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Characterization of Chemical Speciation of Titanyl Sulfate Solutions for Production of Titanium Dioxide Precipitates

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Ion association in concentrated aqueous solutions of titanyl sulfate in sulfuric acid has been investigated at 25 °C by Raman spectroscopy under conditions like those used in the preparation of titania nanoparticles. Systematic variation of titanyl (M), sulfate (L), and hydrogen ion concentrations and a detailed quantitative analysis of the spectra reveal that two weak titanyl sulfato complexes (ML and ML_2) are formed, with ML predominating. This assignment conflicts with the recent results of Baillon et al. (*J. Mol. Liq.* **2008**, *143*, 8−12).

Introduction

Titania (TiO_2) is a multifunctional material with considerable economic importance as a stable white pigment and as a catalyst with photo- and bio-activity.[1] Precipitation from concentrated sulfuric acid solutions is often a key step in the production of titania with desired properties. On the one hand, the hydrometallurgical production of titania is achieved mainly by a sulfate process in which ilmenite ore is leached by sulfuric acid, followed by the separation of iron from the resulting liquor. Alternatively, nano-crystalline TiO_2 catalysts with different anatase-to-rutile ratios and surface areas have recently been prepared by various methods[2] including hydrolysis from sulfuric acid solutions. To manage the precipitation of titania with particular nano- and macrocrystallinities, a quantitative description of the physicochemical properties of these solutions[3] and the precursor species formed therein is needed, which in turn requires a reliable Ti(IV) speciation model.

Some early literature[4] notwithstanding, the only direct study regarding Ti(IV) speciation in sulfuric acid has been reported recently by Baillon et al.[5] In these publications,[5] inconsistencies exist between primary data (Raman intensities) and the evaluated equilibrium constants (see below). Another contradiction concerns Ti(IV) coordination by hydrogensulfate[5a] or sulfate.[5b] The Baillon et al. studies,[5]

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and others,[1–4] indicate a widespread contemporary interest in this topic but, evidently, as yet no consensus view exists. Accordingly, we report here a Raman spectroscopic investigation that elucidates the Ti(IV) speciation in sulfuric acid medium by varying the concentrations of all components systematically.

Experimental Section

Materials. Sulfuric acid-free titanyl sulfate dihydrate used for the measurements was obtained as follows. A 50 g quantity of titanium oxysulfate−sulfuric acid complex hydrate (Aldrich) was suspended in 400 mL of absolute ethanol (Biolab). The mixture was stirred for 1 h, and the solid filtered. This washing step with ethanol was repeated twice. After the final filtration, the white material was dried in an oven at 100 °C overnight. The composition of the solid obtained was then checked by different methods (Calculated: Ti, 5.10 mmol/g; S, 5.10 mmol/g. Found: Ti, 5.08 mmol/g (UV−vis); Ti, 5.15 mmol/g (thermogravimetry); S, 4.92 mmol/g (gravimetry)). All other chemicals (sodium sulfate (Sigma), ammonium hydrogensulfate (Aldrich), ammonium sulfate (Sigma Aldrich), sulfuric acid (Merck), sodium perchlorate (Merck), cyclohexane (Aldrich)) were analytical grade and used without further purification.

Raman Spectroscopy. The Raman spectra were recorded with a Nicolet 6700 FT−IR spectrophotometer equipped with NXR FT−Raman module using an Nd:YVO$_4$ laser operating at 1064 nm and an InGaAs detector. The spectra were measured at (25 ± 1) °C using a 5 mm diameter fluorescence-free NMR tube, collected over the 300−3000 cm^{-1} wavenumber range with 2 cm^{-1} resolution and 512 scans. The position of the sample tube was optimized with cyclohexane which was used on occasion as an external standard (ν_{max}/cm^{-1} = 801) for normalizing the measured intensities. The sodium perchlorate internal standard (ν_{max}/cm^{-1} = 934) was used for quantitative measurements, such as the stability constant determinations. In the analysis of the measured Raman spectra, a Gauss−Lorentz profile was used to determine the bandwidths (full width at half-maximum height, fwhh), the peak heights and positions (ν_{max}), and the integrated intensities. These data were collected by the GRAMS/Al 8.0 (Thermo Fischer Scientific Inc.) computer program. Good agreement (always from 99% to 101%) between the calculated and the measured spectra was found. The species distribution curves were simulated using the PSEQUAD[6] computer package.

