

Chemical behavior of tungstate solutions. Part 1. A spectroscopic survey of the species involved

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Abstract

This study is focused on the composition and the evolution of tungstate ions solutions as a function of pH and increasing concentrations. The Raman analysis showed that, during the titration of the tungstate solutions, WO_4^{2-} , HWO_4^- ions and probably $\text{W}_2\text{O}_7^{2-}$, $\text{HW}_2\text{O}_7^{2-}$ and $\text{H}_2\text{W}_2\text{O}_7$ solvated species could exist in aqueous solutions. For diluted solutions, additions of a strong acid does not cause any precipitation, whereas the formation of the unstable solid tungstic acid (H_2WO_4 or $\text{WO}_3 \cdot \text{H}_2\text{O}$) could occur in concentrated solutions.

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1. Introduction

Electrodeposited nickel–tungsten alloys have a good temperature behavior, as well as a strong resistance to friction and corrosion [1]. They find many applications in fields as varied as tribology, magnetism or protection against corrosion. However, the reaction mechanisms of formation of these alloys are not presently clearly established [2, 3, 4 and 5]. In fact, the chemistry of tungstate solutions in the absence of nickel ions is itself rather unexplained [6].

The aim of this study is to improve the understanding of the reduction reaction mechanisms of the tungstate ions in aqueous solutions, with or without nickel ions, in order to optimize finally the metal tungsten contents in the Ni–W alloys. This first part is devoted to the study, especially by Raman spectroscopy, of the composition and evolution of tungstate ions solutions as a function of pH and increasing concentrations. A detailed complementary study focused on their electrochemical behavior will be presented in a forthcoming paper.

2. Experimental

The tungstate ions solutions were prepared by dissolving pure tungsten oxide WO_3 (Aldrich, 98%) in 2 M sodium hydroxide at 353 K. Sodium sulfate was then added in strong concentration (0.2–1.0 M), in order to increase its electrical conductivity and allow to neglect tungstate ions migration during voltammetric tests. Table 1 gives the list of the solutions tested in this study.

Table 1. Ionic concentrations and pH values

No.	$[\text{WO}_4^{2-}] \text{ mol l}^{-1}$	$[\text{SO}_4^{2-}] \text{ mol l}^{-1}$	$[\text{Na}^+] \text{ mol l}^{-1}$	pH
1	0.222	0.905	0.951	8.0
5	0.066	0.909	2.000	12.4
8	0.062	1.093	1.725	1.8
9	0.145	0.400	1.760	12.7
12	0.132	0.735	1.524	2.
13	0.242	0.333	1.467	12.9
16	0.209	0.843	1.268	2.2
17	0.272	0.250	1.100	13.0
18	0.264	0.368	0.995	7.75
19	0.248	0.581	0.973	4.6
20	0.230	0.830	0.963	2.0

The pH titrations were carried out under magnetic stirring with 4.0 M sulfuric acid, in order to have only Na^+ , SO_4^{2-} and WO_4^{2-} ions in the starting alkaline solution. The pH was measured within 60 s after each acid addition, with a glass electrode (Tacussel), calibrated before each series of measurements with buffer solutions (Bioblock, pH 4.0 and 7.0).

