Article

# On the Nb(V) Electrochemistry in "Dry" Acetonitrile

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A redução de Nb(V) em acetonitrila, contendo até 10 mM de água residual, foi investigada em função das concentrações de cloreto e de Nb(V). O efeito provocado pela adição de HCl e de um doador de prótons sobre o comportamento voltamétrico foi também investigado. Antes de ocorrer uma transferência eletrônica, o NbCl5 inicialmente se hidrolisa resultando na formação de espécies contendo grupos hidroxila e HCl, os quais se encontram em equilíbrio. Nb(IV) formado após uma transferência monoeletrônica se hidrolisa, formando uma espécie eletroinativa ou, dependendo da condições experimentais usadas, se dimeriza (em TEAP) ou se desproporciona (em TEACl). Redução do Nb(IV) a um estado de oxidação menor é possível na presença de cloreto, o qual age como agente estabilizante. A hidrólise de Nb(IV) resulta em HCl, cujos picos de redução se encontram no mesmo intervalo de potencial da redução de Nb(IV). Nb(IV) não se hidrolisa quando concentrações adequadas de HCl e/ou TEACl estão presentes na solução. Uma comparação por simulação do mecanismo eletródico proposto com os dados experimentais é apresentada.

The Nb(V) reduction in acetonitrile, containing up to 10 mM residual water, was investigated as a function of chloride and Nb(V) concentrations. The effect caused by hydrogen chloride and a proton donor was also examined. Before any electron transfer occurs NbCl5 initially hydrolyzes resulting in HCl and hydroxy-species, all being in equilibrium. Nb(IV) formed after a monoelectronic reduction can either hydrolyze, yielding an electroinactive species, or, depending on experimental conditions used, dimerize (in TEAP) or disproportionate (in TEACl). Futher reduction of Nb(IV) is possible in the presence of chloride, which acts as a stabilizing agent. Nb(IV) hydrolysis yields HCl whose reduction wave overlaps with the peaks from futher Nb(IV) reduction. Nb(IV) does not hydrolyze if adequate amounts of HCl and/or TEACl are present in solution. A comparison is made between simulation of the proposed electrode mechanism and experimental data.

**Keywords:** *electrochemistry, niobium, reduction, non-aqueous solvent*

## Introduction

Niobium is known to possess properties which favorably combine mechanical and corrosion resistance[1]. Numerous applications have been proposed such as turbine blades, leading edges for high speed aircraft[2], batteries[3] and superconductors[4].

Despite its potential, there is a lack of information on niobium electrochemistry, especially when compared with the existing knowledge of other metals. Currently, two detailed mechanisms for Nb(V) reduction in non-aqueous media are found in the literature: Sherman and Archer's[5] in dimethylformamide (DMF) and Kirk *et al.*[6] in acetonitrile (AN). The former authors worked with ordinary dry DMF whose residual water content is greater than the Nb(V) concentration investigated; the latter authors worked with carefully dried AN with a residual water content of less than 0.01 mM. So, the actual initial electroactive species investigated in both studies were different, despite the fact that both investigations used NbCl5 as

starting material. In this paper we are concerned with the electroreduction of Nb(V) in AN in the presence of a "normal" water content (~10 mM). These experimental conditions are close to Sherman and Archer's.

Sherman and Archer proposed that Nb(V) is reduced mono-electronically in a first step. Next, Nb(IV) dimerizes and disproportionates intramolecularly before it can be reduced bi-electronically forming NbO, which precipitates. An important point in their work is the fact that they consider HCl formation through reaction of Nb(V) with residual water of the solvent. HCl is detected in the electrochemical experiments as it is electroactive in the potential region considered. The role of HCl has not been considered in earlier mechanistic studies[7,8].

The formation of Nb(II) through electrolysis of Nb(V) in DMF has been criticized by Bosselaar *et al.*[9]. These authors analyzed the precipitate formed and concluded that significant amounts of carbon, nitrogen and hydrogen, together with a small amount of chloride, were present. The amount of niobium present in the precipitate was much lower than expected for NbO. They also argued that the color described in Sherman and Archer's paper does not correspond to that reported previously by other authors.

As far as we know, stable Nb(II) has only been obtained by NbCl$_5$ electroreduction, at temperatures above 170 °C, in non-aqueous media containing ethylene glycol[10].

In view of the limited amount of work done on the non-aqueous electrochemistry of Nb(V) and the conflicting results reported in the literature, we thought it worthwhile to futher investigate Nb(V) in order to gain more insight on its electrochemical behavior in non-aqueous solvents containing small amounts of residual water.

