Cathodic Reactions Involved in Corrosion Processes Occurring in Concentrated Nitric Acid at 100 °C

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In order to explain and analyze the corrosion process of AISI 304 L stainless steel in the presence of nitric acid condensates, the reduction mechanism of nitric acid was studied on a platinum electrode in various nitric acid solutions (4 mol·L^{-1}, 8 mol·L^{-1} and 12 mol·L^{-1}) at 100 °C. Classical electrochemical techniques were used: cyclic voltammetry, chronoamperometry on a stationary electrode as well as on a rotating disk electrode. A reduction mechanism is proposed; this mechanism is autocatalytic and involves a charge-transfer step and a heterogeneous chemical reaction which regenerates the electroactive species at the electrode surface. The electroactive species is assumed to be nitrous acid which is a soluble species. The other compounds involved in the reduction mechanism are NO and NO_2, which are supposed to be adsorbed. The nitric acid concentration influences the major product of the reduction process: NO for concentrations lower than 8 mol·L^{-1} and NO_2 for higher concentrations.

Introduction

Nuclear fuel reprocessing is achieved in France using nitric acid as the dissolution reaction medium. The corrosiveness of nitric acid mixtures leads to the use of corrosion-resistant materials such as austenitic stainless steels or zirconium.

Some potential cases of intergranular corrosion have been identified in experimental devices and studied on non-sensitized stainless steels, for example, in confined and non-renewed nitric acid.[1] However in some specific conditions, uncertainties about the mechanisms involved remain. Corrosion in the presence of nitric acid condensates is one of these cases and can be encountered in any installation handling boiling nitric acid. A specific loop, named ECORCE (Etude de la CORrosion sous Condensat d'Evaporation), designed at the laboratory, revealed a much more severe corrosion of stainless steels by nitric acid condensates than in the liquid bulk under similar conditions of concentration and temperature.[2] In fact, the condensate medium can lead to such highly oxidizing conditions that the corrosion potential of the steel can reach the transpassive domain.

Very few literature data have been found on this phenomenon and no thorough study has been performed. Therefore, in order to understand and analyze the corrosion mechanism of AISI 304 L stainless steel in the presence of nitric acid condensates, a research project was performed in this laboratory. The first step of this study consisted in a thermodynamic analysis of the chemical and electrochemical properties of nitric acid media.[3] This analysis led to a representation of concentrated nitric acid at 100 °C. One of the results of this study concerns the influence of the nitric acid concentration on the reduction species of nitric acid. Major species liable to be found when nitric acid is reduced at potentials close to the equilibrium potential were determined: nitrogen monoxide for nitric acid concentrations lower than 8 mol·L^{-1} and nitrogen dioxide for higher concentrations.[3]

This paper presents the second step of the research project which is the electrochemical investigation of the reduction process of nitric acid at 100 °C occurring on a platinum electrode. The platinum electrode was used as working electrode in order to avoid the oxidation of the electrode material and to focus the research on the reduction process. This electrochemical study appeared necessary as previous corrosion studies performed on AISI 304 L stainless steel in nonrenewed and confined liquid nitric acid[1] revealed the necessity of investigating the cathodic part of the corrosion process by suggesting a major role of the reduction mechanism on the increase in the corrosion rate.

The working temperature in the thermodynamic study[3] and in the electrochemical study was fixed at 100 °C as the metallic wall temperature is close to this value in the condensation zones.

In a last step, it will be necessary to perform a similar electrochemical study on a stainless steel electrode in order to compare the reduction process obtained with the one observed on a platinum electrode and, secondly, to link these results to the results of the corrosion tests performed in the laboratory.[4] The final aim of this research is to ex-

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plain the corrosion mechanism of AISI 304 L stainless steel in the presence of nitric acid condensates.

Literature Data

The Reduction Mechanism of Nitric Acid on a Platinum Electrode

This process has been widely studied over many years.[5–13] All the authors agree on its autocatalytic nature, characterized by the predominant role of the reduction products. It is also generally believed that the nitric acid molecule is not the electroactive species.

In nitric acid solutions of concentrations from 1 to 10 mol·L^{-1}, at 25 °C, containing nitrous acid,[5–12] two different autocatalytic mechanisms have been formulated respectively by Vetter and Schmid.

According to Vetter the mechanism is heterogeneous, as the chemical regeneration of NO_2, assumed to be the electroactive species, occurs at the electrode surface. NO_2 is formed at the interface according to a previous slow heterogeneous chemical reaction. In that case, the stirring of the solution has no influence on the current density.[5–7] This mechanism is described as:

$$(HNO_2)_{ads.} + H^+ = (NO^+)_{ads.} + H_2O$$
$$(NO_3^-)_{ads.} + (NO^+)_{ads.} = (N_2O_4)_{ads.}$$
$$(N_2O_4)_{ads.} = 2(NO_2)_{ads.}$$
$$(NO_2)_{ads.} + e^- = (NO_2^-)_{ads.}$$
$$(NO_2^-)_{ads.} + H^+ = (HNO_2)_{ads.}$$

According to Schmid the mechanism is homogeneous, as the chemical regeneration of NO^+, assumed to be the electroactive species, occurs in the bulk. NO^+ (equivalent to HNO_2) is obtained from the nitrous acid formed in the layer near the electrode. In that case the stirring of the solution provokes a decrease of the current density.[8–12] This mechanism is described as:

$$HNO_2 + H^+ = NO^+ + H_2O$$
$$NO^+ + e^- = NO$$
$$2NO + NO_3^- + H^+ + H_2O = 3HNO_2$$

These two mechanisms, for a long time opposed, have both been validated by Razygraev who worked in a large range of concentrations and temperatures.[13] He supposed that both mechanisms occur on a platinum electrode, but for different potentials, leading to NO_2 (heterogeneous mechanism) or NO (homogeneous mechanism).

The Reduction Mechanism of Nitric Acid on a Stainless Steel Electrode

The same study was performed on stainless steels and alloys by Razygraev.[14] He concluded that an identical sequence of reactions was taking place on the different materials as on the platinum electrode, except that both mechanisms occurred simultaneously on stainless steels.

A recent study on the effect of dissolved chromium species on the corrosion of stainless steel in nitric acid confirmed the autocatalytic characteristic of the reduction of nitric acid on a gold electrode as well as on a stainless steel electrode.[15] This study revealed the lack of influence of Ar, N_2 and N_2O on the corrosion rate of stainless steel and the effect of a continuous bubbling of NO and NO_2, which leads to an increase in the corrosion rate by a catalytic mechanism. However, no reduction mechanism of nitric acid was proposed and the role of the different nitric acid species was not clearly specified.