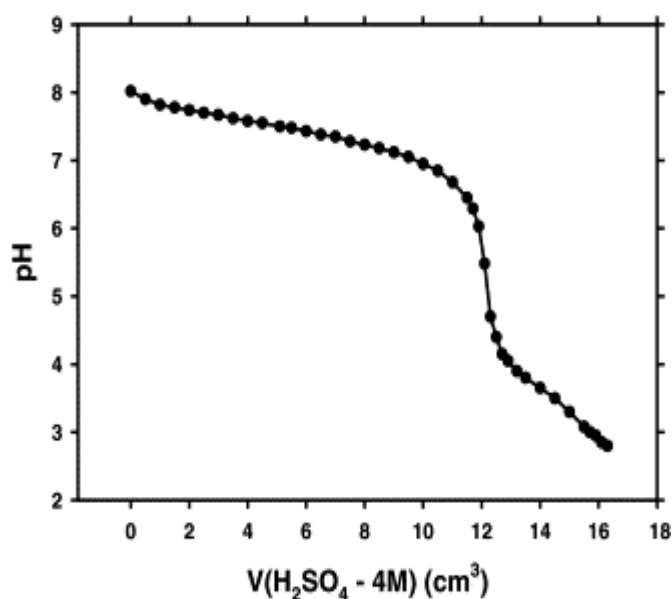
The Raman measurements were made with a Labram (DILOR) microspectrometer equipped with a He–Ne laser ($\lambda = 632.8 \text{ nm}$, 2 mW) and a “notch” filter at 600 nm. The Raman signal was collected through the objective of a microscope ($G = *50$), then passed through a holographic monochromator (1800 lines/mm). It finally fell on a CCD detector (Wright) cooled at 243 K. For this preliminary study, each spectrum was measured over 60 s, which ensured a satisfactory signal-to-noise ratio.

3. Results

3.1. Acidic titration

Fig. 1 presents the titration curve corresponding to solution 1. When the pH, initially very alkaline, reached a value around 7, a precipitation of a substance having a white, milky appearance was observed. However, the precipitate, not very stable in our conditions, dissolved after a few seconds. As soon as pH reached 4, the addition of acid no longer caused the formation of precipitate. Finally, it should be noted that, during the dissolution of the white-milky precipitate, the pH of the solution decreased notably.

Fig. 1. Titration curve of the tungstate solution 1.



3.2. Influence of the pH

Fig. 2 reports the Raman diffusion spectra for solutions 17–20 (with high tungstate ions concentrations; $c \approx 0.25$ M), at pHs ranging from 13 to 2, respectively. Two main intense Raman bands are located in the region $900\text{--}1050\text{ cm}^{-1}$, while the arrows placed on this figure indicate the positions of the secondary, less intense emission bands. The emission lines associated with the presence of sulfate ions are clearly indicated. The wavenumber range has been enlarged in Fig. 3, in order to allow a better separation of all the peaks present in this zone. According to this figure, the value of pH has a drastic influence on the Raman spectra. Compared to the pure sulfate solutions, new peaks appear, in particular at 930 cm^{-1} for basic and neutral solutions. By acidifying solution 17, the intensity of this peak decreases (solution 18), then disappears drastically when the pH lowers from 7.8 to 4.6 (solution 19) and finally to 2.0 (solution 20). At the same time, new bands appear, at 960 and 995 cm^{-1} for solutions 19 and 20, respectively.

Fig. 2. Raman spectra ($200\text{--}1600\text{ cm}^{-1}$) of the concentrated tungstate solutions (no. 17–20) ($c \approx 0.25$ M) with decreasing pH values.