## Experimental

All reagents used were *purum*, P.A., *supra-purum* or spectroscopic grade. The purity of tetraethylammonium perchlorate, TEAP, (Eastman) and chloride, TEACl, (Schuchardt) in acetonitrile, AN, (Merck), used as supporting electrolytes, was checked by cyclic voltammetry. Before use, TEAP and TEACl solutions were left over activated 0.3 nm molecular sieve (Merck) for several hours. Karl-Fischer titration revealed a residual water content of 6-10 mM. Solutions were stored in bottles fitted with stopcocks. From them, aliquots were drawn and transferred to the electrochemical cell by means of a syringe and a surgical catheter, thus minimizing contact with atmospheric humidity. The electrochemical cell was heated at 150 °C and cooled down under nitrogen flow, before transference of any supporting electrolyte. Nitrogen was purified by passing the gas through: a catalyst (BASF), H$_2$SO$_4$ (conc.), solid KOH, activated molecular sieve and, finally, AN. After deaerating the supporting electrolyte for 30 min, nio-

bium stock solution was added and the solution further deaerated for 3 min. The faintly yellow 30-50 mM niobium pentachloride (Koch & Light) stock solution in AN (previously dried over molecular sieve) was stored in a volumetric flask inside a desiccator containing CaCl$_2$. HCl in AN was prepared by bubbling the dry gas through the solvent.

Cyclic voltammetric experiments were carried out with either a PAR 273 potentiostat or a PAR 173 equipped with a PAR 175 function generator and a HP7090 measurement system connected to a microcomputer through a HPIB card (IEEE protocol). Coulometric experiments were executed using a PAR 173 potentiostat equipped with a PAR 179 module. Polarograms were recorded using a Polarecord (Metrohm/Switzerland) E506 plus E505 equipment. A 10 mV p/p amplitude and 75 Hz frequency a.c. signal was used. The working electrode was Hg, the auxiliary electrode Pt and the reference electrode a silver wire inserted in a Luggin capillary filled with 0.1M TEAP/0.01 M AgNO$_3$ solution. All potentials reported are referred against this reference electrode. The solution ohmic resistance, determined by Schultze's method[11], was approximately 170 and 120 $\Omega$ for 0.1 M TEAP and 0.1 M TEACl solutions, respectively.

## Results and Discussion

### Polarography

A single dc wave or ac peak was observed in the polarograms recorded in 0.1 M TEAP. Two peaks were observed in 0.1 M TEACl. Logarithmic analysis of the first dc wave resulted in a straight line for both TEACl and TEAP solutions. Table 1 summarizes the dc and ac polarographic parameters of the first wave. The values for the slope (dc) and width at half-height(ac), $\Delta E_{peak/2}$, are greater than the theoretically expected values for a reversible monoelectronic process (59 mV and 91.1 mV[12] for the dc and ac case, respectively), indicating deviation from reversibility. For irreversible electron transfers, theory predicts a very small ac signal for experimental conditions such as the ones used by us (Nb(V) = 0.47 mM). Since a significant ac current signal was obtained (see Table 1) irreversibility of the first ac peak can be excluded. A comparison of the slopes (dc) and $\Delta E_{peak/2}$ (ac) values for both supporting electrolytes (see Table 1) demonstrates a slightly more pronounced deviation from reversible behavior for the TEAP system.

The nature of the second wave in TEACl proved to be complex, so no meaningful analysis could be made. No evidence of adsorption in the potential range investigated was obtained from the ac polarographic results.

Changing systematically the perchlorate to chloride in the supporting electrolyte resulted, for the first Nb(V)

**Table 1.** Polarographic parameters, dc and ac, for the Nb(V)/Nb(IV) wave. 0.47 mM NbCl₅ in 0.1 M TEAP/AN and 0.1 M TEACl/AN.

| | $-E_{1/2}$ (V) | $i_{lim}$ (μA) | slope (mV) | $-E_{peak}$ (V) | $\Delta E_{peak}$ (V) | $i_{peak}$ (μA) |
|---|---|---|---|---|---|---|
| TEAP | 1.021 | 0.80 | 76 | 1.056 | 132 | 0.28 |
| TEACl | 1.036 | 0.86 | 69 | 1.176 | 110 | 0.44 |

wave, in a cathodic shift in the half-wave potential (ac peak potential) with a simultaneous increase of the current.

Polarographic data obtained with the TEACl supporting electrolyte, where Nb(V) hydrolysis is much less pronounced (see cyclic voltammetric results), allowed the calculation of the Nb(V) species diffusion coefficient, using the Ilkovic equation; a value of $1.1 \times 10^{-5}$ cm² s⁻¹ was obtained
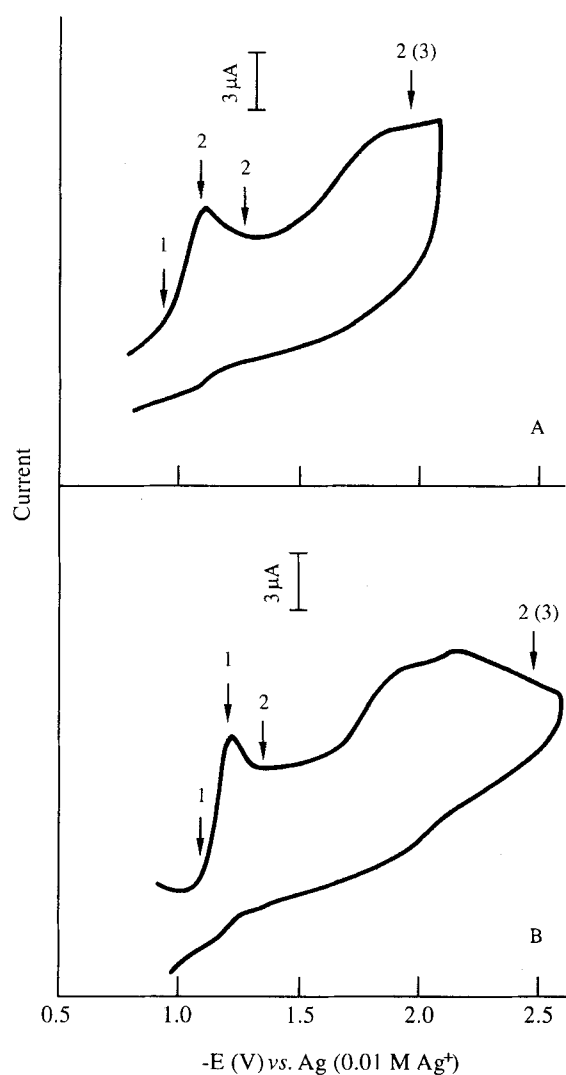