Conclusions from Literature Data

The knowledge of the corrosion mechanism of AISI 304 L stainless steel in the presence of nitric acid condensates involves the understanding and the analysis of the reduction process of nitric acid.[1]

Literature data on the reduction process of nitric acid occurring on a platinum electrode are very numerous and sometimes contradictory. However, the studies presented in the literature agree on two major points: the reduction mechanism is autocatalytic and the electroactive species is not nitric acid.

The major uncertainties remaining are:

- the identity of the electroactive species at low overvoltages (potential range investigated for the corrosion study): HNO_2, NO^+, NO_2,
- the regeneration site of the electroactive species: electrode surface, solution,
- the influence of the concentration of nitric acid on the reduction process,
- the relationship between the reduction process and the thermodynamic behavior of nitric acid.

In this paper, our aim is to clarify these uncertainties, to identify the major species involved in the reduction process of nitric acid, and to propose a sequence of reactions explaining the experimental facts observed.

Results and Discussion

Various electrochemical techniques have been used: cyclic voltammetry, chronoamperometry with a stationary electrode as well as with a rotating disk electrode.

The values of the Open Circuit Potential (OCP) of the platinum electrode in the nitric acid solutions are given in Table 1. The values of the nitrous acid concentrations are estimated from thermodynamic calculations.[3]

Table 1. Experimental values of the Open Circuit Potential of the platinum electrode in the three nitric acid solutions at 100 °C – corresponding calculated nitrous acid concentration

$[HNO_3]$ [mol·L^{-1}]	OCP [V/SSE][a]	$[HNO_2]$ [mol·L^{-1}]
4	0.550	3.1×10^{-5}
8	0.630	7.5×10^{-6}
12	0.680	7.5×10^{-6}

[a] SSE: $Hg/Hg_2SO_{4(sat.)}$, $K_2SO_{4(sat.)}$.

The electroactivity domain of a solution of nitric acid 4 mol·L^{-1} is presented in Figure 1. The potentials were investigated between 0.400 V/SSE and 1 V/SSE. For higher overvoltages a gaseous evolution occurs.

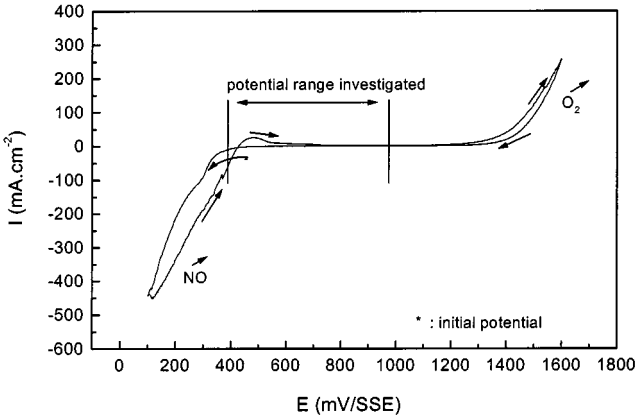

Figure 1. Electroactivity domain of HNO_3 4 mol·L^{-1} at 100 °C at a scan rate of 10 mV·s^{-1}; in reduction, NO evolution; in oxidation, O_2 evolution

Nitric Acid Solutions With No External Additions

Current-Potential Curves at a Low Scan Rate

Figures 2 and 3 show voltammograms obtained on a stationary electrode for nitric acid concentrations of 4 mol·L^{-1}, 8 mol·L^{-1} and 12 mol·L^{-1} at a scan rate of 10 mV·s^{-1}. The curves are presented in a log scale.

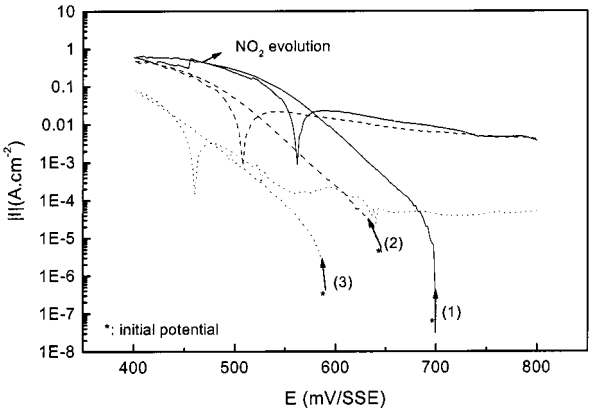

Figure 2. Cyclic voltammograms for HNO_3 solutions of different concentrations at 100 °C at a scan rate of 10 mV·s^{-1}. (1): 12 mol·L^{-1} (2): 8 mol·L^{-1} (3): 4 mol·L^{-1}

For the three solutions, the scans were performed from the OCP to the same potential of 0.400 V/SSE and then reversed (Figure 2). For HNO_3 4 mol·L^{-1}, another curve was placed on the diagram for which the scan was performed down to 0.250 V/SSE (Figure 3).

The oxidation peak is assigned to the oxidation of species formed during the reduction of nitric acid, which is confirmed by the absence of this peak when a scan is performed directly on oxidation.

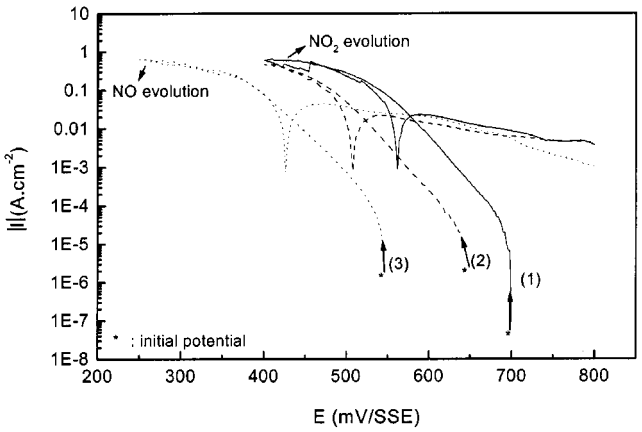

Figure 3. Cyclic voltammograms for HNO_3 solutions of different concentrations at 100 °C at a scan rate of 10 mV·s^{-1}. (1): 12 mol·L^{-1} (2): 8 mol·L^{-1} (3): 4 mol·L^{-1}

The analysis of the experiments and the visual observations show that:

– for the three concentrations, the voltammograms are similar: current densities are almost equal for the same overvoltage (taken from the OCP);
– a red gaseous evolution of NO_2 is observed for HNO_3 12 mol·L^{-1} and 8 mol·L^{-1};
– a colorless gaseous evolution (probably NO) is observed for HNO_3 4 mol·L^{-1} for a potential of 0.250 V whereas no evolution is observed for 0.400 V/SSE.

