Study of titanium(IV) speciation in sulphuric acid solutions by FT-Raman spectrometry

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ABSTRACT

The effects of the addition of titanium(IV) to aqueous solutions of sulphuric acid were studied by FT-Raman spectroscopy. Solutions containing 0 M to 4.01 M of titanium(IV) and 1.98 M to 6.17 M of sulphuric acid were analysed. A new peak, characteristic of titano-sulphate complexes, has been observed, in addition to the peaks characterising ions SO_4^{2-} and HSO_4^-. Free HSO_4^- and SO_4^{2-} concentrations have been determined from the Raman peak areas. From mass balance it was deduced that two complexes are present in the solution: $[Ti(OH)_2SO_4]$ (aq) and $[Ti(OH)_2(SO_4)_2]^{2-}$ (aq). Their apparent constants of formation have been estimated.

1. Introduction

1.1. Context of the study

Titanium dioxide, because of its optical properties, plays a significant role in the chemical industry, in particular in the form of anatase pigment powders. Precipitation by thermal hydrolysis in sulphuric medium of a titanyl sulphate solution is the usual process for the production of anatase. The anatase form is specifically used in papers, catalysts and cosmetics.

To be able to improve the performances of this process, its simulation implies a realistic modelling of the system, and thus, in the first instance, a knowledge of the species in solution. Although the speciation of aqueous solutions of sulphuric acid has been often studied in the past, in particular using Raman spectroscopy, very few works have focused on the study of titanium(IV) sulphate solutions. Furthermore, in these few studies, the concentrations of sulphuric acid and of titanium were low, compared with the range of concentrations considered in the present work. Hence the aim of our study is to get information about the speciation in H_2O–Ti(IV)–H_2SO_4 solutions over a large range of composition, our laboratory having conducted several works devoted to the characterisation of "strong acids" solutions using Raman spectroscopy [1–3].

1.2. Speciation of aqueous sulphuric acid

In aqueous solutions, sulphuric acid dissociates in two steps:

$$H_2SO_4 + H_2O = H_3O^+ + HSO_4^-$$

$$HSO_4^- + H_2O = H_3O^+ + SO_4^{2-}$$
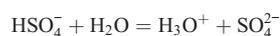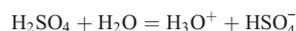
Various authors studied [4–10], mainly by Raman spectroscopy, the distribution of HSO_4^-, SO_4^{2-} and of the molecular H_2SO_4 in aqueous sulphuric acid solutions from 0 to 100 wt.% in acid, generally at 298.15 K. Spectra indicate that the molecular form appears only at acid concentrations larger than 20 M (M≡mol/L).

The Raman spectrum of an aqueous solution of sulphuric acid in the $400\ cm^{-1}$–$1600\ cm^{-1}$ range is given in Fig. 1. In the traditional approach [3–5] the spectrum contains several peaks ($425\ cm^{-1}$, $590\ cm^{-1}$ and $1200\ cm^{-1}$) corresponding to both SO_4^{2-} and HSO_4^- species. The peaks at $900\ cm^{-1}$ and $1050\ cm^{-1}$ are attributed to HSO_4^-, the last one at $980\ cm^{-1}$ being specific to SO_4^{2-}. In fact the location of this peak may vary, in the various papers, from $978\ cm^{-1}$ to $987\ cm^{-1}$, a discussion of the peak position being made in Rudolph's paper[11], but to simplify we will use $980\ cm^{-1}$ in the following. Other approaches [6–8] take into account ion pairs formed by SO_4^{2-} or HSO_4^- and H_3O^+, leading to specific peaks: at $948\ cm^{-1}$ ($H_3O^+\ SO_4^{2-}$ or $H_3O^+\ HSO_4^-$) and $1024\ cm^{-1}$ ($H_3O^+\ HSO_4^-$). More recently Lund Myhre et al. [9] consider that the $948\ cm^{-1}$ line is not necessary to describe the spectrum. Moreover, they conclude that the peaks at $1024\ cm^{-1}$ and $1050\ cm^{-1}$, necessary to represent the asymmetry of the $1050\ cm^{-1}$ peak correspond to the stretching vibrations of HSO_4^- ions only. In this study, we focus on the $950\ cm^{-1}$–$1150\ cm^{-1}$ range, because, in this range each peak is specific to only one species (HSO_4^- or SO_4^{2-}). We will then consider the following peaks: $980\ cm^{-1}$(SO_4^{2-}), $1050\ cm^{-1}$ (HSO_4^-).