Figure 1. Cyclic voltammograms of 0.47 mM NbCl₅ in AN. (A) 0.1 M TEAP; (B) 0.1 M TEACl. $v = 1.0$ V s⁻¹. Arrows indicate $E_{app}$ used in the coulometric experiments. The numbers on the curves show the n-values obtained in the absence (without parenthesis) and in the presence (with parenthesis) of 7.4 mM HCl added on purpose.

## Cyclic voltammetry

### Preliminary investigations

Representative Nb(V) cyclic voltammograms, CV, are shown in Fig. 1. All voltammograms show a first, well defined peak, followed by a second, broad, ill defined wave. Using 0.1 M TEAP as supporting electrolyte, independently of the switching potential used, no anodic wave was observed even at sweep rates of 20 V s⁻¹. Using 0.1 M TEACl as supporting electrolyte and low sweep rates the general form of the CV is similar to the one obtained using 0.1 M TEAP.

The only difference observed is a cathodic shift together with a slight increase of the current. At sweep rates ≥ 800 mV s⁻¹ (see Fig. 5), however, an anodic peak corresponding to the first cathodic peak is obtained with this electrolyte. For both supporting electrolytes no modification in the voltammograms is observed whether they are recorded immediately after dilution of Nb(V) stock solution or after waiting for 30 min. Gradual addition of water, dissolved in AN, to 0.47 mM Nb(V)/0.1 M TEAP solutions initially resulted in a decrease of the voltammetric curve. Futher addition of water turned the solution turbid, indicating Nb(V) hydrolysis. Since TEAP is only moderately soluble in water, an alternative explanation for the turbidity could be TEAP precipitation. This possibility was ruled out by adding identical water quantities to the same volume of pure supporting electrolyte. No turbidity was observed. Similar tests executed with 0.47 mM Nb(V)/0.1 M TEACl revealed higher water contents are necessary to obtain identical behavior, suggesting that chloride ions stabilize the Nb(V) species. This preliminary investigation also showed that a ≈10mM residual water content of AN is not capable of hydrolysing Nb(V) to the extent that insoluble species are formed. The formation, however, of partially hydrolyzed soluble Nb(V) species (e.g. Nb(OH)ₓCl(5-x), etc.) must be taken into account.

The processes occuring at potentials more cathodic than the first peak are not well characterized. The wave observed in this potential region is quite broad, probably due to more than one process occurring simultaneously. It exhibits irreversible behavior (no anodic peak is observed even at sweep rates as high as 20 V s⁻¹). The irreversible behavior of the second wave is observed for both 0.1 M TEACl and 0.1 M TEAP.

Sherman and Archer[5] considered HCl formation in their mechanistic proposal. We therefore found it necessary to
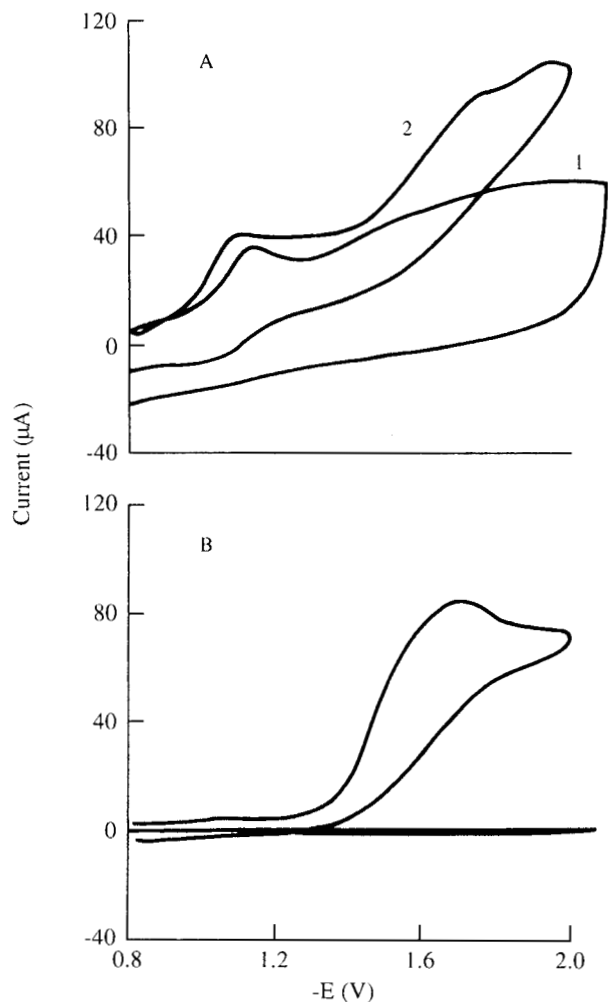
**Figure 2.** Cyclic voltammograms of (A) 1: 0.47 mM NbCl5; 2: 0.47 mM NbCl5 + 2.8 mM HCl. Supporting electrolyte: 0.1 M TEAP. $v = 10$ V s$^{-1}$. T = 25 °C. (B) 2.8 mM HCl.