Figure 4 shows the representation [log$p$(O_2)] versus [–log$p$(HNO_3) and pH] of nitric acid at 100 °C established previously.[3] The curves represent the calculated values of the oxygen pressure for which the partial pressures of NO and NO_2 are equal to 1 bar and the concentration of nitrous acid to 10^{-2} mol·L^{-1}. The links between the oxygen pressure and the experimental potential values are determined by potentiometric measurements for 4 mol·L^{-1}, 8 mol·L^{-1} and 14.4 mol·L^{-1} solutions (determination of the potential for p_{NO2} = 1 bar at the different concentrations) and by considering that $\Delta\log p(O_2) = 1$ for $\Delta E = 2.303RT/4F = 18.5$ mV.[3] For a given potential, the oxygen pressure varies with the nitric acid concentration.

At 100 °C, the electroactivity domain of nitric acid in reduction (nonhatched domain) under a pressure of one bar is divided into two parts. The formation of NO limits the stability domain for concentrations lower than 8 mol·L^{-1} and the formation of NO_2 for higher concentrations. With this diagram, the voltammetric results can be analyzed:

– for HNO_3 12 mol·L^{-1} and 8 mol·L^{-1}, a potential of 0.400 V/SSE applied to the platinum electrode corresponds to oxygen pressures far outside the stability domain of nitric acid and an evolution of NO_2 occurs;
– for HNO_3 4 mol·L^{-1}, the potential of 0.400 V is very near the stability domain of HNO_3. Thus, no gaseous evolution occurs. However, the potential of 0.250 V is located far outside the stability domain and then a gaseous evolution of NO is observed.

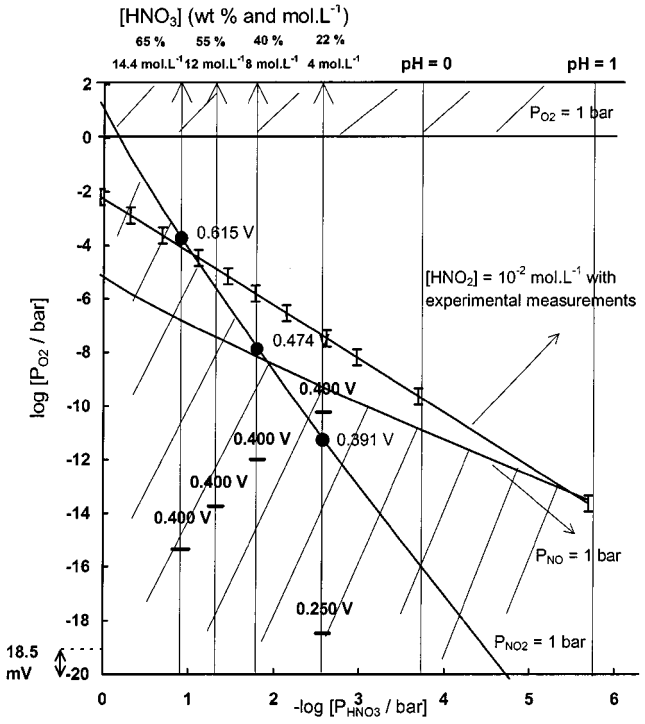

Figure 4. Representation of the chemical and electrochemical properties of concentrated nitric acid at 100 °C. •: Potential values for $p_{NO2} = 1$ bar (V/SSE at 25 °C); –: potential limits of the electrochemical investigations (V/SSE at 25 °C)

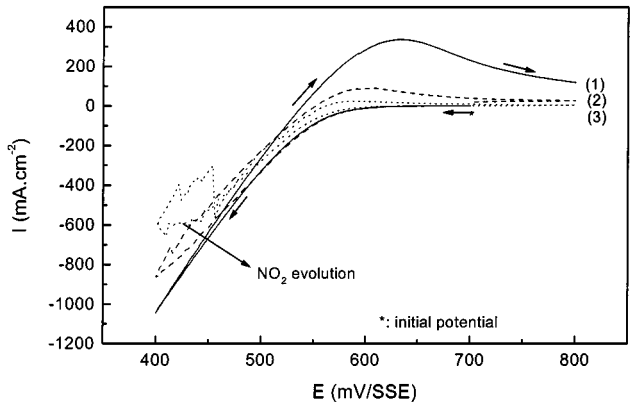

Figure 5. Cyclic voltammograms for HNO_3 12 mol·L^{-1} at 100 °C at different scan rates. (1): 500 mV·s^{-1} (2): 100 mV·s^{-1} (3): 10 mV·s^{-1}

These first results show the dependence of the reduction process on the nitric acid concentration.

Voltammetry

Figure 5, Figure 6 and Figure 7 show, for 12 mol·L^{-1}, 8 mol·L^{-1} and 4 mol·L^{-1} solutions, the voltammograms obtained for scan rates varying from 10 mV·s^{-1} to 500 mV·s^{-1}.

The results obtained are the following:

– for HNO_3 12 mol·L^{-1}, a regular variation of the voltammograms with the scan rate is obtained;

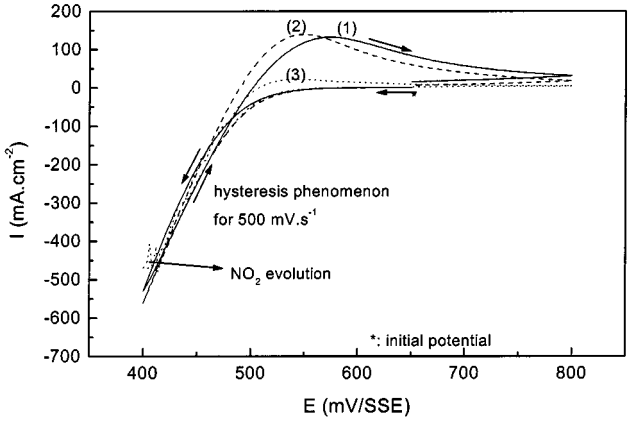

Figure 6. Cyclic voltammograms for HNO_3 8 mol·L^{-1} at 100 °C at different scan rates. (1): 500 mV·s^{-1} (2): 100 mV·s^{-1} (3): 10 mV·s^{-1}

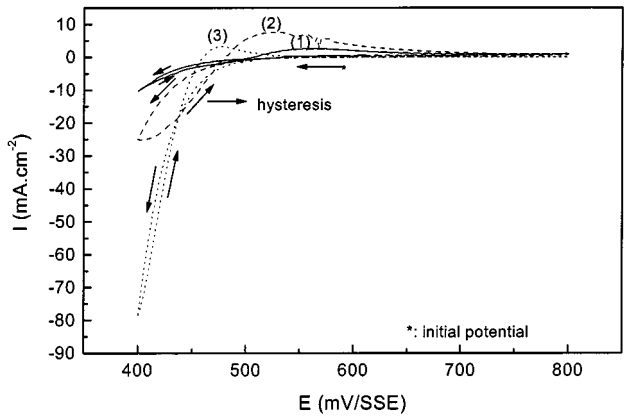

Figure 7. Cyclic voltammograms for HNO_3 4 mol·L^{-1} at 100 °C at different scan rates. (1): 500 mV·s^{-1} (2): 100 mV·s^{-1} (3): 10 mV·s^{-1}

– for HNO_3 8 mol·L^{-1}, a slight hysteresis phenomenon appears for 500 mV·s^{-1};

– for HNO_3 4 mol·L^{-1}, a sharp hysteresis phenomenon appears and the current density in reduction decreases when the scan rate increases;

– for a given scan rate, the current density increases with the nitric acid concentration.