Results and Discussion

Raman spectroscopy has proven particularly useful for the investigation of sulfate−hydrogensulfate[7] and metal sulfate[8] systems. This tool is better suited than most for the investigation of concentrated electrolyte solutions.

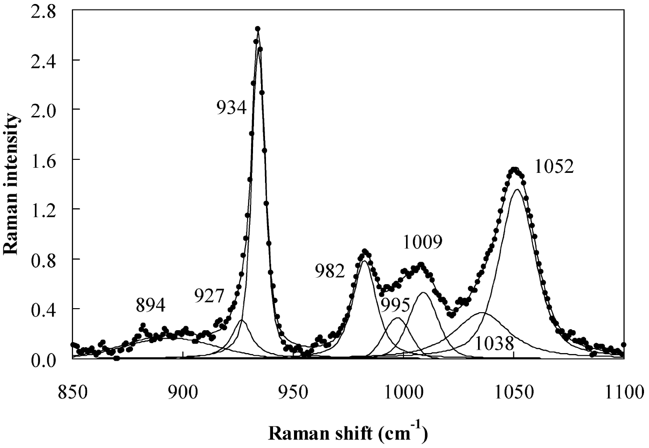

Figure 1. Decomposed Raman spectrum of a solution of titanyl sulfate (1.3 mol/L), sodium perchlorate (as internal standard, 0.3 mol/L) and sulfuric acid (0.8 mol/L). The measured spectrum is indicated by symbols (●) with the calculated individual peaks by lines.

Peak Assignment. Raman active vibrations of the free and/or coordinated sulfate and hydrogensulfate species appear in the wavenumber range of (850 to 1100) cm^{-1}, so our analysis here (with baseline correction) concentrates on this region. The bands of the Raman active species in this range overlap with each other, but eight individual Raman peaks were resolved after deconvolution of the spectrum of titanyl sulfate dissolved in sulfuric acid (using a small amount of sodium perchlorate as an internal standard). Figure 1 shows that the free (non-coordinated) hydrogensulfate ion has three Raman peaks (ν_{max}/cm^{-1} = 1052.2 ± 0.4, 1038.3 ± 0.4, and 894.2 ± 0.5) with that from the free sulfate ion being at ν_{max}/cm^{-1} = 981.8 ± 0.2.[7] Besides the peaks from sodium perchlorate (ν_{max}/cm^{-1} = 934.4 ± 0.2 and 927.1 ± 0.4), two Raman bands were identified and assigned to the sulfate ions coordinated by Ti(IV) (ν_{max}/cm^{-1} = 995.2 ± 0.7 and 1008.7 ± 0.3, hereafter denoted Ti(995) and Ti(1009) respectively). These peak positions are similar to those of other metal sulfates in Raman spectroscopy.[8] In contrast, Baillon et al.[5] report only one Ti peak even at their highest Ti concentration. Although Figure 3.19 of Baillon's thesis[5c] suggests that a possible second peak at ~990 cm^{-1} appears, this was not taken into account. Their deconvolution procedure also resulted in only one peak for hydrogensulfate at ~1050 cm^{-1}.[5b]

