pt(110)/Pd; (C, D) Pt(111)/Pd and (E, F) Pt(100)/Pd in D$_2$O (solid) and H$_2$O (doted). Line + symbol curves: nitrate consumption band area from FTIR experiments in D$_2$O (– –) and H$_2$O (– –). Insets in A and B: N$_2$O band area for FTIR experiments in D$_2$O (– –) and H$_2$O (– –).
NH₄⁺ preferentially. When H⁺ are substituted by D⁺ the reaction rates change. While changes in the rate of reaction (1) \( (k_1) \) do not interfere with the final products, changes in the rate of reactions (2) and (3) do. In D₂O, because of the lower availability of protons or higher activation energy for the cleavage of hydrogen bonds, reaction (3) would be favored. Dima and coworkers proposed that N₂O is only produced when NO is observed in solution, according to reaction (3) where one NO molecule in solution is involved. Although no spectroscopic evidence of NO in solution was obtained using s polarized light in FTIR experiments (Fig. 4 shows the results for nitrate reduction on Pt(110)/Pd electrode in HClO₄ and D₂O) NO gas was detected in the DEMS experiments, as described below. Most likely the NO concentration is below the detection limit for the FTIR measurement. However, it is not possible to discard an alternative pathway for the production of N₂O involving two adsorbed NO molecules. Production of dinitrogen on Pt(100) has been proposed to proceed through the recombination of NO and NH₃ species. However, this mechanism seems to be very specific for this surface, which seems to possess an optimum geometry for the stabilization of adsorbed NH₃. The isotopic effect reported here has not been observed in the same extent for the reduction of other nitrogenated compounds with lower oxidation state or for nitrate reduction on platinum. Nitrite reduction on palladium adlayers has been demonstrated to produce N₂O, similarly to nitrate reduction, but no isotopic effect is reported in this case. Without isotopic effect. Regarding NO reduction, the final product depends on the presence or not of NO in solution. In the absence of solution NO, only ammonia is detected as final product, while N₂O is detected when NO is present in solution. Again, no isotopic effect is reported in this case. These observations suggest that the balance between rates of reactions (2) and (3) is very delicate and small changes in either the amount or energy of adsorption of adsorbed NO, or in the availability and concentration of solution NO, are strongly determinant for the final product distribution.

### Table 2

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ionic conductivity, ( \mu \Omega \text{cm}^2 \text{mol}^{-1} )</th>
<th>Ion concentration, ( \mu \text{mol L}^{-1} )</th>
<th>Transport number, ( t ) (in H₂O)</th>
<th>Transport number, ( t ) (in D₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M KNO₃ + 0.1 M H₂SO₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H⁺</td>
<td>349.65</td>
<td>0.2</td>
<td>0.696</td>
<td>0.621</td>
</tr>
<tr>
<td>D⁺</td>
<td>249.9</td>
<td>0.2</td>
<td>0.073</td>
<td>0.091</td>
</tr>
<tr>
<td>K⁺</td>
<td>73.5</td>
<td>0.1</td>
<td>0.071</td>
<td>0.089</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>71.42</td>
<td>0.1</td>
<td>0.160</td>
<td>0.199</td>
</tr>
<tr>
<td>( \frac{1}{2} ) SO₄²⁻</td>
<td>80.0</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 M KNO₃ + 0.1 M HClO₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H⁺</td>
<td>349.65</td>
<td>0.1</td>
<td>0.622</td>
<td>0.541</td>
</tr>
<tr>
<td>D⁺</td>
<td>249.9</td>
<td>0.1</td>
<td>0.131</td>
<td>0.159</td>
</tr>
<tr>
<td>K⁺</td>
<td>73.5</td>
<td>0.1</td>
<td>0.127</td>
<td>0.155</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>71.42</td>
<td>0.1</td>
<td>0.120</td>
<td>0.146</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>67.3</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 6 Influence of the solvent in the electric field of the infrared radiation: (A) on the electrode surface and (B) in solution.
It is noteworthy that the consumption band of nitrate is more intense in heavy water for all the electrodes. Then, it is necessary to discuss whether the effect of the isotopic substitution is limited to a change of the reaction rate or, as proposed in the previous paragraphs, it causes also a change in the product distribution. In other words, it could be argued that N$_2$O is not seen in the spectra collected in H$_2$O simply because the corresponding band is below the detection limit, since the extent of the reaction is smaller. This is not the case for Pt(111), where the N$_2$O band is well above the detection limit even after normalization to account for the different magnitude of the nitrate consumption band. However, for Pt(100) after the same normalization, the N$_2$O band is hardly distinguishable from the background noise. Then, it cannot be unambiguously concluded that the N$_2$O is not produced on Pt(100) when the reaction takes place in water, although this is the most likely explanation from the comparison with the result for Pt(111). The absence of the vibrational band assigned to N$_2$O in the spectra collected in H$_2$O suggests that in water the reaction follows a pathway that would finally lead to the formation of NH$_4^+$. The corresponding vibrational band of ammonia, expected at 1460 cm$^{-1}$ could not be detected because of the combined interference of O–H bending, nitrate consumption and NO formation (at ca. 1500 cm$^{-1}$).