These observations suggest the existence of a relatively slow reaction in the reduction process which is promoted by a high nitric acid concentration.

The analysis of the charges (Table 2) shows that, during the reduction process, some matter is lost: at all concentrations the ratio $| Q_{ox}/Q_{red} |$ is lower than 1 and increases when the scan rate increases. For high nitric acid concentrations, this phenomenon is more marked; the overvoltage applied in reduction is high and the stability domain of nitric acid is exceeded: the small ratio (0.04) obtained at a low scan rate is due to a gaseous evolution (NO_2).

For HNO_3 4 mol·L^{-1}, the overvoltage imposed in reduction is relatively low, the stability domain of nitric acid is not exceeded: no gaseous evolution occurs and the ratio $|Q_{ox}/Q_{red}|$ tends towards 1 for high scan rates.

Chronoamperometry

Experiments on the influence of the nitric acid concentration were performed using chronoamperometry. This tech-

Table 2. Oxidation charge, $Q_{ox.}$ [mC·cm^{-2}], reduction charge, $Q_{red.}$ [mC·cm^{-2}], and ratio $|Q_{ox.}/Q_{red.}|$, as a function of the nitric acid concentration and of the scan rate

$[HNO_3]$ [mol·L^{-1}]	**4**			**8**			**12**		
V [mV·s^{-1}]	$Q_{ox.}$	$Q_{red.}$	$\lvert Q_{ox.}/Q_{red.}\rvert$	$Q_{ox.}$	$Q_{red.}$	$\lvert Q_{ox.}/Q_{red.}\rvert$	$Q_{ox.}$	$Q_{red.}$	$\lvert Q_{ox.}/Q_{red.}\rvert$
500	1.06	−1.5	0.71	51.5	−100.3	0.51	131.1	−297.5	0.44
300	2.05	−3.4	0.60	77.5	−154	0.50	177.2	−490.3	0.36
100	10.4	−20.2	0.51	222.2	−514.6	0.43	144.3	−1305	0.11
30	25.0	−104.0	0.24	592.1	−1958	0.30	182.9	−4430	0.04

nique was used to determine the influence of the stirring of the solution. A reduction potential (near the equilibrium potential) is imposed and when the current is stabilized, the electrode is stirred. The stirring is regulated with a rotating disk electrode (ω = 2000 rpm).

Figure 8 shows the variation of the current density with time for a potential of 0.400 V/SSE and for the different nitric acid concentrations.

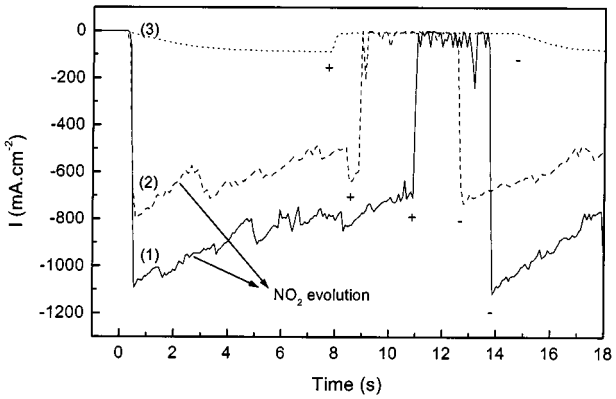

Figure 8. Influence of the stirring on the limiting current density of different nitric acid solutions at 100 °C for a potential of 0.400 V/SSE. ω = 2000 rpm; +: stirring; −: no stirring. (1): 12 mol·L^{-1} (2): 8 mol·L^{-1} (3): 4 mol·L^{-1}

An evolution of nitrogen dioxide is observed for HNO_3 8 mol·L^{-1} and 12 mol·L^{-1}. For all the concentrations the rotation of the electrode leads to a sharp decrease (it becomes nearly equal to zero) of the current density (in magnitude). This inverse dependence of the current density vs. stirring shows that the electroactive species is a soluble species formed at the electrode which diffuses into the solution. When the solution is stirred, the electroactive species is expelled from the electrode. This result is in agreement with Schmid's observations.[8–12] From these first experiments, it is possible to conclude that nitric acid is reduced indirectly through a mechanism involving at least a charge-transfer step and a chemical reaction which regenerates the electroactive species. The electroactive species is a soluble species produced at the electrode by a chemical reaction which is promoted by a high nitric acid concentration.

Influence of the Addition of Nitrous Acid in Solution and of a Flow of Nitrogen Monoxide in the Cell

In order to clarify the species involved, some voltammetric experiments were performed in nitric acid solutions containing reduction products of nitric acid at a significant concentration. The first series was performed with an addition of nitrous acid (nitrites) in solution and the second series with a flow of nitrogen monoxide in the cell.

Current-Potential Curves at a Low Scan Rate

The same experiments (as with nitric acid solutions with no external additions) were performed with an initial nitrite concentration of 10^{-2} mol·L^{-1} in solution. Table 3 gives the OCP of the platinum electrode in the different solutions for a nitrite concentration of 10^{-2} mol·L^{-1}. The values are lower than without nitrites according to the Nernst law:

$$E = E^{0'} - RT/2F \ln[HNO_2]$$

Table 3. Experimental values of the Open Circuit Potential of the platinum electrode in the three nitric acid solutions at 100 °C for a nitrite concentration of 10^{-2} mol·L^{-1}

$[HNO_3]$ [mol·L^{-1}]	OCP [V/SSE]
4	0.457
8	0.514
12	0.564

The experimental values of the apparent standard potentials, for the different nitric acid solutions at 100 °C, have been determined previously.[3]

The influence of the nitric acid concentration was studied for a scan rate of 10 mV·s^{-1} (Figure 9).