There is considerable disagreement in the literature[4,5] as to whether sulfate (L) or hydrogensulfate (HL) coordinates to the titanyl ion (M), and other bivalent ions, in sulfuric acid medium. To clarify this, Raman spectra of solutions with constant total titanyl and sulfate concentrations were measured at varying total sulfuric acid concentrations. Since free sulfate concentration decreases with increasing total [H$^+$], the observed decrease of the integrated intensities of Ti(995) and Ti(1009) with proton concentration clearly corresponds to formation of a titanyl sulfate, rather than a titanyl hydrogensulfate, species (Supporting Information, Figure S1). Since these peaks persist in increasingly acidic solutions, they cannot be attributed to titanyl hydroxo or

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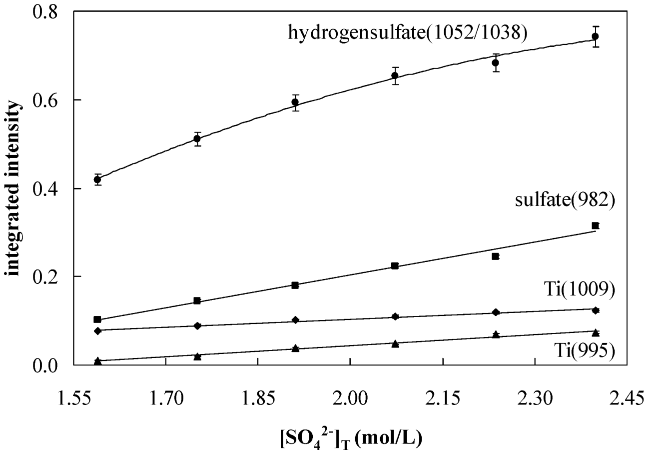

Figure 2. Integrated Raman intensity of the peaks for titanyl sulfate solutions as a function of the total sulfate concentration at constant total sulfuric acid and total titanyl concentrations: $[H_2SO_4]_T = 0.8$ mol/L; $[Na_2SO_4]_T = (0$ to $0.8)$ mol/L; $[TiOSO_4]_T = 0.8$ mol/L. The intensities were normalized using cyclohexane as an external standard.

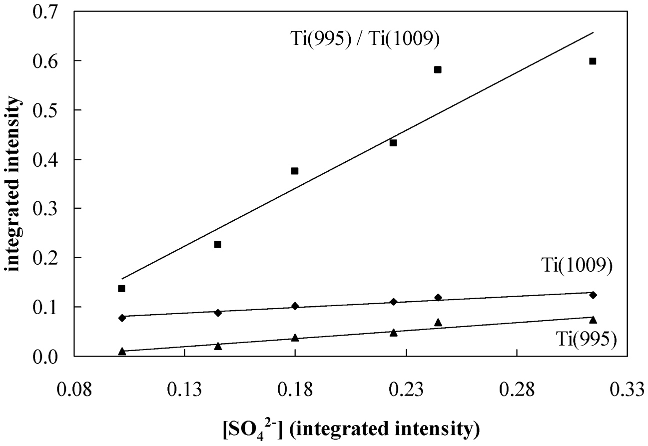

Figure 3. Ratio and individual integrated Raman intensities of the peaks assigned to the titanyl sulfate species as a function of the free (non-coordinated) sulfate concentration ($[H_2SO_4]_T = 0.8$ mol/L; $[Na_2SO_4]_T = (0$ to $0.8)$ mol/L; $[TiOSO_4]_T = 0.8$ mol/L). The intensities were normalized using cyclohexane as an external standard.

mixed sulfato−hydroxo complexes. The sulfate coordination is also preferred even in solid state.[9]

Stoichiometry. Further measurements were carried out at constant total $[H^+]$ but varying titanyl-to-sulfate ratios to determine the stoichiometry of the titanyl sulfate complexes (Ti(995) and Ti(1009), Figure 2 and Supporting Information, Figure S2). The following were observed.

(1) Both Ti(995) (Figure 2) and Ti(1009) (Figure 2 and Supporting Information, Figure S2) increase with sulfate and/or titanyl concentrations.