In the case of Pt(110)/Pd, the reaction in water must follow two parallel pathways, producing NH$_4^+$ and N$_2$O, but in heavy water the pathway that produces N$_2$O is favored in comparison with the other one producing NH$_4^+$, consuming more nitrate ions. To help in the qualitative discussion of this data, Table 1 summarizes the ratio of the integrated intensities of nitrate consumption bands in the two solvents, together with the ratio for N$_2$O formation band at Pt(110) and the ratio between voltammetric charges. The increase in N$_2$O production when heavy water is used is around 2 for both electrolytes. However, the increase in nitrate consumption is higher (around 3-4). This suggests that other products, besides N$_2$O, are generated. The most likely product would be N$_2$, which is produced from N$_2$O reduction (N$_2$O + 2H$^+$ + 2e$^-$ → H$_2$O + N$_2$). Since N$_2$ is formed through a path that involves N$_2$O, we can still conclude that N$_2$O is favored for Pt(110)/Pd in D$_2$O.

The variation of band intensities due to the isotopic substitution can be compared with the corresponding variation of the magnitude of voltammetric currents. In any case, the comparison between voltammetric currents and band intensities should be made with caution since experimental conditions are not identical in both cases. In the voltammetric experiment the potential is linearly swept at 2 mV s$^{-1}$ while in the IR experiment the potential is sequentially stepped and held at each value during spectra acquisition. The reactants concentration is also limited by the thin layer. Moreover, different reflectivity values of the interface and transport numbers in the two solvents need also to be taken into account. This will be discussed below.

The voltammetric profiles of the first cycle for nitrate reduction in 0.1 M HClO$_4$ and 0.1 M H$_2$SO$_4$ for both solvents are presented in Fig. 5, together with the integrated area of nitrate band measured in FTIR experiments. The voltammetric behavior for the two solvents is again different.

Analyzing the voltammetric profiles for 0.1 M HClO$_4$ (Fig. 5A, C and E) and data in Table 1, no significant increase of the reduction current can be observed when H$_2$O is substituted by D$_2$O, although the nitrate consumption band is always more intense in the latter solvent. In fact, for Pt(110)/Pd, the reduction current in D$_2$O is lower than in H$_2$O. The Pt(110)/Pd electrode could be more sensitive to contaminants present in the solvent than the other basal plane electrodes and thus lead to a lower current. However, the interpretation of the results for Pt(111)/Pd and Pt(100)/Pd offer another possibility to understand why the current is lower in the case of Pt(110)/Pd.

As discussed before, the FTIR experiments for Pt(111)/Pd and Pt(100)/Pd showed different products for nitrate reduction in H$_2$O and D$_2$O, and a higher consumption of NO$_3^-$ However, the voltammetric currents recorded in HClO$_4$ electrolyte solutions are almost the same for both solvents.

From FTIR results it was possible to suggest that in H$_2$O the reaction follows a pathway that leads to the formation of NH$_4^+$. This reaction consumes 8 e$^-$/NO$_3^-$ in D$_2$O, the substitution of H$^+$ for D$^+$ makes the reaction preferentially follow a different mechanism, producing N$_2$O and consuming more nitrate ions in this case. The electron transfer is lower for N$_2$O (4 e$^-$/NO$_3^-$), but as more nitrate ions are reduced, the final reduction current is essentially the same. For Pt(110)/Pd, considering that the reaction follows two parallel pathways as suggested above, with the production of N$_2$O being favored in D$_2$O, we can propose that, even with a higher rate of nitrate consumption, the current generated is not enough to compensate a lower contribution from the path that involves 8e$^-$/NO$_3^-$ leading to NH$_4^+$.