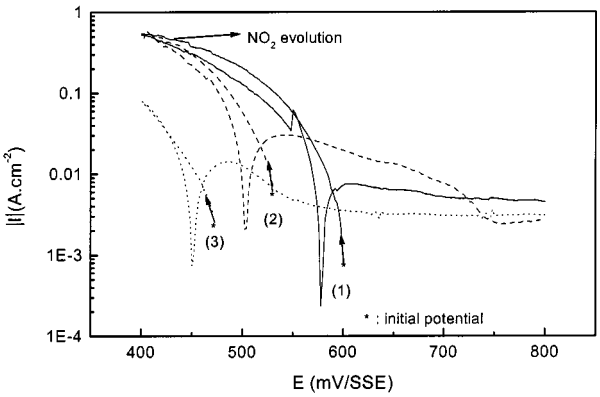

Figure 9. Cyclic voltammograms for HNO_3 solutions of different concentrations at 100 °C containing $[HNO_2] = 10^{-2}$ mol·L^{-1} at a scan rate of 10 mV·s^{-1}. (1): 12 mol·L^{-1} (2): 8 mol·L^{-1} (3): 4 mol·L^{-1}

If the voltammograms are compared with the ones without nitrites, no major differences are observed. The current

densities in reduction are nearly the same with or without nitrites for this scan rate. In oxidation, an increase of the oxidation peak is observed for HNO_3 4 mol·L^{-1} and 8 mol·L^{-1}, which is easily explained as nitrites present in solution undergo oxidation into nitric acid. For HNO_3 12 mol·L^{-1}, a slight decrease of the oxidation current is observed; this phenomenon cannot be readily explained at the moment.

Voltammetry

Figure 10, Figure 11 and Figure 12 show, for 12 mol·L^{-1}, 8 mol·L^{-1} and 4 mol·L^{-1} solutions containing nitrites, respectively, the voltammograms obtained for scan rates varying from 10 mV·s^{-1} to 500 mV·s^{-1}.

The influence of nitrites is more marked for low nitric acid concentrations and high scan rates. The results obtained are:

– for HNO_3 4 mol·L^{-1}, the charge in reduction is multiplied by 1.5 for 50 mV·s^{-1} and by 4 for 500 mV·s^{-1}. Moreover, in the presence of nitrites, the hysteresis disappears even for high scan rates; the evolution of the reoxidation peak current density becomes regular and charges in oxidation are multiplied by 20 for all the scan rates. The chemical regeneration reaction of the active species is slow and limits

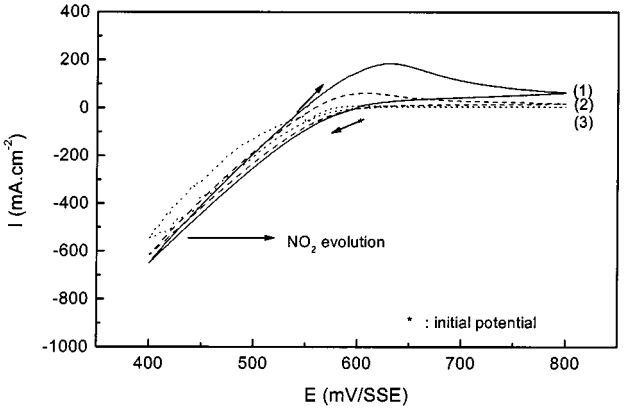

Figure 10. Cyclic voltammograms for HNO_3 12 mol·L^{-1} at 100 °C containing [HNO_2] = 10^{-2} mol·L^{-1} at different scan rates. (1): 500 mV·s^{-1} (2): 100 mV·s^{-1} (3): 10 mV·s^{-1}

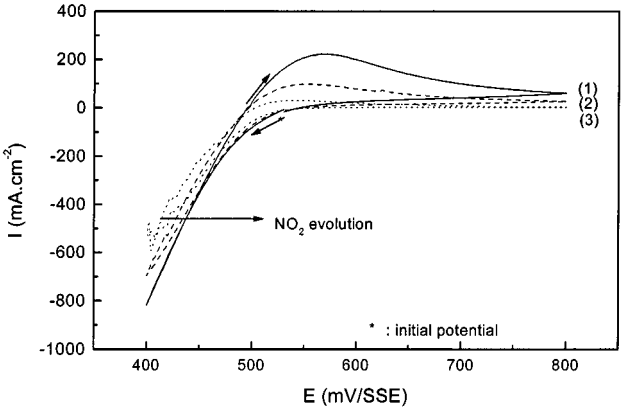

Figure 11. Cyclic voltammograms for HNO_3 8 mol·L^{-1} at 100 °C containing [HNO_2] = 10^{-2} mol·L^{-1} at different scan rates. (1): 500 mV·s^{-1} (2): 100 mV·s^{-1} (3): 10 mV·s^{-1}

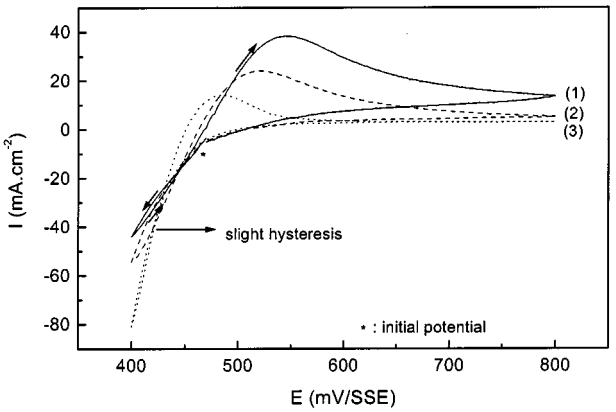

Figure 12. Cyclic voltammograms for HNO_3 4 mol·L^{-1} at 100 °C containing [HNO_2] = 10^{-2} mol·L^{-1} at different scan rates. (1): 500 mV·s^{-1} (2): 100 mV·s^{-1} (3): 10 mV·s^{-1}

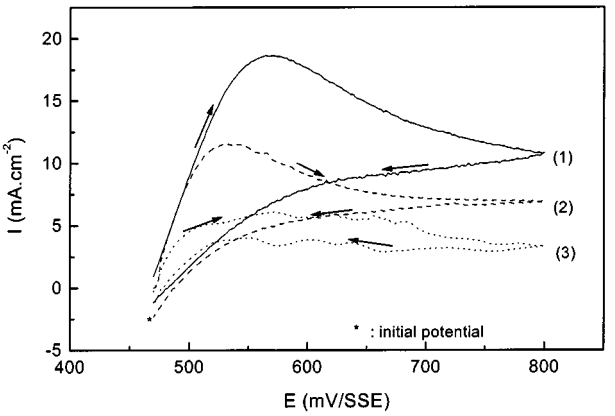

Figure 13. Voltammograms in oxidation for HNO_3 4 mol·L^{-1} containing [HNO_2] = 10^{-2} mol·L^{-1} at 100 °C at different scan rates. (1): 500 mV·s^{-1} (2): 100 mV·s^{-1} (3): 10 mV·s^{-1}

the reduction process. Therefore, the presence of nitrites in solution accelerates the chemical reaction and provokes the disappearance of the hysteresis and the increase in the reduction current densities for high scan rates;

– for HNO_3 8 mol·L^{-1}, the charges in reduction are multiplied by 1.5 for scan rates higher than 30 mV·s^{-1}; in oxidation they are multiplied by 2 for scan rates higher than 300 mV·s^{-1};

– for HNO_3 12 mol·L^{-1}, no major differences are observed with nitrites.