(2) In the case of Ti(995), a greater increase occurs at higher sulfate-to-titanyl ratios indicating the formation of a complex with sulfate-to-metal ratio >1:1 (Supporting Information, Figure S3).

(3) The ratio of the integrated intensities of the two peaks assigned to the titanyl sulfate species increases linearly with the free sulfate concentration (Figure 3) in accordance with the following equation.

$$\frac{[ML_2]}{[ML]} = \frac{\beta_2[M][L]^2}{\beta_1[M][L]} = \frac{\beta_2[L]}{\beta_1} \qquad (1)$$

(4) Simulation of the individual concentrations of the components (Figure 4 and Supporting Information, Figure S5) gave the best fit with this model.

The peak at 1009 cm^{-1} (Ti(1009)) can thus be assigned convincingly to the titanyl sulfate species with 1:1 stoichiometry, that is, ML ($TiOSO_4^o$) whereas the Ti(995) peak is due to ML_2 ($TiO(SO_4)_2^{2-}$). These species were also identified by Baillon et al.[5b] but without corresponding resolution into their individual peaks.

Stability Constants. To characterize the interaction between the titanyl and sulfate ions quantitatively, measurements were performed using sodium perchlorate as an internal standard. First, the relative Raman molar scattering coefficients (*MSC*) of sulfate (Na_2SO_4 (0.797 ± 0.012) and $(NH_4)_2SO_4$ (0.833 ± 0.007)) and hydrogensulfate (NH_4HSO_4 (0.446 ± 0.009) and H_2SO_4 (0.448 ± 0.015)) were determined (Supporting Information, Table S1 and Figure S4). Good agreement was found between the values obtained with the different substances (although a slight difference was found with sulfate itself, probably resulting from the weak interaction between the sodium and sulfate ions[8b]). These *MSC* values were used to determine the free (non-coordinated) sulfate and hydrogensulfate concentrations quantitatively in the present acidic titanyl sulfate solutions.

Raman spectra of solutions containing titanyl sulfate, sulfuric acid, sodium sulfate, and sodium perchlorate were recorded and analyzed. To determine the stability constants of the ML and ML_2 complexes, the sulfate-to-titanyl ratio was varied systematically (Supporting Information, Table S2), and the concentrations of the free sulfate and hydrogensulfate ions were determined from the integrated intensi-

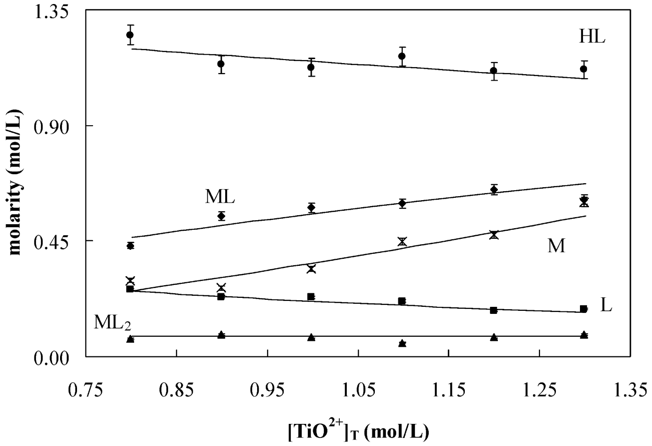

Figure 4. Measured (symbols, from Raman intensities) and calculated (lines, stability constants from Supporting Information, Table S3) concentrations of the species in the titanyl sulfate−sulfuric acid system at different total titanyl concentrations ($L = SO_4^{2-}$, $M = TiO^{2+}$ and $[H^+]_T = 1.6$ mol/L; $[SO_4^{2-}]_T = 2.1$ mol/L; $[TiO^{2+}]_T = (0.8$ to $1.3)$ mol/L, $I_c \approx 7.6$ mol/L). Error bars show measured uncertainties of Raman peak integrations; actual errors in concentrations will be considerably larger, especially for minor species.