2. Experimental section

2.1. Sample preparation

The sulphuric acid solutions were prepared from concentrated acid of p.a. quality (98%, Aldrich) and distilled water. The titanyl sulphate solutions were prepared by hydrolysis of commercial titanate isopropoxide (from Aldrich, 97%) in concentrated sulphuric acid
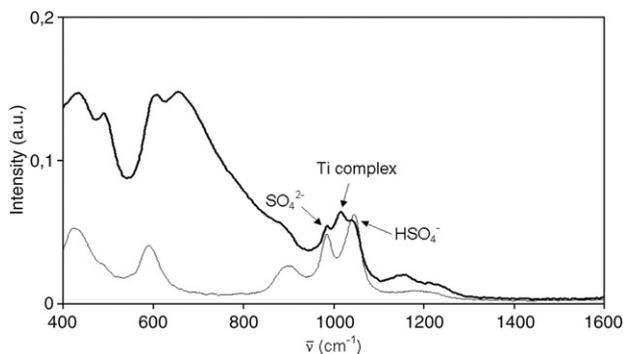
Fig. 1. Effect of Ti(IV) addition on the Raman spectrum of sulphuric acid. — $c_{H_2SO_4}^{apparent}$ = 5.98 M and c_{Ti} = 3.01 M, — $c_{H_2SO_4}^{apparent}$ = 6.03 M and c_{Ti} = 0 M.

solutions, following the protocol described by Raskopf [12], according to the reaction: $Ti(OC_3H_7)_4 + H_2O + H_2SO_4 \rightarrow TiOSO_4 + 4C_3H_7OH$

The total concentrations of Ti(IV) and sulphate, respectively denoted $c_{Ti}^{apparent}$ and $c_{H_2SO_4}^{apparent}$, are adjusted by addition of water and concentrated (98 wt.%) sulphuric acid. Titanium(IV) in solution within the samples is titrated using a spectrophotometer Shimadzu UV 160 at 400 nm wavelength, after complexation by hydrogen peroxide.

All Raman spectra were obtained at 25 °C and at concentrations ranging between 0 M and 4.01 M for $c_{Ti}^{apparent}$ and between 1.98 M and 6.17 M for $c_{H_2SO4}^{apparent}$.

2.2. Raman experiments

To acquire the Raman spectra of Ti(IV) in sulphuric medium, we used a Bruker IFS 66 FTIR spectrometer equipped with the FRA 106 FT-Raman module. The source is the 1064 nm line of a Nd:YAG laser and the effective maximum power on the sample is 1 W. A DTGS detector, cooled with liquid nitrogen, collects the diffused intensity. The nominal resolution was of 2 cm^{-1} and the spectra resulted from 120 averaged interferograms.

The studied solutions were placed in a 5 mm quartz cell (Hellma 110 QS), closed by a PTFE stopper. This cell was then placed in a brass sample holder. The temperature was controlled by circulating a thermostated liquid through the metallic sample holder.

The spectra were corrected for the instrument response using a tungsten lamp as a blackbody source.

To avoid signal fluctuation among the experiments, we used an external reference. This reference solution is an aqueous NaNO$_3$ saturated solution (C_{NaNO_3} = 6.65 M). Its spectrum is recorded before and after the analysis of each studied solution and presents a well-defined peak at 1050 cm^{-1} corresponding to the nitrate ion. Hence, the experimental values used to get species concentrations are normalized peak areas defined by the ratio of the area A_i^α of peak α characteristic of a species i over the average area $A_{reference}$ of the reference peak of the reference solution. The concentration c_i of the species i is then given by:

$$c_i = k_i^\alpha \cdot A_i^\alpha / A_{reference}$$

This relation defines k_i^α, the relative response coefficient of the peak α characterizing species i. It has to be determined by calibration experiments.