The presence of nitrites promotes the establishment of the steady state in reduction: nitrites in the bulk accelerate the attainment of the concentration in active species near the electrode to reduce nitric acid. For concentrated nitric acid, this concentration is reached rapidly as the chemical regeneration of the active species proceeds easily and therefore a supplementary addition of nitrites does not influence the reduction process.

Direct scans were also performed in oxidation. Figure 13 shows the voltammograms obtained for different scan rates in HNO_3 4 mol·L^{-1}. The same experiments performed in pure nitric acid display a voltammogram without peak which means that the oxidation peak is attributable to the

oxidation of nitrites into nitric acid; this is confirmed by literature data.[16]

If the current density of the oxidation peak is plotted versus the square root of the scan rate for HNO_3 4 mol·L^{-1}, 8 mol·L^{-1} and 12 mol·L^{-1} (Figure 14), a linear variation is obtained in a large range. Thus it is possible to assume that the current is diffusion controlled.

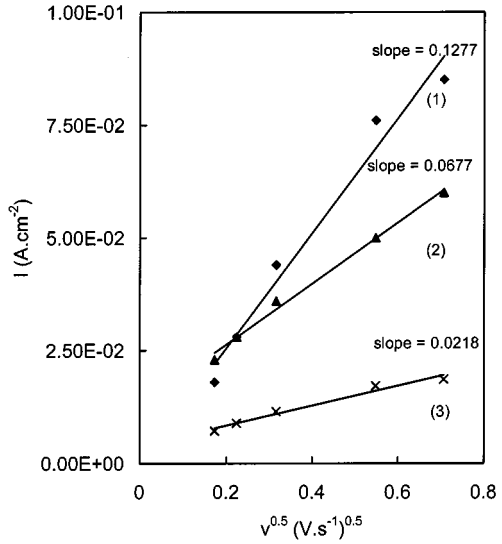

Figure 14. Influence of the scan rate on the variation of the oxidation peak current density for different nitric acid solutions at 100 °C containing approximately [HNO_2] = 10^{-2} mol·L^{-1}. (1): 12 mol·L^{-1} (2): 8 mol·L^{-1} (3): 4 mol·L^{-1}

A diffusion coefficient has been deduced according to:[17a]

$I_p = (2.40 \times 10^5) n^{3/2} D_0^{1/2} v^{1/2} C_0^*$

where

I_p = peak current density [A·cm^{-2}]

n = number of electrons involved in the oxidation charge transfer step

D_0 = diffusion coefficient [cm^2·s^{-1}]

v = scan rate (V·s^{-1})

C_0^* = nitrite concentration [mol·cm^{-3}]

The value of n is $n = 2$, as the oxidation reaction is supposed to be the oxidation of nitrites into nitric acid:

$$HNO_2 + H_2O = HNO_3 + 2H^+ + 2e^-$$

Table 4 shows the diffusion coefficients obtained for a nitrous acid concentration of approximately 10^{-2} mol·L^{-1}, in the different nitric acid solutions.

Table 4. Diffusion coefficient of nitrous acid in nitric acid solutions at 100 °C as a function of nitric acid concentration

[HNO_3] [mol·L^{-1}]	D_0 [cm^2.s^{-1}] and interval of error
4	3×10^{-5} [$8 \times 10^{-6} - 9 \times 10^{-5}$]
8	2×10^{-5} [$5 \times 10^{-6} - 6 \times 10^{-5}$]
12	7×10^{-4} [$2 \times 10^{-4} - 2 \times 10^{-3}$]

The interval of error of the diffusion coefficient is calculated from the error in the value of the concentration of nitrous acid in solution. The concentration of nitrous acid was not directly measured in these experiments. It was calculated from the OCP according to the thermodynamic data obtained previously.[3] The error in the OCP is supposed to be ± 10 mV. The error in the nitrous acid concentration and the error in the diffusion coefficient can then be deduced.

Table 4 shows higher diffusion coefficients for more concentrated HNO_3. This variation may be due to a difference in the chemical form of the diffusing species: for example HNO_2 in less concentrated medium and NO^+ in more concentrated medium. The uncertainty in the measurement minimizes this interpretation and supplementary measurements would be necessary to confirm this result.

Chronoamperometry

Figure 15 shows the variation of the current density with time for a potential of 0.400 V/SSE for the different nitric acid concentrations.

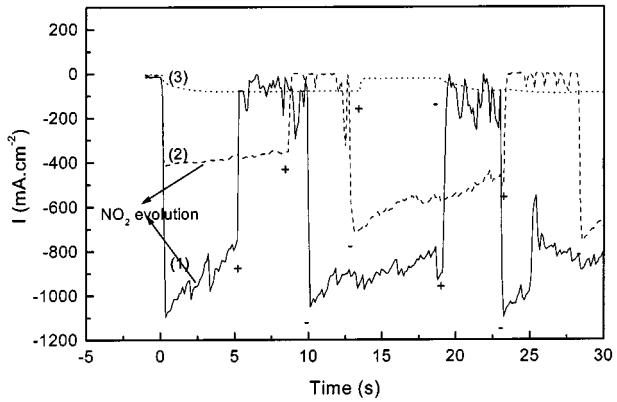

Figure 15. Influence of the stirring on the limiting current density of different nitric acid solutions at 100 °C containing [HNO_2] = 10^{-2} mol·L^{-1} for a potential of 0.400 V/SSE. ω = 2000 rpm; +: stirring; −: no stirring. (1): 12 mol·L^{-1} (2): 8 mol·L^{-1} (3): 4 mol·L^{-1}

The current densities are the same as when there are no nitrites in solution and the stirring of the solution provokes a similar decrease of the current density. Nitrites do not influence the stationary current densities (without stirring) as was already observed with the voltammograms performed at low scan rates.

For HNO_3 4 mol·L^{-1}, the stirring of the electrode provokes a decrease of the stationary current density which stabilizes at a value different from zero: this current is due to the nitrites present in solution.

For HNO_3 8 mol·L^{-1} and 12 mol·L^{-1}, the stirring of the electrode provokes a decrease of the current density similar to when there were no nitrites initially present in solution: the value of the current becomes nearly equal to zero. This result can be explained by the fact that in concentrated nitric acid, nitrites are less stable and an evolution of NO_2 occurs.

Influence of a Flow of Nitrogen Monoxide for HNO_3 4 mol·L^{-1} at 100 °C

The influence of a flow of nitrogen monoxide (flow rate = 1 L·h^{-1}) on the reduction process was studied in

HNO_3 4 mol·L^{-1}. A pressure of p_{NO} = 0.8 bar was imposed by fixing the flow rates of nitrogen monoxide and of an inert gas.