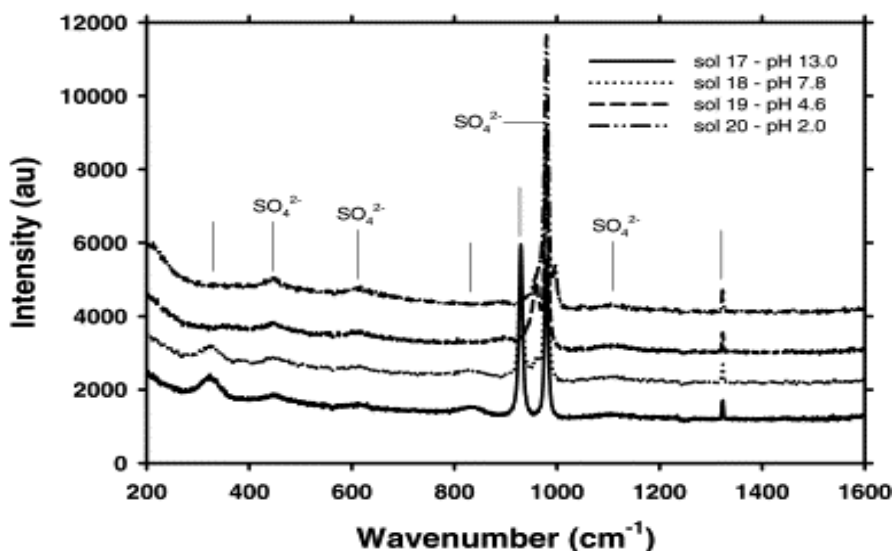
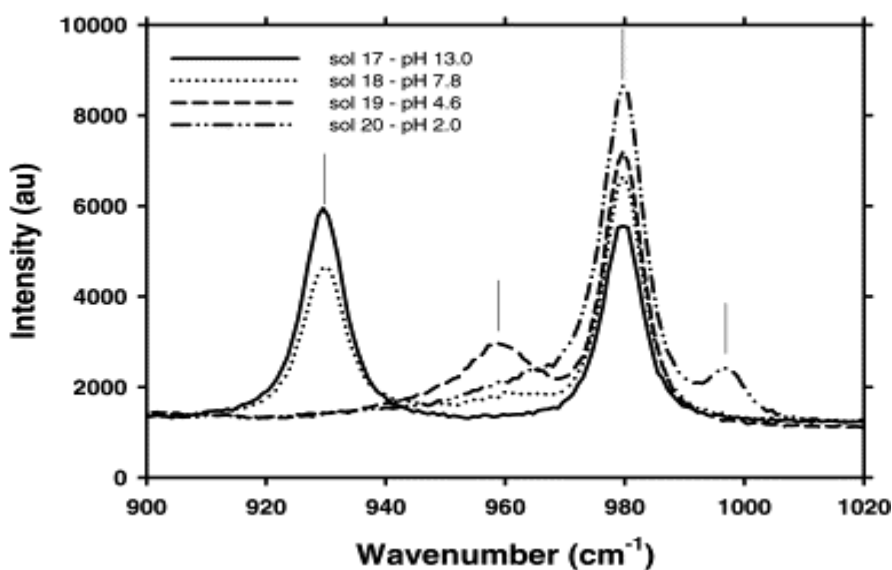


Fig. 3. Detailed Raman spectra ($900\text{--}1030\text{ cm}^{-1}$) of the concentrated tungstate solutions (no. 17–20) ($c \approx 0.25\text{ M}$) with decreasing pH values.



In addition to these changes, small variations of intensity are recorded in the wavenumber ranges $280\text{--}380\text{ cm}^{-1}$, $780\text{--}900\text{ cm}^{-1}$ and $1300\text{--}1350\text{ cm}^{-1}$. The emission peak located around 320 cm^{-1} disappears as the solution passes from neutral to acidic. In the range $780\text{--}900\text{ cm}^{-1}$, i.e. next to the region where the main variations occur in the spectrum, the same evolution appears as a function of pH: a peak emitted in the neutral and basic media disappears when the pH becomes acidic. Moreover, comparison of spectra corresponding to solutions 17 and 18 reveals that the half width of the peak at 840 cm^{-1} increases notably with decreasing pH. [Table 2](#) gathers these main Raman characteristics directly correlated with pH modifications of the concentrated tungstate solutions.

Table 2. Summary of Raman emission lines linked with tungsten species

	pH			
	13	7.8	4.6	2
Main peak	930 cm ⁻¹	930 cm ⁻¹	960 cm ⁻¹ (weak)	995 cm ⁻¹ (weak)
	320 cm ⁻¹	320 cm ⁻¹		
Secondary peak	830 cm ⁻¹	830 cm ⁻¹	1325 cm ⁻¹	–
	1325 cm ⁻¹	1325 cm ⁻¹		

In order to distinguish specific contributions of the sulfate and tungstate ions, the influence of tungstate concentration will now be investigated.