A deconvolution process is necessary to determine the peak areas. This was done using a fixed Lorentz Gaussian function for the representation of each peak. Its position, its area and its width at half maximum then characterise each peak. The area will be used for the quantitative determination of species concentrations.

2.3. Spectra analysis

In acid aqueous solutions, titanium(IV) forms, with hydroxyl groups, complexes whose general formula is: $[Ti(OH)_n(H_2O)_{(6-n)}]^{(4-n)+}$ [13,14],
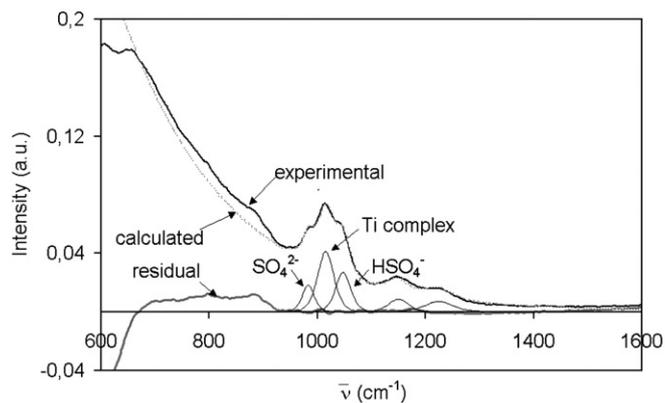

Fig. 2. Representation of the spectra through the deconvolution process.

with $0 \leq n \leq 4$. Previous studies provide apparent constants for the formation of the various complexes [15–18]. According to Nabivanets' conclusions [17], it appears that, for strong acidic solutions as in the case of the systems considered in the present work, the $[Ti(OH)_2(H_2O)_4]^{2+}$ ion is dominating in solution. As reported by Sole [19], some authors assume that the divalent titanium(IV) ion is TiO^{2+} or $[Ti(OH)_2(H_2O)_4]^{2+}$ but, as there is no strong evidence of the existence of the titanyl ion TiO^{2+}, we assume that divalent Ti (IV) ion is $[Ti(OH)_2(H_2O)_4]^{2+}$.

In the presence of sulphate and hydrogensulphate ions, this ion can form complexes containing one or two HSO_4^- or SO_4^{2-} ligands [20–23].

As it may be observed in Fig. 1, when titanium(IV) is added to sulphuric acid solutions, several significant changes in the Raman spectrum appear. The 950–1150 cm^{-1} wavelength range is particularly interesting because a new peak appears at 1010 cm^{-1}. It is located between the SO_4^{2-} peak at 980 cm^{-1} and the HSO_4^- peak at 1050 cm^{-1}. Fig. 2 gives an example of the deconvolution process. As it may be seen, knowledge of the position of the SO_4^{2-} and HSO_4^- peaks helps to locate the three peaks in the 900 cm^{-1}–1100 cm^{-1} range during the deconvolution process.

Fig. 3 gives the intensity of the deconvoluted peaks for sulphuric solutions containing various titanium(IV) concentrations, the total concentration of SO$_4$, expressed as apparent H$_2$SO$_4$ concentration, being about 6 M. It may be observed that the intensity of the peak at 1010 cm^{-1} increases with increasing titanium concentration and that, simultaneously, the intensities of the SO_4^{2-} peak (980 cm^{-1}) and of the HSO_4^- peak (1050 cm^{-1}) decrease.