compare a Nb(V) voltammogram with a voltammogram of pure HCl, recorded under the same experimental conditions (Fig. 2). A comparison of both CV's revealed the irreversible HCl reduction wave to fall in the same potential region as the second, ill defined Nb(V) wave.

The irreversible nature of the HCl reduction was described earlier by Coetze and Kolthoff[13]. Deliberate addition of dry HCl/AN solution to the Nb(V) solution resulted in an increase of the current over the whole potential range investigated (first and second wave, Fig. 2A).

### Investigation of the Nb(V)/Nb(IV) peak

The influence of chloride ion on the first voltammetric peak was investigated by gradually substituting TEACl for TEAP, keeping the total ionic strength constant at 0.1 M. An aproximately 30% increase in the current was observed when [TEACl] = 0.03 M. The current no longer increased

for higher TEACl concentrations. Independently of sweep rate (0.2 - 20 V s$^{-1}$) E$_{peak}$ shifts 50-59 mV with log[TEACl].

This experimental behavior can be explained assuming the existence of an equilibrium involving the electroactive species and chloride ions. Such a mechanism was theoretically treated by Matsuda and Ayabe[14].

Based on the experimentally observed E$_{peak}$ shift of about 59 mV the ratio between the number of ligands and electrons, m/n, can be assumed to be unity. Since in the coulometric study the number of electrons transferred in the first peak was found to be one it must be concluded that the number of Cl-ligands involved in this reduction is also one.

It has been suggested that the first one-electron Nb(V) electrode process behaves irreversibly in DMF[5]. For 0.1 M TEAP our results also point to an irreversible overall electrode process of the Nb(V)/Nb(IV) peak. In fact, for this supporting electrolyte, no anodic peak was observed even at sweep rates as high as 20 V s$^{-1}$. For 0.01-0.1 M TEACl, however, mechanistic criteria support q-reversibility for the first peak: (a) an anodic peak is observed at the higher sweep rates; (b) E$^{I}_{p,c}$ is independent of v; (c) i$_{p,a}$/i$_{p,c}$ tends to unity at the higher sweep rates. Using the working curve proposed by Nicholson[15] for a q-reversible electron transfer and the Nb(V) diffusion coefficient estimated from the polarographic results, a value of 0.011 cm s$^{-1}$ was calculated for the heterogeneous rate constant, k$^{o}_{sh}$, of the first one-electron transfer. During simulations (see later) no modification of this value was necessary in order to fit the theoretical and experimental voltammograms obtained in TEAP. For TEACl a slightly higher k$^{o}_{sh}$ value was necessary.

The results of our study strongly suggest the overall electrode process representing the first CV peak to behave irreversibly due to hydrolysis of the electroformed Nb(IV). However, the electron transfer itself Nb(V) → Nb(IV) is reversible as supported by the k$^{o}_{sh}$ value. Futher, the fact that with TEACl an anodic peak is already observed at modest sweep rates (0.8 V s$^{-1}$) supports the Nb(IV) hydrolysis rate to be lower in this supporting electrolyte, suggesting the chloride ion to exert a stabilizing effect on the Nb-species.

To evaluate the importance of the hydrolysis of the intermediate, a study was conducted investigating the influence of a proton donor as a function of its concentration and the sweep rate. Trifluoroacetic acid, TFAA, is suitable for such a study. In the presence of TFAA the discharge of the supporting electrolyte is anticipated to lie around -1.3 V, fortunately not interfering with the first Nb(V) reduction peak (except for TEACl at low sweep rates).

The effects observed on the CV with increasing TFAA concentration are: i) an increase of the peak current and ii) an anodic shift of the peak potential. The current increases

approximately 50% in the presence of about 30 mM TFAA. For both 0.1 M TEAP and 0.1M TEACl the peak potential shifts linearly with log[TFAA]. For the TEAP supporting electrolyte the slope, $\partial E_{peak}/\partial log[TFAA]$ varies between -40 to -60mV for sweep rates between 0.02 and 1 V s$^{-1}$. For the TEACl supporting electrolyte, the slope decreases monotonically from 23 mV at 50 mV s$^{-1}$ to zero at 5 V s$^{-1}$. So the importance of protons on the niobium behavior decreases in the presence of chloride. At 5 V s$^{-1}$, the time window of the experiment is small enough to prevent chemical reactions involving protons to exert a significant influence on the electrode behavior.