3.3. Influence of concentration

Solutions labeled 5, 9, 13 and 17 have increasing tungstate concentrations but very similar alkalinity, around 12.4–13.0, pH range where the Raman modifications are weak in view of the results presented above. Fig. 4 gathers all corresponding Raman spectra, while Fig. 5 allows to pinpoint the influence of the tungstate ions concentration on the main emission line, located at 930 cm⁻¹. The intensity of this peak increases proportionally to [WO₄²⁻] (Fig. 6). On the other hand, the decrease of the peak at 980 cm⁻¹ (related to the solvent) is due to the decrease of the sulfate ions concentration.

Fig. 4. Raman spectra (200–1600 cm⁻¹) of alkaline solutions 5, 9, 13 and 17 (pH ≈ 13) with increasing tungstate concentrations.

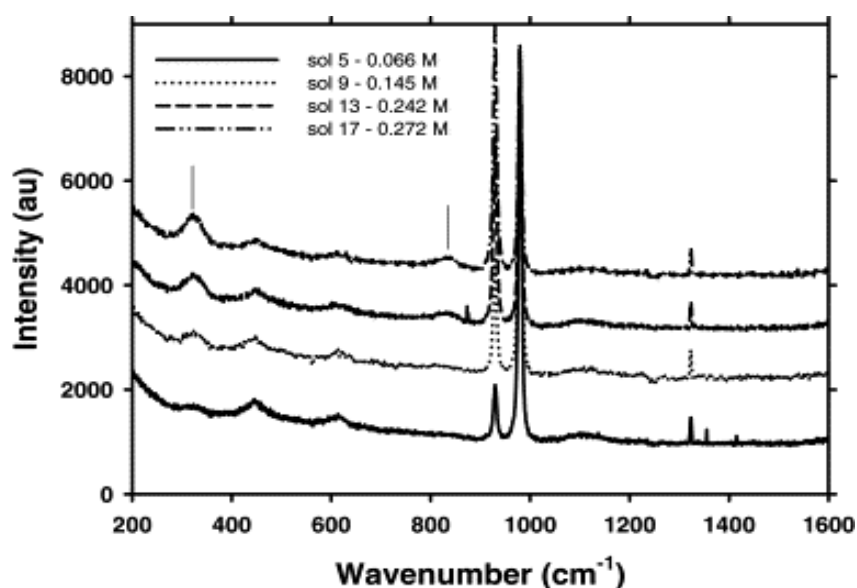


Fig. 5. Detailed Raman spectra (900–1020 cm⁻¹) of alkaline solutions 5, 9, 13 and 17 (pH ≈ 13) with increasing tungstate concentrations.