On the base of its position in the spectrum and of its relation to titanium concentration, the 1010 cm^{-1} peak has been attributed to HSO_4^- (or SO_4^{2-}) molecules complexing titanium(IV).
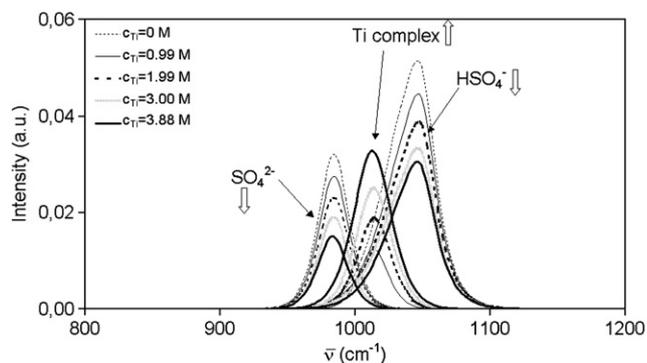

Fig. 3. Changes of Raman spectrum of H$_2$SO$_4$ solutions for increasing Ti(IV) concentrations at $c_{H_2SO_4}^{apparent}$ ≈ 6 M.

3. Results

The normalized experimental areas of the peaks at 980 cm^{-1} (SO$_4^{2-}$), 1050 cm^{-1} (HSO$_4^-$) and 1010 cm^{-1} (Ti complex) for the solutions studied during the present work are presented in Table 1.The treatment of Raman spectra of sulphuric aqueous solutions at various acid concentrations (1.02 to 9.85 M) allows the determination of the $k_{SO_4^{2-}}^{980}$ and $k_{HSO_4^-}^{1050}$ relative response coefficients defined in Section 2.2 because the speciation in these solutions is well known from the literature [4–6].

The values are : $k_{SO_4^{2-}}^{980} = 4.14M$ and $k_{HSO_4^-}^{1050} = 6.59M$.

Assuming that these values are still valid in systems containing titanium(IV), it is possible to deduce the values of HSO$_4^-$ and SO$_4^{2-}$ concentrations, $c_{HSO_4^-}$ and $c_{SO_4^{2-}}$ respectively, from the areas of the peaks at 980 cm^{-1} and 1050 cm^{-1} present in the spectrum of solution containing titanium(IV).

In the solutions considered here, the H$_2$SO$_4$ apparent concentration ($c_{H_2SO_4}^{apparent}$) is always significantly lower than the concentration limit (20 M) where molecular H$_2$SO$_4$ becomes significant. It has to be pointed out that $c_{H_2SO_4}^{apparent}$ includes the concentration of sulphuric acid used to prepare TiOSO$_4$ as well as the concentration of sulphuric acid used to adjust the total amount of SO$_4$, as explained in Section 2.1. Thus the difference between $c_{H_2SO_4}^{apparent}$ and the measured values of $c_{HSO_4^-}$+$c_{SO_4^{2-}}$ could be attributed to the concentration of species containing sulphur in titanium(IV) complexes.

This quantity noted $c^{complex}$ is then calculated by mass balance on H$_2$SO$_4$:

$$c^{complex} = c_{H_2SO_4}^{apparent} - c_{HSO_4^-} - c_{SO_4^{2-}}$$

The variation of the peak area located at 1010 cm^{-1} with $c^{complex}$ is presented in Fig. 4. The proportional tendency is in accordance with our assumption concerning the peak attribution.

4. Discussion

The variation of $c^{complex}$ as a function of the total concentration of titanium(IV) noted $c_{Ti}^{apparent}$, at three values of $c_{H_2SO_4}^{apparent}$ is presented in Fig. 5. In this figure, the plain line corresponds to the behaviour expected if there is only one 1–1 complex, neglecting the amount of free titanium(IV). For Ti(IV) complexes with two SO$_4^{2-}$ or HSO$_4^-$ ligands, the same assumptions give results represented by the dotted line.