These experimental results also suggest the participation in the electrode mechanism of an equilibrium, involving the electroactive species, preceding the first electron transfer. The observed TFAA effects on $i^I_p$ and $E^I_p$ are explained as the result of a displacement of the pre-equilibrium in favour of the electroactive species, resulting in an increase of its equilibrium concentration.

The behavior of $E^I_p$ and $i^I_p$ as a function of Nb(V) concentration is shown in Figs. 3 and 4, for both supporting electrolytes.

For 0.1 M TEACl and sweep rates between 0.2 and 5 V s$^{-1}$, the peak potential is independent on log[Nb(V)]. On the other hand, for 0.1 M TEAP a linear dependence on log[Nb(V)] is observed showing a slope of 59 m V at 0.2 V s$^{-1}$ and 21 mV at 1 V s$^{-1}$. The deviation from linearity, observed at the higher Nb(V) concentrations, is due to ohmic drop taking effect and is more pronounced at the higher sweep rates.

Figure 4 shows the linear dependence between $i^I_p$ and the concentration, observed for both supporting electrolytes, up to approximately [Nb(V)] = 1.5 mM. At higher
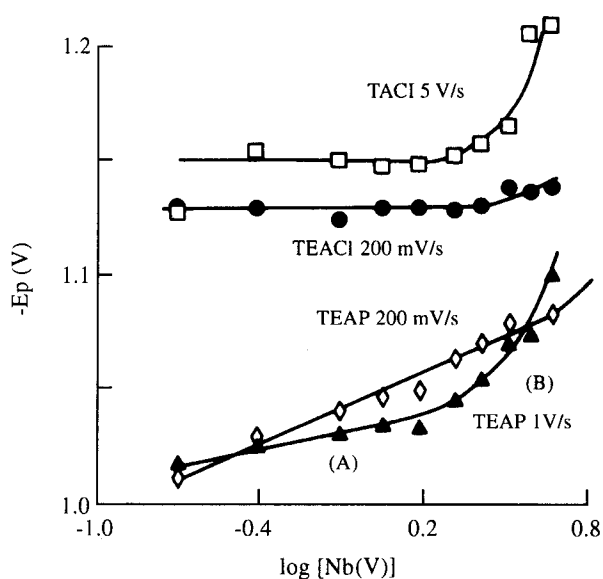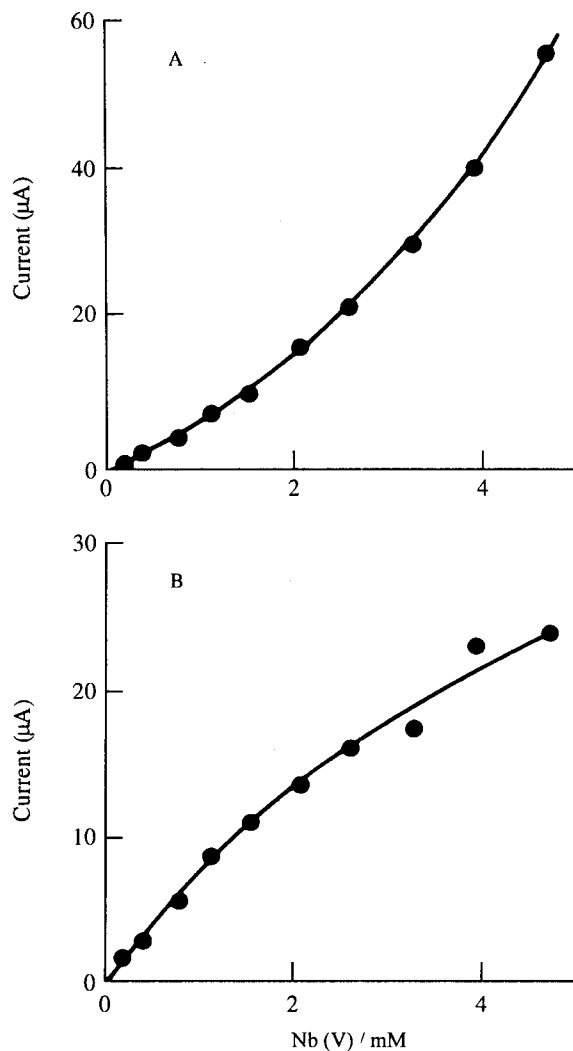


**Figure 4.** Influence of Nb(V) concentration on the peak current of the first voltammetric wave. $v = 0.2$ V s$^{-1}$. (A) 0.1 M TEACl. (B) 0.1 M TEAP.

concentrations, the deviation from linearity of the $i^I_p$ vs. [Nb(V)] plot, observed for 0.1 M TEACl, can be explained assuming disproportionation of Nb(IV). The linear dependence of the $E^I_p$ vs. log[Nb(V)] plot, observed for 0.1 M TEAP, suggests the occurence of a second order reaction, probably dimerization of Nb(IV), following the first electron transfer. A dimerization reaction involving Nb(IV) has no effect on $i_pI$. So, the negative deviation from linearity observed in the $i^I_p$ vs. [Nb(V)] plot (see Fig. 4) must be a consequence of the preceding equilibrium (see electrode mechanism, step 1) which is displaced to the right with increasing Nb(V) concentration, resulting in a decrease of the equilibrium concentration. It should be noted that for the experimental conditions used in the other electrochemical techniques ([Nb(V)] = 0.47 mM) such second order reactions do not have significant influence on the electrode process.