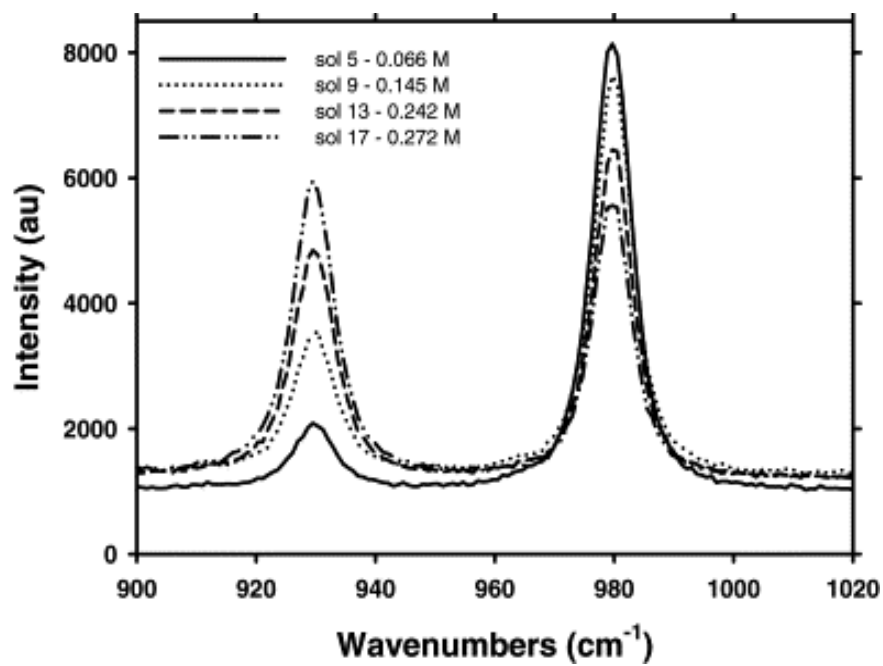
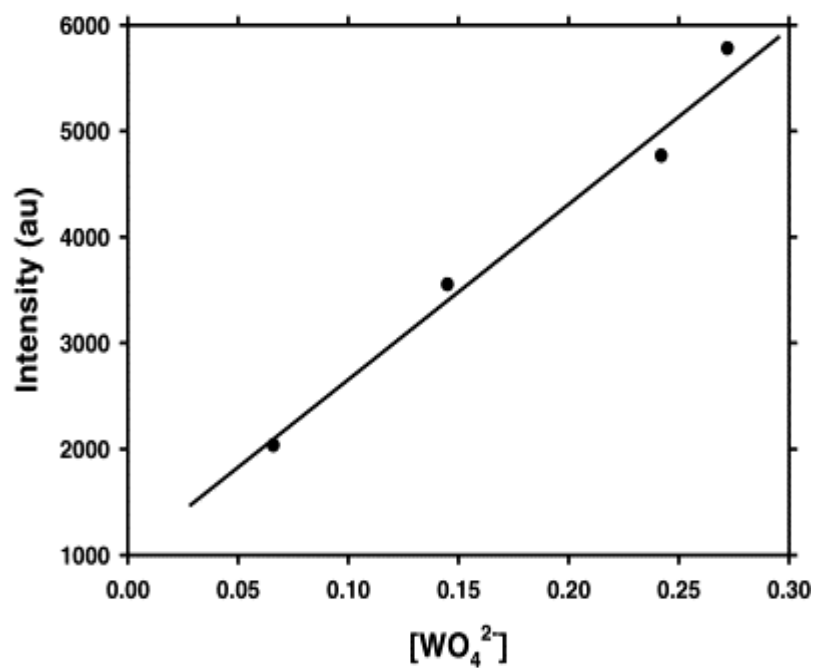


Fig. 6. Variation of the Raman emission intensity at 930 cm^{-1} as a function of the tungstate concentration for alkaline solutions.



For the acidic solutions ($\text{pH} \approx 2$), labeled 8, 12, 16 and 20, the Raman spectra are shown in Fig. 7. As previously seen, the secondary emission peaks related to the non-sulfated species disappear completely, while only remain the lines around 995 cm^{-1} , as well as the peak at 1325 cm^{-1} (Fig. 8). The intensity of this latter peak is not influenced by the tungstate ions concentration, except for solution 20 for which it disappears.

Fig. 7. Raman spectra ($200\text{--}1600 \text{ cm}^{-1}$) of acidic solutions 8, 12, 16 and 20 ($\text{pH} \approx 2$) with increasing tungstate solutions.