The actual variation lies between these two limiting cases. It indicates that both complexes (1–1 and 1–2) are present in the studied
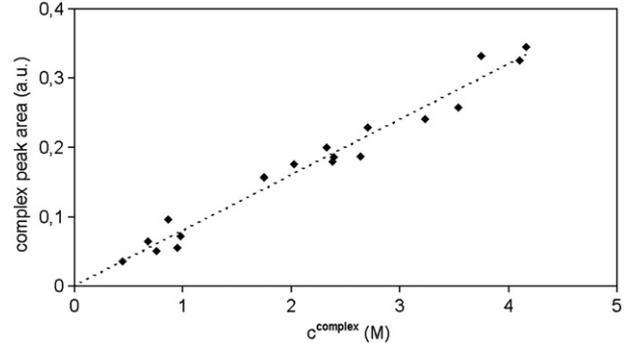

Fig. 4. Variation of the complex peak area with $c^{complex}$.

systems, with, as expected, an increase of 1–1 complex and a decrease of 1–2 complex when the ratio $c_{Ti}^{apparent}/c_{H_2SO_4}^{apparent}$ increases. Experimental scatter and the assumption that there is no free Ti(IV) could explain why two experimental points are outside the sector determined by the two lines.

We suppose that the two complexes present in the solution can be formed with [Ti(OH)$_2$(H$_2$O)$_4$]$^{2+}$(whose concentration is denoted c_{Ti}^{free}) and HSO$_4^-$ or SO$_4^{2-}$.

With HSO$_4^-$, the complexes would be [Ti(OH)$_2$HSO$_4$(H$_2$O)$_3$]$^+$ and [Ti(OH)$_2$(HSO$_4$)$_2$(H$_2$O)$_2$], and their respective concentrations are denoted $c_{cpx1}^{HSO_4^-}$ and $c_{cpx2}^{HSO_4^-}$. If they are formed with sulphate, the complexes would be [Ti(OH)$_2$SO$_4$(H$_2$O)$_3$]^0 and [Ti(OH)$_2$(SO$_4$)$_2$(H$_2$O)$_2$]$^{-2}$ and their respective concentration are denoted $c_{cpx1}^{SO_4^{2-}}$ and $c_{cpx2}^{SO_4^{2-}}$.
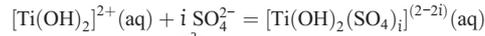
The equilibria corresponding to the complexes formation are, depending on the assumption concerning the ligand:

$$[Ti(OH)_2]^{2+}(aq) + i\ HSO_4^- = [Ti(OH)_2(HSO_4)_i]^{(2-i)}(aq)$$
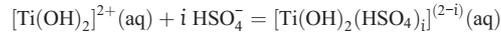
with

$$K_i^{HSO_4^-} = \frac{c_{cpx\ i}^{HSO_4^-}}{c_{Ti}^{free} \cdot (c_{HSO_4^-})^i}$$

and i=1 or 2 or:

$$[Ti(OH)_2]^{2+}(aq) + i\ SO_4^{2-} = [Ti(OH)_2(SO_4)_i]^{(2-2i)}(aq)$$

with $K_i^{SO_4^{2-}} = \dfrac{c_{cpx\ i}^{SO_4^{2-}}}{c_{Ti}^{free} \cdot (c_{SO_4^{2-}})^i}$ and i=1 or 2

As the aim of the study is to characterise the solutions, we only consider apparent equilibrium constants. To estimate the complex

Table 1
Normalized area of HSO$_4^-$ peak at 1050 cm^{-1}, of SO$_4^{2-}$ peak at 980 cm^{-1} and of 1010 cm^{-1} peak corresponding to Ti complex, as a function of $c_{Ti}^{apparent}$ and $c_{H_2SO4}^{apparent}$