In Figure 16, the voltammograms obtained in the presence of NO and nitrites are compared with the voltammogram obtained without any addition, at a scan rate of 100 mV·s^{-1}. The presence of NO has the same influence as the addition of nitrites: it provokes an increase in the current densities in oxidation and in reduction and the disappearance of the hysteresis. The slight increase in the current densities with NO relative to nitrites is due to the fact that the pressure of NO imposed fixes a concentration in nitrites in solution higher than the concentration added in the other experiments: [HNO_2] = 3.5×10^{-2} mol·L^{-1} (experimental measurement) for p_{NO} = 0.8 bar.

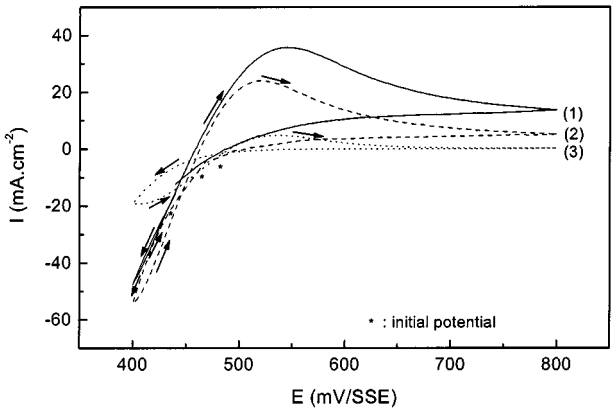

Figure 16. Cyclic voltammograms for HNO_3 4 mol·L^{-1} at 100 °C under different conditions at a scan rate of 100 mV·s^{-1}. (1): p_{NO} = 0.8 bar (2): [HNO_2] = 10^{-2} mol·L^{-1} (3): no addition

Voltammograms were performed at different scan rates in oxidation. Figure 17 presents the results obtained. If the current density of the oxidation peak is plotted versus the square root of the scan rate (Figure 18), a linear variation is obtained similar to the variation obtained in the presence of nitrites.

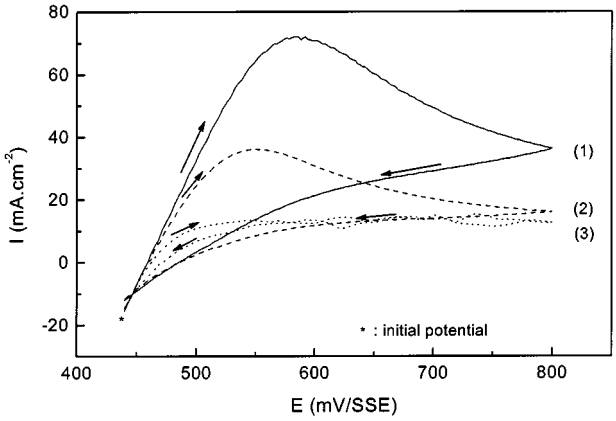

Figure 17. Voltammograms in oxidation for HNO_3 4 mol·L^{-1} under p_{NO} = 0.8 bar at 100 °C at different scan rates. (1): 500 mV·s^{-1} (2): 100 mV·s^{-1} (3): 10 mV·s^{-1}

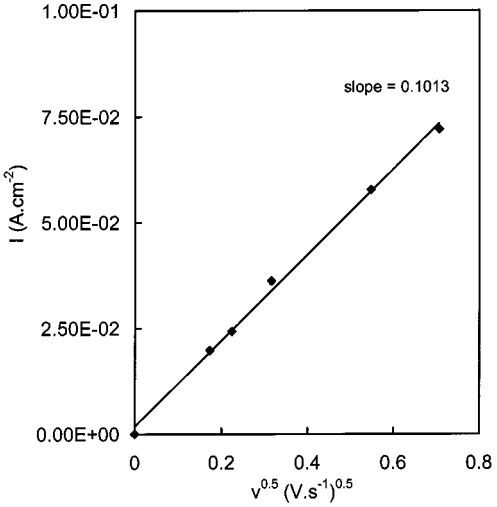

Figure 18. Influence of the scan rate on the variation of the oxidation peak current density for HNO_3 4 mol·L^{-1} at 100 °C under p_{NO} = 0.8 bar

The diffusion coefficient of nitrous acid can be calculated (the interval of error is estimated as in section 'voltammetry'), assuming that the reoxidation peak observed is attributed to the oxidation of nitrites into nitric acid:

$$D_0 = 2 \times 10^{-5}\ \text{cm}^2\cdot\text{s}^{-1}\ [5 \times 10^{-6} - 6 \times 10^{-5}]$$

Chronoamperometric measurements were also performed (Figure 19). The influence of the stirring causes a decrease in the reduction current which stabilizes for a value different from zero. This current is due to the presence of nitrites in solution.

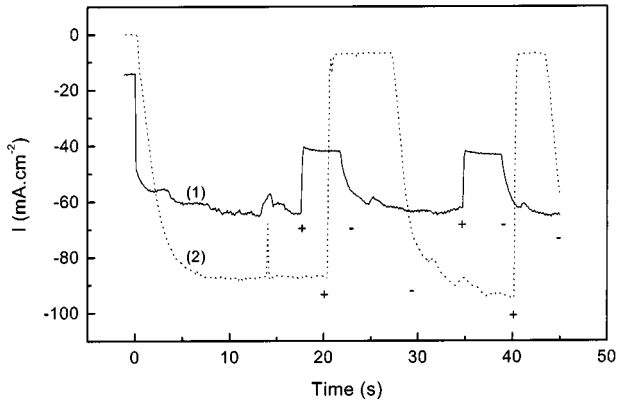

Figure 19. Influence of the stirring on the limiting current density of HNO_3 4 mol·L^{-1} at 100 °C under different conditions for a potential of 0.400 V/SSE. ω = 2000 rpm; +: stirring; −: no stirring. (1): p_{NO} = 0.8 bar (2): no addition

In fact, without stirring, at the steady state, the nitrous acid concentration at the electrode is much higher than in the bulk and this difference is larger for low nitric acid concentrations. When the solution is stirred, the nitrous acid concentration at the electrode is equal to the concentration in solution.

Mechanism of Reduction of Nitric Acid at a Platinum Electrode at 100 °C

It appears from this study that the major parameters for explaining the reduction of nitric acid are firstly the concentration range of nitric acid, and secondly the concentration of nitrous acid. The nitric acid molecule is not directly reduced; it is reduced through an autocatalytic mechanism involving an electrochemical step and a chemical reaction regenerating the active species. The electroactive species is formed at the electrode and diffuses into the solution: this explains the influence of the stirring on the current density. Moreover, it is possible to assume that the electroactive species is a soluble compound. The regeneration reaction is rapid for high HNO_3 concentrations and slow for low concentrations; this provokes the appearance of the hysteresis phenomenon. The electroactive species is believed to be nitrous acid which is the major soluble species present in nitric acid. This is confirmed by the increase in the current densities in reduction in the presence of nitrous acid in solution: this increase is sharp for low nitric acid concentrations and high scan rates and becomes nonexistent for HNO_3 12 mol·L^{-1}. Moreover nitrous acid suppresses the hysteresis phenomenon.