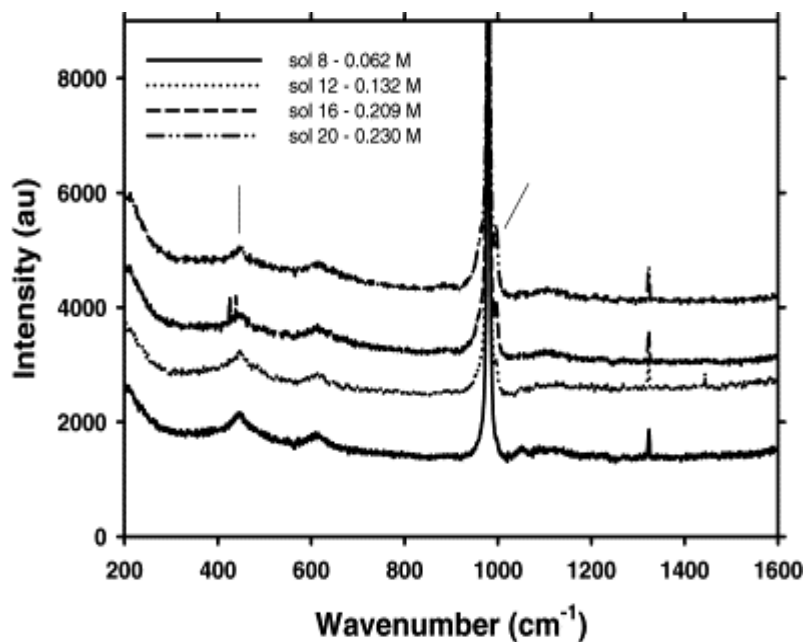
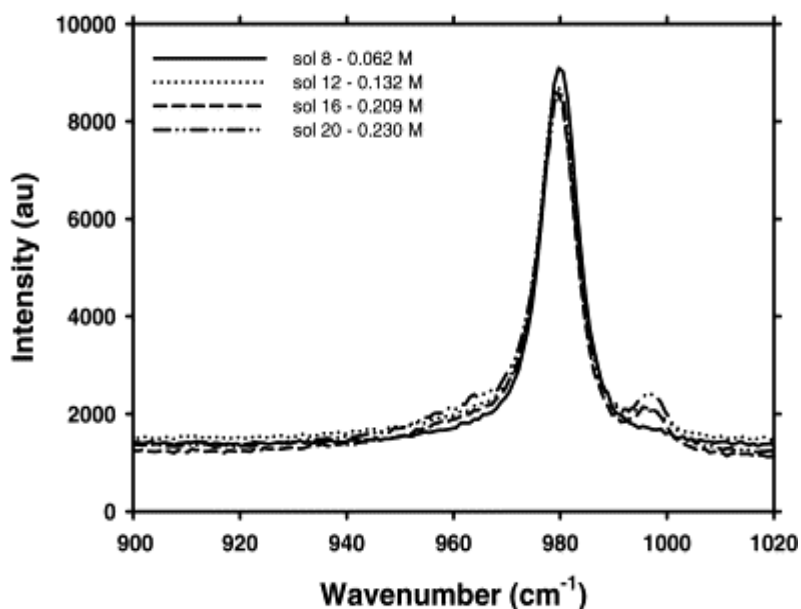


Fig. 8. Detailed Raman spectra ($900\text{--}1020 \text{ cm}^{-1}$) of acidic solutions 8, 12, 16 and 20 ($\text{pH} \approx 2$) with increasing tungstate solutions.



For solution 8, the most diluted one ($[\text{WO}_4^{2-}] = 0.062 \text{ mol l}^{-1}$), the band located at 995 cm^{-1} is present only as a shoulder. About basic solutions, four main spectral emission regions are observed, within the same limits as those fixed in the previous part. Additionally to the main emission line (at 930 cm^{-1}), the secondary emission lines also increase with the tungstate ions concentration. Similarly with the acidic solutions, the lines located at 1325 cm^{-1} are not influenced by the variations of the tungstate contents and are therefore not presented separately here.

4. Discussion

4.1. Predominant compounds during titration

According to Pourbaix's diagram for tungsten, there should be only one ionic species present in aqueous solution, i.e. the tungstate ion WO_4^{2-} , stable compound in basic media, whereas the existence of pertungstic ion WO_5^{2-} remains hypothetical. This equilibrium diagram implies that this ion is not stable in acidic medium ($\text{pH} < 7$) and induces precipitation of the tungsten oxide WO_3 according to the following reversible reaction, with a solubility constant equal to $10^{14.1}$:



According to our preliminary experiments, this reaction is very slow, since tungsten oxide precipitate is only observed in very acidic conditions ($\text{pH} < 1$) and for reaction times of several weeks. From the chemical point of view, it is then interesting to study the titration curve of a tungstate alkaline solution in order to ascertain precipitation and/or solubility as a function of pH zones. At first, it should be noted that the equivalent point here is around $\text{pH} = 5$ (Fig. 1), whereas the titration of a strong base (sodium hydroxide) with a strong acid (sulfuric acid) should lead to an equivalent point centered at $\text{pH} = 7$. So, according to our tests, the titration of tungstates would involve, in the pH range 4–7, the precipitation of an intermediate solid as $\text{WO}_3 \cdot x\text{H}_2\text{O}$ ($1 \leq x \leq 3$), that remains very unstable.