$c_{Ti}^{apparent}$ (M)	$c_{H_2SO4}^{apparent}$ (M)	$A_{SO_4^{2-}}^{980}/A_{reference}$	$A_{HSO_4^-}^{1050}/A_{reference}$	$A_{Ti\ cpx}^{1010}/A_{reference}$
0.25	1.98	0.069	0.017	0.036
0.50	1.98	0.059	0.014	0.065
0.76	1.99	0.054	0.013	0.051
1.00	2.00	0.046	0.011	0.072
1.26	2.01	0.054	0.013	0.055
0.50	3.52	0.113	0.027	0.096
1.01	3.93	0.084	0.020	0.156
1.51	3.93	0.066	0.016	0.176
1.77	3.98	0.055	0.013	0.200
1.98	4.03	0.062	0.015	0.179
2.26	4.32	0.061	0.015	0.186
1.00	5.88	0.139	0.034	0.186
1.51	5.93	0.108	0.026	0.229
2.02	5.96	0.107	0.026	0.240
2.51	5.95	0.098	0.024	0.258
3.00	5.97	0.095	0.023	0.332
3.51	6.17	0.050	0.012	0.325
4.01	6.00	0.049	0.012	0.345

Fig. 5. Variation of $c^{complex}$ with Ti concentration and $c_{H_2SO_4}^{apparent} \approx 2$ M (experimental ■, calculated □),$c_{H_2SO_4}^{apparent} \approx 4$ M (experimental ▲, calculated △), $c_{H_2SO_4}^{apparent} \approx 6$ M (experimental ●, calculated ○).)

formation constants, it is necessary to calculate $c_{\text{cpx } i}^{\text{HSO}_4^- \text{ or } \text{SO}_4^{2-}}$ and $c_{\text{Ti}}^{\text{free}}$, $c_{\text{SO}_4^{2-}}$ or $c_{\text{HSO}_4^-}$.

The concentrations $c_{\text{SO}_4^{2-}}$ and $c_{\text{HSO}_4^-}$ are directly deduced from the corresponding peak areas and, by mass balance on sulphuric acid. If only one kind of complex is present, the quantity of ligand and then of complex may be calculated using only a mass balance relation on sulphur. However as it has been found that there are probably two complexes, the determination of complex formation constants has to be made through an optimisation method. For instance in the case of sulphate ligand, at fixed values of $K_1^{\text{SO}_4^{2-}}$ and $K_2^{\text{SO}_4^{2-}}$, the concentration of free titanium may be calculated by:

$$c_{\text{Ti}}^{\text{free}} = \frac{c_{\text{Ti}}^{\text{apparent}}}{1 + K_1^{\text{SO}_4^{2-}} c_{\text{SO}_4^{2-}} + K_2^{\text{SO}_4^{2-}} c_{\text{SO}_4^{2-}}^2}$$

Then it becomes possible to check the mass balance on sulphur as well as on titanium. The deviations on both mass balance conditions have been used as an objective function to get the formation constant values allowing calculation of the concentration of all species.

We obtain:

$$K_1^{\text{HSO}_4^-} = 1.1\text{M and } K_2^{\text{HSO}_4^-} = 0.9\text{M}^2$$

$$K_1^{\text{SO}_4^{2-}} = 3.4\text{M and } K_2^{\text{SO}_4^{2-}} = 12.1\text{M}^2$$

Both assumptions (complex with HSO_4^- or with SO_4^{2-}) lead to satisfactory results on the base of mass balances. On Fig. 5 is presented, together with the values deduced from mass balance, the values calculated c^{complex} using the preceding formation constants with the assumption of complexes with SO_4^{2-}.

To find the actual complexes, the concentration of H⁺, denoted $c_{\text{H+}}$, has been calculated by two different ways:

– from HSO_4^- dissociation
– from electroneutrality condition

The first method is based on the relation between H⁺ and the concentrations of SO_4^{2-} and HSO_4^- through the HSO_4^- dissociation apparent constant.