**Figure 3.** Influence of Nb(V) concentration on the peak potential of the first voltammetric wave.

**Table 2.** Coulometric results for 0.47 mM NbCl₅ in 0.1 M TEAP/AN and 0.1 M TEACl/AN

| TEAP | | TEACl | |
|---|---|---|---|
| Applied Potential (V) | number of electrons | Applied Potential (V) | number of electrons |
| -0.950 | 0.75 | -1.078 | 1.17 |
| -1.100 | 1.95 | -1.228 | 1.08 |
| -1.277 | 1.90 | -1.350 | 2.09 |
| -2.000 | 1.93 | -2.500 | 1.93 |
| -2.000 | 2.80* | -2.500 | 2.93* |

* Results obtained in the presence of 7.4 mM HCl deliberately added.

These results corroborate literature data where, for both aqueous and non aqueous media, Nb(IV) dimerization or disproportionation have frequently been proposed[5,6,16-19].

*Controlled potential coulometry, CPC*

Coulometric experiments were carried out at selected potentials. Figure 1 shows Nb(V) voltammograms in 0.1 M TEAP and 0.1 M TEACl, the arrows indicating the potentials utilized in the CPC experiments together with the n-values obtained. The results are summarized in Table 2.

For TEACl and an applied potential, $E_{app}$, localized at the top of the first peak, a 1 Fmol⁻¹ value was obtained. The same result was obtained with $E_{app}$ at the foot of the peak. In the latter experiment the time needed to observe complete Nb(V) reduction was, as expected, much longer. So the first peak represents the monoelectronic reduction of Nb(V) to Nb(IV).

For TEAP, a 1 Fmol⁻¹ value is only obtained when $E_{app}$ is set at the foot of the first wave (-0.95 V). Nb(V) species in TEAP solutions hydrolyze more easily than in TEACl solutions. So, in exhaustive experiments such as CPC, the 0.75 n-value (see Table 2) can be explained as being a consequence of Nb(V) loss due to its hydrolysis. With a slightly more cathodic $E_{app}$, *e.g.* -1.1 V, a 2 Fmol⁻¹ n-value is found (Table 2). As the first Nb(V) reduction step was found to be monoelectronic, this result can be explained assuming that electrogenerated Nb(IV) hydrolyzes, producing HCl. This is quite reasonable since all Nb-species contain chloride. Thus, the second electron uptake must be due to HCl reduction, formed *in situ*. Since coulometry is an exhaustive technique, HCl reduction is feasible despite the fact that the HCl wave falls at a somewhat more cathodic potential than the Nb(V)/Nb(IV) peak potential. Indeed, in the -1.1 V potential region, a contribution of HCl reduction can already be observed in the voltammograms, so that after 5000 s (the duration of the experiment) it is reasonable to assume that all HCl generated *in situ* was depleted. The same interpretation can be given to the results in TEAP at more cathodic potentials.
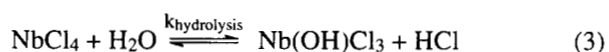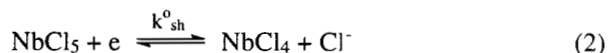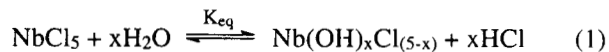
A comparison of the n-values for TEAP and TEACl, obtained with $E_{app}$ at the foot of the first peak, when confronted with the n-values obtained at the respective peak potential (see Table 2 and Fig. 1), clearly demonstrates the stabilizing effect exerted by the chloride ion on the Nb(V) species, preventing its hydrolysis. The stabilizing effect of the chloride ion is, however, not strong enough to prevent hydrolysis of the Nb(IV) species explaining the 2 Fmol⁻¹ value obtained with $E_{app} \geq -1.35$ V when TEACl is used as supporting electrolyte.
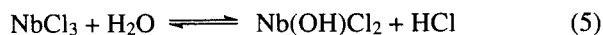
Because of the importance of HCl in the electrode mechanism, we also investigated the influence of HCl/AN, added on purpose, on the coulometric results. Coulometric experiments were carried out electrolyzing Nb(V) in the presence of a known amount of HCl (7.4 mM). Nb(V) and HCl aliquots were injected simultaneously into the supporting electrolyte (TEAP or TEACl). The total charge ($Q_T = Q_{Nb} + Q_{HCl,hydrolysis} + Q_{HCl,added}$) was corrected for the contribution of the charge due to the reduction of the HCl deliberately added ($Q_{HCl,added}$) so that the net charge is solely due to the reduction of Nb-species and HCl formed *in situ* trough hydrolysis of Nb-species ($Q_{net} = Q_{Nb} + Q_{HCl,hydrolysis}$). $Q_{HCl,added}$ was determined from independent experiments, electrolysing the same amount of HCl (without Nb being present) keeping all other experimental conditions carefully constant.