Looking in detail the results in 0.1 M H$_2$SO$_4$ (Fig. 5B, D and F), it can be seen that the increase of the nitrate consumption band in FTIR experiments is consistent with the increase in current in the voltammetric experiments. The FTIR results show the same changes in the mechanism when D$_2$O is used as solvent, but in this case the increase in nitrate consumption is high enough to increase the voltammetric current. As mentioned above, voltammetric currents and band intensities are not directly comparable. Still, the higher increase in voltammetric current in comparison with the band intensity may suggest that another non-hydrogenated product, which consumes more electrons than N$_2$O and cannot be seen by FTIR is being formed. Again, the suggestion is that this species would be N$_2$, that needs 5 e$^-$/NO$_3^-$ to be produced. This hypothesis is in agreement with the comparison of the ratio of band intensities shown for Pt(110) in Table 1 and the insets in Fig. 5A and B. The latter show the integrated area of N$_2$O peak from FTIR experiments and, as discussed before, since the increase in N$_2$O production is lower than the increase in nitrate consumption, another product must be being formed. DEMS experiments, that will be discussed later, showed production of molecular nitrogen confirming this hypothesis.

Other factors need to be considered to make the quantitative analysis of IR bands. The first one arises from the fact that a fraction of nitrate consumption is due to migration of anions outside the thin layer to carry the charge needed for the electrochemical reaction. The fraction of the total current carried by a particular species is measured by the transport number of this species ($t_i$)$^{34}$ and it depends on the current transported by all the other species. Hence, if an ion is substituted by another ion with a different ionic conductivity, even if the concentrations are the same, the transport number of the other ions will change too.$^{34}$ Table 2 shows the ionic conductivity$^{36}$ and transport number for

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the ionic species of the experiments presented in Fig. 1–5. Since the ionic conductivity for D+ is significantly lower than for H+, when H2O is replaced by D2O, the transport number of nitrate will increase. This effect would also contribute to the increase of the intensity of the nitrate consumption band observed in D2O. However, a look at the data in Table 2 reveals that transport numbers for nitrate are relatively low and therefore, migration can only account for around a 20% of the total band intensity.

Another factor that needs to be considered when comparing the band intensity for spectra collected under different experimental conditions is the change in the radiation electric field caused by the different optical properties for each situation. Fig. 6 show the influence of the thin layer thickness on the electric field, for H2O and D2O, calculated for 1300 cm−1 using Fresnel 1 software.58 Both, the electric field at the electrode surface (Fig. 6A) and the average electric field in the solution (Fig. 6B), are higher, for a same thickness, when the solvent is D2O. In the case of a species in solution, such as NO3−, the electric field in the solution must be considered (Fig. 6B). For a typical thickness of 3 μm, the ratio between the electric field in ordinary and heavy water is 1.5. This difference cannot be neglected and influences the NO3− consumption band.

Since all the volatile products can be monitored by DEMS, the production of N2 can be investigated to confirm the hypothesis presented above. In this way, some DEMS measurements were conducted to follow N2, NO and N2O production during the course of nitrate reduction in water (A, C and E) and in heavy water (B, D and F). The results as a function of the electrode potential (Fig. 7) are in agreement with those from FTIR. For Pt(110)/Pd in water, the only observed volatile product is N2O, but when heavy water is used as solvent, N2O, NO and N2 are observed as products, in agreement with the hypothesis presented above. For both Pt(111)/Pd and Pt(100)/Pd, no volatile products were observed in H2O, but an increase in mlz = 44 was observed in D2O, indicating the production of N2O. These results are essentially the same as those observed for FTIR experiments.

Conclusions

From spectroelectrochemical experiments of nitrate reduction on palladium-modified electrodes it was possible to conclude that the use of deuterium instead of hydrogen can deeply interfere in the reaction mechanism. The results showed that the isotopic nature of the solvent affects the final distribution of products. The use of D2O favors in all cases the formation of N2O. For Pt(111)/Pd and Pt(100)/Pd, N2O is only observed in those experiments carried out in D2O, while NH4+ is the preferred product in H2O. For Pt(110)/Pd, N2O and NH2OH were observed in both water and heavy water, although band intensity and DEMS results indicate that the formation of N2O and N2 is favored in D2O for this crystallographic orientation. The change in the reaction pathway was also observed in the voltammetric results, showing in all cases that the substitution of H2O for D2O leads to different reaction pathways. This is in agreement with changes in the reaction rates when the solvent is substituted. The increase of the transport number of the ionic species involved in the reaction and changes in the thin layer electric field was also considered as factors that partially affect the band intensity.

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