The dissociation of HSO_4^- leads to

$$\text{HSO}_4^- = \text{SO}_4^{2-} + \text{H}^+ \quad \text{with } K_d = \frac{c_{\text{SO}_4^{2-}} c_{\text{H}^+}}{c_{\text{HSO}_4^-}}$$
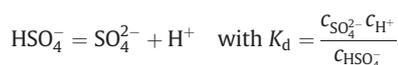
The apparent dissociation constant K_d has been calculated from our experiments on sulphuric acid solutions without titanium. In our range of H_2SO_4 concentration, K_d is quite proportional to $c_{\text{H}_2\text{SO}4}^{\text{apparent}}$: $K_d = 0.51\ c_{\text{H}_2\text{SO}_4}^{\text{apparent}}$ with σ (standard deviation)$=\pm0.15$ M. It has to be pointed out that in the case of systems with titanium, the value of $c_{\text{H}_2\text{SO}4}^{\text{apparent}}$ corresponds to the initial apparent H_2SO_4 concentration less the part involved in the complexes. This expression is used to fit the experimental points and cannot be extrapolated outside the concentration range used for the fitting. Knowing $c_{\text{HSO}_4^-}$ and $c_{\text{SO}_4^{2-}}$ in the solutions containing titanium from Raman experiments and K_d as a function of $c_{\text{H}_2\text{SO}_4}^{\text{apparent}}$, it was possible to estimate $c_{\text{H+}}$.

$c_{\text{H+}}$ may also be calculated by applying the electroneutrality condition, the concentration of all other species being deduced from mass balance and from the analysis of Raman spectra.

Fig. 6 represents $c_{\text{H+}}$ calculated from HSO_4^- dissociation constant as a function of $c_{\text{H+}}$ calculated from electro neutrality.

It can be seen from Fig. 6 that the assumption linked to complexes formed with SO_4^{2-} leads to the best results. The remaining difference could be explained by the experimental scattering and by the fact that we have considered free titanium only as $[\text{Ti(OH)}_2(\text{H}_2)_4]^{2+}$ and have not taken into account the other titanium(IV) hydroxide species.
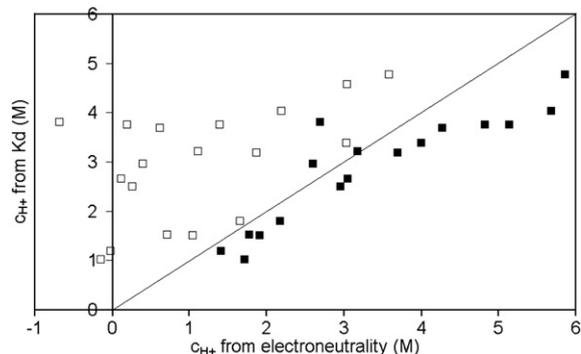

Fig. 6. Comparison between values of $c_{\text{H+}}$ calculated from HSO_4^- dissociation constant and from electroneutrality condition, assuming HSO_4^- complexes (□) or assuming SO_4^{2-} complexes (■).

Our values for $K_1^{\text{SO}_4^{2-}}$ (3.4 M) and $K_2^{\text{SO}_4^{2-}}$ (12.1 M²) differ from the values obtained by the authors who have considered the same complexes: Nabivanets [23] has obtained $K_1^{\text{SO}_4^{2-}} = 248.8$ M and $K_2^{\text{SO}_4^{2-}} = 157.5$ M² while Babko et al. [20] obtained $K_1^{\text{SO}_4^{2-}} = 169.5$ M and $K_2^{\text{SO}_4^{2-}} = 76.9$ M². Moreover, Babko has considered a third complex containing three SO_4^{2-}. The differences can be explained by the difference in the concentrations of H⁺, of SO_4^{2-}, and of Ti(IV). In the literature studies, c_{Ti} is lower than in our work ($c_{\text{Ti}}^{\text{apparent}} = 2.10^{-4}$ M for Nabivanets, and $c_{\text{Ti}}^{\text{apparent}} = 10^{-3}$ M for Babko). The formation constants have then been extrapolated to infinite dilution and are thermodynamic constants, contrary to the apparent constants that we have determined. Tur'yan and Maluka [24], who have considered a complex with Ti(OH)³⁺ and one SO_4^{2-}, have shown than the apparent constant of formation decreases when the ionic strength increases. Hence the apparent discrepancies between the published values are probably due to significant differences in the concentration ranges considered as well as to the use of different assumptions concerning the species.