Coulometric experiments executed with $E_{app}$ localized at the switching potentials (see Fig. 1) furnished a 3 Fmol⁻¹ value for both TEAP and TEACl. These results can be understood in the light of the stability of the different niobium oxidation states, which decrease in the sequence: Nb(V)-Nb(IV)-Nb(III)[22]. Results obtained in 0.1 M TEAP (no HCl deliberately added) yielded a 2 Fmol⁻¹ value, showing Nb(IV) to be hydrolyzed by the AN residual water content resulting in HCl, formed *in situ*, which is reduced, explaining n = 2 (1e for Nb(V)/Nb(IV), 1e for HCl). The experimental result of 3 Fmol⁻¹, obtained in the presence of 7.4 mM HCl deliberately added, demonstrates that Nb(IV) hydrolysis was prevented, permitting further reduction to Nb(III). The stabilization effect caused by the added HCl is, however, not enough to prevent hydrolysis of Nb(III), explaining the 3 Fmol⁻¹ result (1e for Nb(V)/Nb(IV); 1e Nb(IV)/Nb(III); 1e for HCl reduction formed *in situ* because of Nb(III) hydrolysis).

## Conclusions

The experimental results for TEAP can be rationalized according to the reduction scheme shown below :

$$NbCl_5 + xH_2O \; \overset{K_{eq}}{\rightleftharpoons} \; Nb(OH)_xCl_{(5-x)} + xHCl \qquad (1)$$

$$NbCl_5 + e \; \overset{k^o{}_{sh}}{\rightleftharpoons} \; NbCl_4 + Cl^- \qquad (2)$$

$$NbCl_4 + H_2O \; \overset{k_{hydrolysis}}{\rightleftharpoons} \; Nb(OH)Cl_3 + HCl \qquad (3)$$

$$NbCl_4 + e \rightleftharpoons NbCl_3 \qquad (4)$$

$$NbCl_3 + H_2O \rightleftharpoons Nb(OH)Cl_2 + HCl \qquad (5)$$

Since Nb(V) is known to hydrolyze easily and the AN used has a residual water content of $\approx 6$-10 mM, it is reasonable to assume an equilibrium between the electroactive $NbCl_5$ and the electroinactive $Nb(OH)_xCl_{(5-x)}$ (step (1)). It is necessary to consider $NbCl_5$ the electroactive form in order to explain the current increase observed with increasing $H^+$, $Cl^-$ and HCl concentrations. Step (1) also explains the $i_{peak}$ vs. [Nb(V)] behavior observed.

The reduction of Nb(V) to Nb(IV) with the simultaneous liberation of one $Cl^-$ ligand (step (2)) is supported by the results of the Matsuda and Ayabe treatment[14] of the $E_p$ vs. $[Cl^-]$ CV data.

For pure 0.1M TEAP steps (1)-(3) are operative, explaining the number of electrons found in the controlled potential coulometry experiments: one electron for step (2) and another for the reduction of HCl formed in situ in step (3). In the presence of an extra amount of HCl, added on purpose, step (3) is prevented. So for these experimental conditions, the Nb(V) reduction mechanism follows steps (1), (2), (4) and (5). In this case, two electrons are consumed in the Nb(V)/Nb(III) reduction (steps (2) and (4)) a third electron being consumed in the reduction of the HCl formed in situ as a consequence of step (5).

The Nb(V) reduction in 0.1 M TEACl, both in the presence and absence of an extra amount of HCl, follows the same electrode mechanism described for 0.1 M TEAP. Literature data[23-25] as well as our simulation results show HCl to behave as a weak acid in AN. So, use of TEACl instead of TEAP, both being strong electrolytes, results in a drastic decrease of the free proton concentration, due to the $Cl^-$ effect on the HCl dissociation equilibrium. This explains why the HCl reduction is not detected with $E_{app}$ localized at the first peak resulting in a n-value equal to one for 0.1 M TEACl while for the 0.1M TEAP supporting electrolyte a n-value of two was found.