4.2. Specific Raman contribution of tungstate ions

The Raman studies enabled us to assign the emission lines characteristic of the tungstate ions, in basic or acidic solutions. The peaks appearing at 320 cm^{-1} (secondary band), 830 cm^{-1} (secondary band) and 930 cm^{-1} (main band) with increasing tungstate concentrations, were assigned to the presence of WO_4^{2-} ions. On the contrary, the peak located at 1325 cm^{-1} does not seem to belong to this system, because the concentration modifications cause no variation of its intensity. All these specific lines are only detected in neutral and basic conditions, whereas important changes are observed in more acidic solutions ($\text{pH} < 5$).

There is indeed an important influence of the acidity in the medium, particularly between $1 < \text{pH} < 5$, on the activity of the tungstate ions, inducing significant modifications of the Raman spectra. Acidifying the solutions first causes a complete disappearance of the main and secondary emission peaks previously present at neutral and basic pH. Furthermore, a new single peak

centered at 960 cm^{-1} appears at $\text{pH} = 4.6$, while it is shifted to 995 cm^{-1} at $\text{pH} = 2.0$. In addition, at these pH values, the intensities appear to be very low in view of the concentrations involved and compared to the height of the lines observed for the basic solutions. This low intensity could undoubtedly explain the absence of secondary emission lines for these acidic solutions.

4.3. Identification of stable compounds in alkaline solutions

Kloprogge and Frost [7] identified the main Raman emission band of the WO_4^{2-} species in solid phase (in scheelite, for example), while Tsaryuk et al. [8] located it at 930 cm^{-1} in aqueous solutions. Taking into account our results, and considering the influence of the pH , it may be concluded that the tungstate ion WO_4^{2-} exists in sulfated aqueous solution for alkalinities ranging from $\text{pH} = 7$ to 13 and that the main Raman band is located at 930 cm^{-1} .

According to the previous studies, no data exist presently concerning the secondary peaks in aqueous solutions. Nevertheless, Kloprogge and Frost [7] mentioned low intensity lines at 795 and 380 cm^{-1} for WO_4^{2-} species in the ionic crystal CaWO_4 . Moreover, Huang and Butler [9] already reported bands characteristic of WO_4^{2-} groups in potassium tungstate (K_2WO_4) at 925 , 823 and 350 cm^{-1} (with decreasing intensity, respectively). Despite the fact that they are observed in solid phase, these values are fairly close to our results (secondary peaks at 830 and 320 cm^{-1}) in aqueous solutions. Thus, it seems to exist some continuity in the Raman emission of the tungstate species, whether they are in the solid state (such as CaWO_4 , K_2WO_4 , etc., by forming crystals with ionic bonds) or in solution (ionic species solvated by water molecules).

4.4. Identification of stable compounds in acidic solutions

If the WO_4^{2-} ions in basic conditions are clearly identifiable by comparison with data reported in the literature, the ionic species existing in acidic solutions have not yet been identified. However, Zolin et al. [10], in their studies on ionic crystals of tungstates of the lanthanides series, showed that the formation of tungsten compounds with low coordination numbers caused an increase in the wavenumbers of the $\text{W}=\text{O}$ stretching vibrations. In other words, a decrease of the O/W ratio is accompanied by a spectral upshift of the Raman bands. For example, ionic crystals having WO_5^{4-} groups ($\text{O}/\text{W} = 5$) yield a main line around 860 cm^{-1} . On the other hand, with the species $\text{W}_2\text{O}_9^{6-}$ ($\text{O}/\text{W} = 4.5$), this line is upshifted to 885 cm^{-1} , while $\text{W}_2\text{O}_7^{2-}$ ions ($\text{O}/\text{W} = 3.5$) emit mainly at 930 cm^{-1} . The reverse statement also seems true, since WO_4^{2-} ions (for $\text{O}/\text{W} = 4$) display a strong band between 930 and 950 cm^{-1} , that is downshifted to 880 cm^{-1} for WO_5^{4-} groups ($\text{O}/\text{W} = 5$) and between 795 and 840 cm^{-1} for WO_6^{6-} species ($\text{O}/\text{W} = 6$).