5. Conclusions

When Ti(IV) is added to aqueous solutions of sulphuric acid, a new Raman peak appears at 1010 cm⁻¹ that may be attributed to sulphate ions present in titanium complexes. Based on the results of various tests, it appears that the best assumption is the formation of the two following titanium complexes: $[\text{Ti(OH)}_2\text{SO}_4(\text{H}_2\text{O})_3]^0$ and $[\text{Ti(OH)}_2(\text{SO}_4)_2(\text{H}_2\text{O})_2]^{-2}$. The corresponding apparent equilibrium constants have been evaluated and compared with literature values.

References

[1] M. Cherif, A. Mgaidi, M.N. Ammar, W. Fürst, J. Solution Chem. 29 (2000) 255.
[2] J-P. Passarello, W. Fürst, Fluid Phase Equilib. 116 (1–2) (1996) 177.
[3] J-P. Passarello, W. Fürst, Proceedings of XXIV JEEP, Université H. Poincaré, Nancy-France, 1998.
[4] T.F. Young, L.A. Blatz, Chem. Rev. 44 (1949) 93.
[5] D.J. Turner, J. Chem. Soc., Faraday Trans. II 68 (1972) 643.
[6] H. Chen, D.E. Irish, J. Phys. Chem. 75 (1971) 2672.
[7] R.A. Cox, Ü.L. Haldna, K.L. Idler, K. Yates, Can. J. Chem. 59 (1981) 2591.
[8] Ü. Haldna, R.A. Cox, R. Juga, E. Rajavee, EESTI NSV Tead. Akad. Toim. Keemia 36 (1987) 261.
[9] C.E. Lund Myhre, D.H. Christensen, F.M. Nicolaisen, C.J. Nielsen, J. Phys. Chem. A 107 (2003) 1979.
[10] S. Kratsis, G. Hefter, P.M. May, Pal Sipos, Aust. J. Chem. 53 (2000) 363.
[11] W.W. Rudolph, G. Irmer, G.T. Hefter, Phys. Chem. Chem. Phys. 5 (2003) 5253.
[12] G. Raskopf, PhD dissertation. Ecole des Mines de Paris, Paris (1990).
[13] C.F. Baes, R.E. Mesmer, The Hydrolysis of Cations, Krieger Publi. Comp., Hefty fellow, Florida, 1976.
[14] J.-P. Jolivet, M. Henry, J. Livage, Savoirs Actuels, InterEdition/CNRS Editions, Paris, 1994.
[15] A. Liberti, V. Chiantella, F. Corigliano, J. Inorg. Nucl. Chem. 25 (1963) 415.

[16] V.A. Nazarenko, V.P. Antonovich, E.M. Nevskaya, Russ. J. Inorg. Chem. 16 (1971) 530.

[17] B.I. Nabivanets, V.V. Lukachina, Ukrain. Khim. Zhur. 30 (1964) 1123.

[18] F.I. Lobanov, V.M. Savostina, L.V. Serzhenko, V.M. Peshkova, Russ. J. Inorg. Chem. 14 (1969) 562.

[19] K.C. Sole, Hydrometallurgy 51 (2) (1999) 239.

[20] A.K. Babko, E.A. Mazurenko, B.I. Nabivanets, Russ. J. Inorg. Chem. 14 (1969) 1091.

[21] A.B. Lundin, T.V. Luzgina, I.I. Kalinichenko, Russ. J. Inorg. Chem. 31 (1986) 44.

[22] J. Beukenkamp, K.D. Herrington, J. Am. Chem. Soc. 82 (1960) 3025.

[23] B.I. Nabivanets, Russ. J. Inorg. Chem. 7 (1962) 210, 352.

[24] Ya.I. Tur'yan, L.M. Maluka, J. Gen. Chem. URSS 51 (3) (1981) 531.