For [Nb(V)] > 1.5 mM evidence was found for second order processes envolving Nb(IV) (see *Investigation of the Nb(V)/Nb(IV) Peak* section). So, for the higher Nb(V) concentrations the electrode mechanism should incorporate step (3'), in case where TEAP is used as supporting electrolyte,

$$2NbCl_4 \longrightarrow dimer \qquad (3')$$

or step (3"), in case where TEACl is used as supporting electrolyte:

$$2NbCl_4 \longrightarrow NbCl_5 + NbCl_3 \qquad (3")$$
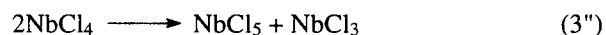
It is worthwhile to emphasize that both step (3') and (3") do not give significant contributions to the electrode mechanism for ordinary CV conditions.
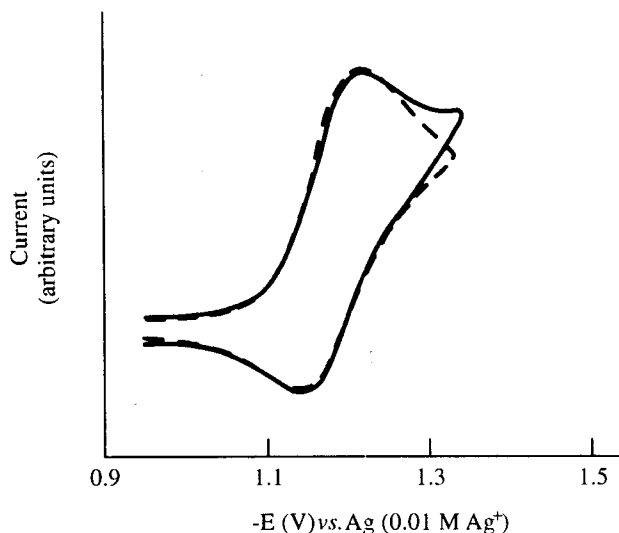


**Figure 5.** Cyclic voltammograms of the Nb(V)/Nb(IV) peak: (—) experimental curve; (----) simulated curve. 0.47 mM $NbCl_5$ in 0.1 M TEACl/AN. $v = 0.8$ V s$^{-1}$.

The proposed mechanism was employed as the basis of simulation using the finite difference point method.[26] Figure 5 shows a representative result of the comparison between the experimental and simulated voltammetric curves. For all systems, the fitting of the first peak is quite reasonable, being slightly better for TEACl than for TEAP. Because of the complex nature of the voltammogram at potentials more negative than the first peak, the fitting is not totally satisfactory for this potential region.

Parameters kept constant during the simulations were the transfer coefficient (0.5) and the diffusion coefficients (considered to be equal). For the 0.1 M TEAP simulation the graphically found $k^0_{sh}$-value was used without modification. For the 0.1 M TEACl supporting electrolyte (Fig. 5) a larger value was necessary in order to obtain a perfect fit between the cathodic and anodic peaks.

Table 3 summarizes the parameters obtained from simulation. The equilibrium constant, $K_{eq}$, of step (1) determines the broadness of the first peak. The $K_{eq}$-value was determined based on the adjustment, which was very satisfactory, of the first peak. The values obtained for both supporting electrolytes are in good agreement. On the other hand, the hydrolysis of Nb(IV) (see step (3) of the reduction mecha-

**Table 3.** Physic-chemical parameters for the proposed mechanism obtained through digital simulation.

| parameter | TEAP | TEACl |
|---|---|---|
| $k_{sh}^0$ | 0.011cm s$^{-1}$ | 0.039 cm s$^{-1}$ |
| $K_{EQ}$ | 0.3 | 0.2 |
| $k_{hydrolysis}$ | 3.5 L mol s$^{-1}$ | 1.0 L mol s$^{-1}$ |
| $K_{HCl}$ | 3.8 x $10^{-8}$ mol L$^{-1}$ | --- |

nism), described by $k_{hydrolysis}$, determines the magnitude of the anodic peak observed in 0.1M TEACl. Based on this principle, a value for $k_{hydrolysis}$ of 1.0 L mol$^{-1}$ s$^{-1}$ was obtained (see Table 3).

For simulation of the potential region beyond the first peak, we assumed this part of the voltammogram to be adequately described by a composite wave made up of the HCl and Nb(IV) reductions, the degree of overlap of these reduction peaks depending on the formal potentials. The height of the Nb(IV) wave, and so its contribution to the composite wave, depends on the $k_{hydrolysis}$ value (step (3)). Thus, fitting of the theoretical voltammogram to the experimental one allowed $k_{hydrolysis}$ to be obtained from TEAP solutions, independently of the previously obtained value from TEACl. The values obtained from both approaches are in reasonable agreement (see Table 3). Since the $k_{hydrolysis}$ value obtained from voltammograms in TEACl solutions is reliable, as the fitting in this case is very good, the model used can be considered reasonable. However, because of the less succesful adjustment obtained for the potential region beyond the first peak, one must keep in mind that, for this potential region, only the order of magnitude of the constant is meaningful.

With regard to HCl, Sherman and Archer[5] suggested molecular HCl to be the electroactive species. If this hypothesis is correct and taking into account step (1) of the proposed mechanism, digital simulation results in a pronounced HCl peak which was not observed experimentally in the Nb(V) cyclic-voltammogram. A reasonable fit, however, is obtained if dissociation of HCl in AN is taken into account and H$^+$ is considered the electroactive species. This means HCl behaves as a weak acid in AN, in agreement with the findings of Janz and Danyluk[25] who, based on conductometric measurements of HCl in AN, also concluded HCl to behave as a weak acid in this solvent. Based on this proposal a value of $10^{-8}$ mol L$^{-1}$ was obtained for the HCl dissociation constant by simulation.

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