The influence of nitrogen monoxide was shown to be the same as nitrous acid. Therefore it is possible to assume that nitrogen monoxide reacts partly with nitric acid to form nitrous acid. The reduction of nitric acid leads to the formation of NO or NO_2 depending on the potential and the nitric acid concentration.

These conclusions, along with the literature data, allow us to propose a unique reduction mechanism of nitric acid valid for the whole nitric acid concentration range with reaction rates depending on the nitric acid concentration. This mechanism can be divided into two limiting cases, one for the lower concentrations and one for the higher concentrations. In all cases, the charge transfer step is the reduction of nitrous acid into nitrogen monoxide:

$$(HNO_2)_{el.} + H^+ + e^- + s = (NO)_{ads.} + H_2O \quad (1)$$

where 's' represents a free adsorption site.

Then, the chemical regeneration of the active species occurs; this reaction is heterogeneous and produces the electroactive species, HNO_2. It also produces nitrogen dioxide (reduction product for high nitric acid concentrations):[3]

$$HNO_3 + (NO)_{ads.} = (HNO_2)_{el.} + (NO_2)_{ads.} \quad (2)$$

The rate of reaction (2), which is the regeneration reaction, depends on the nitric acid concentration and on the nitrogen monoxide pressure. The rate of the charge transfer step (1) is also influenced, and usually promoted, by a high nitric acid concentration.

A third reaction (3) also occurs:

$$HNO_3 + (HNO_2)_{el.} + 2s = 2(NO_2)_{ads.} + H_2O \quad (3)$$

Reactions(1), (2), (3) are the elementary reactions of the reduction mechanism of nitric acid valid over the whole concentration range. For HNO_3 4 mol·L^{-1}, the regeneration reaction (2) is slow: this causes the hysteresis phenomenon appearing for high scan rates. Therefore, NO formed during the charge transfer step can accumulate and eventually evolve. Reaction (3), in low concentrated medium, promotes the formation of HNO_2, as NO_2 is not stable for concentrations lower than 8 mol·L^{-1}.

Finally, for nitric acid concentrations lower than 8 mol·L^{-1}, the reduction mechanism of nitric acid can be expressed as:

$$(HNO_2)_{el.} + H^+ + e^- + s = (NO)_{ads.} + H_2O \quad (1)$$

$$HNO_3 + 2(NO)_{ads.} + H_2O = 3(HNO_2)_{el.} + 2s \quad (4)$$

where (4) = 2 × (2) – (3)

$$(NO)_{ads.} = (NO)_{g.} + s \quad (5)$$

$$(HNO_2)_{el.} \rightarrow (HNO_2)_{sol.} \quad (6)$$

In the case of HNO_3 12 mol·L^{-1}, the chemical regeneration, reaction (2), promoted by a high nitric acid concentration, is fast and leads to an evolution of NO_2, the stable reduction product for high nitric acid concentrations. The overall reduction mechanism can be described as:

$$(HNO_2)_{el.} + H^+ + e^- + s = (NO)_{ads} + H_2O \quad (1)$$

$$HNO_3 + (NO)_{ads} = (HNO_2)_{el.} + (NO_2)_{ads} \quad (2)$$

$$(NO_2)_{ads} = (NO_2)_{g.} + s \quad (7)$$

$$(HNO_2)_{el.} \rightarrow (HNO_2)_{sol.} \quad (6)$$

Reaction (3) also occurs and is supposed to be at equilibrium. The gaseous species NO and NO_2 are supposed to be adsorbed at the electrode surface, and nitrous acid is a soluble compound formed at the electrode which diffuses into the solution. Therefore, in the reduction mechanism, desorption steps of gaseous species and a diffusion step for nitrous acid have to be added.

Conclusion

The major species involved in the reduction process of nitric acid at low overvoltages have been determined to be HNO_2, NO and NO_2. A mechanism has been proposed, which takes into account the literature data and the experimental results of this paper. It has been shown that: – nitric acid is not the electroactive species; it is reduced indirectly through an autocatalytic process; – nitrous acid is the electroactive species which is reduced into nitrogen monoxide; – nitrous acid is regenerated at the electrode according to a heterogeneous chemical reaction involving nitrogen monox-

ide and nitric acid; – a reduction mechanism for the whole nitric acid concentration range has been proposed depending on the nitric acid concentration: for concentrations higher than 8 mol·L^{-1}, the reduction of nitric acid leads to an evolution of NO_2 and for lower concentrations, it leads to an evolution of NO.

This electrochemical study of the reduction process of nitric acid on a platinum electrode allows us to propose a unique reduction mechanism valid over the whole concentration range. In the next step of our work, similar electrochemical experiments will be performed on a stainless steel electrode to compare the reduction mechanism observed on both materials and then to link the final reduction mechanism with the results of the corrosion tests performed in the laboratory.[4] This last step will be presented in a subsequent paper.

Experimental Section

Reactor Cell: The reactor containing 50 mL of solution was regulated at 100 °C. The working electrode consisted of a platinum disk electrode (area 0.0314 cm^2) polished to a mirror finish. The following circuit was set up for measuring the electrode potential: working electrode/HNO_3, solution 100 °C/HNO_3 solution, 25 °C/saturated KNO_3 solution, 25 °C/saturated K_2SO_4 solution, 25 °C/mercurous sulfate electrode, 25 °C. The reference electrode was a mercurous sulfate electrode (SSE) and is described as: $Hg/Hg_2SO_{4(sat.)}$, $K_2SO_{4(sat.)}$. The potential of this reference electrode versus the standard hydrogen electrode at 25 °C is E_{SSE} = 0.640 V/SHE.[17b]

Electrochemical Apparatus and Procedure: The potential measurements were made with an EGG PAR Model 273 potentiostat. A rotating disk electrode Tacussel EDI 101 T was used to evidence the hydrodynamic effect on the reduction process. Experiments were carried out in 4 mol·L^{-1}, 8 mol·L^{-1}, and 12 mol·L^{-1} nitric acid solutions at 100 °C. The influence of nitrous acid was studied by adding sodium nitrite at a concentration of about 10^{-2} mol·L^{-1} in the solution. The influence of nitrogen monoxide was investigated by imposing a pressure of p_{NO} = 0.8 bar in the cell. The concentration of nitrous acid (nitrite ions) in solution was measured by colorimetry with a Perkin–Elmer UV/Visible spectrometer according to the Griess method.[18]

Acknowledgments

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