These effects of spectral shifts with the tungsten coordination number were confirmed by Wang et al. [11], via studies on ternary glasses based on tungsten oxide. Nevertheless, the values they report are slightly different from those showed by Zolin et al. [10], with an emission between 890 and 930 cm^{-1} for WO_4^{2-} and 850 cm^{-1} for WO_6^{6-} .

However, our results obtained in aqueous solution clearly showed that the main peak of the tungstate ion (at 930 cm^{-1}) shifts to 960 and 995 cm^{-1} when the pH is lowered to 4.6 and 2.0 , respectively. According to these observations, a similar phenomenon of tungsten coordination's

decrease could be considered in aqueous solution: starting from the WO_4^{2-} ion ($\text{O/W} = 4$), the appearance of ions of the type $\text{W}_2\text{O}_7^{2-}$ ($\text{O/W} = 3.5$) could be thus expected in acidic conditions.

Moreover, it should be noted that protonating tungstate ions does not modify the coordination number of tungsten. So, according to this spectroscopic study, the existence of species HWO_4^- does not seem the most probable. Finally, it should be noted that the decrease of the coordination of the central atom does not inevitably involve a change of its oxidation state. Thus, the tungsten element has always the same oxidation state +VI in the reaction mechanisms that we suggest.

4.5. Global reaction mechanisms

Thus, the following reactions can occur during the acidification of tungstate solutions:



This latter reaction (4) fits in well with our experimental observations because during titration there are on the one hand the appearance of a metastable precipitate ($7 > \text{pH} > 4$) and on the other hand a pH decrease linked to its dissolution. So, $\text{W}_2\text{O}_7^{2-}$, WO_4^{2-} and HWO_4^- ions should be the ionic species, while the precipitate would be solid tungstic acid (H_2WO_4 or $\text{WO}_3 \cdot \text{H}_2\text{O}$). Its metastability should directly depend on the solvation of $\text{W}_2\text{O}_7^{2-}$ ion: upon addition of concentrated (4 mol l^{-1}) sulfuric acid, the proton concentration is briefly and locally very high, inducing the H_2WO_4 precipitation (reaction (4)), whereas after a few seconds of diffusion this concentration decreases, implying the reverse reaction. These interpretations meet Li and Nonaka's study [12] on complex solutions, including tungstate, chlorides and phosphates ions, as well as organic compounds of the sulfoxide type, at mildly acidic pHs.

The HWO_4^- ion is usually considered as the conjugated base of the tungstic acid H_2WO_4 . But for not too low pH and at low tungstate concentrations, the dimerization reaction (3) can take place. Afterwards, at even lower pHs, $\text{W}_2\text{O}_7^{2-}$ ions could react with one or more protons, thus inducing the following hydrogenated form:



5. Conclusions

The Raman study showed that, during the titration of the tungstate solutions, WO_4^{2-} ,

HWO_4^- ions and probably $\text{W}_2\text{O}_7^{2-}$, HW_2O_7^- and $\text{H}_2\text{W}_2\text{O}_7$ solvated species could exist in aqueous solutions. For diluted solutions, additions of a strong acid does not cause any precipitation, whereas the formation of the unstable solid tungstic acid (H_2WO_4 or $\text{WO}_3 \cdot \text{H}_2\text{O}$) could occur in concentrated solutions ($\text{WO}_4^{2-} > 0.2 \text{ mol l}^{-1}$). The second part of this study will be devoted to the electrochemical reactivity of these solutions.

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