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[9] Trojanov, S.; Stiewe, A.; Kemnitz, E. *Z. Naturforsch.* **1996**, *51*, 19–24.

ties of their Raman peaks and the *MSC* values. The following assumptions were made.

(1) The ML and ML_2 complexes belong to the Ti(1009) and Ti(995) peaks respectively (see above).

(2) The *MSC* values of coordinated sulfate were considered to be equal in both ML and ML_2 because of the very similar chemical environment in these complexes. (Neither is this assumption likely to be problematic given the limited extent of formation attributed to ML_2 below.)

(3) The difference between the total sulfate concentration ($[SO_4^{2-}]_T$) and the sum of the equilibrium concentrations of sulfate and hydrogensulfate is the concentration of sulfate coordinated to the titanyl ion in ML and ML_2 ($[SO_4^{2-}]_{bound}$). This can be described by the following mass balance relationships.

$$\begin{aligned} [SO_4^{2-}]_{bound} &= [SO_4^{2-}]_T - ([SO_4^{2-}] + [HSO_4^-]) \\ [SO_4^{2-}]_T &= [TiOSO_4]_T + [Na_2SO_4]_T + [H_2SO_4]_T \end{aligned} \tag{2}$$

(4) The integrated intensities of the Ti(995) and Ti(1009) Raman peaks relate to the amount of sulfate coordinated in ML and ML_2, so that the equilibrium concentrations of the individual titanyl sulfate complexes can be calculated as follows.

$$\begin{aligned} [TiOSO_4^o] = [ML] &= \frac{I_{Ti(1009)}}{I_{Ti(1009)} + I_{Ti(995)}}[SO_4^{2-}]_{bound} \\ [TiO(SO_4)_2^{2-}] = [ML_2] &= \frac{[SO_4^{2-}]_{bound} - [TiOSO_4^o]}{2} \end{aligned} \tag{3}$$

(5) Polynuclear Ti(IV) species were neglected because (i) [ML] and [ML_2] changed essentially linearly with total composition and (ii) no "aging effects" were observed over 3 weeks which excludes slow reactions like polymerization.

Relatively low stability constant values were obtained for the ML ($\log\beta_1 = 0.85 \pm 0.08$) and ML_2 ($\log\beta_2 = 0.68 \pm 0.07$) species at room temperature (Supporting Information, Table S3). As is well understood, stability constants of cation−anion complexes determined by thermodynamic techniques such as potentiometry are in general greater than is reflected in spectroscopic quotients.[8f] However, the difference due to solvent−separated ion pairing is typically small. The protonation constant of the sulfate ion ($\lg K_{sulfate} = 1.10 \pm 0.06$) was calculated from the same experimental data achieving a good agreement with previously published data.[7]

Our quantitative analyses were confirmed by the simulation of the species distribution curves (Figure 4) calculated by the PSEQUAD[6] computer program. Equilibrium concentrations of free titanyl ion (M) and the species containing sulfate ion (ML, ML_2, L, and HL) were calculated using the determined stability constant values. Good agreement was found between the calculated and the measured values. As clearly shown in the distribution curves, ML is the main titanyl species, whereas the ML_2 complex forms only in slight amount.

Similar stability ($\log\beta_1 = 0.99 \pm 0.08$ and $\log\beta_2 = 0.97 \pm 0.06$) and protonation constant ($\lg K_{sulfate} = 1.14 \pm 0.08$) values were obtained from independent experiments performed at different total sulfate concentrations (Supporting Information, Table S4). Satisfactory agreement was again found between the calculated and the measured values (Supporting Information, Figure S5) and also between the two sets of stability constants (Figure 5 and Supporting Information, Figure S6). Given the small fraction of total sulfate present as ML_2, the differences in the $\log\beta_2$ values calculated from these two sets of measurements are well within experimental error, which is larger than the standard deviations of the average values.

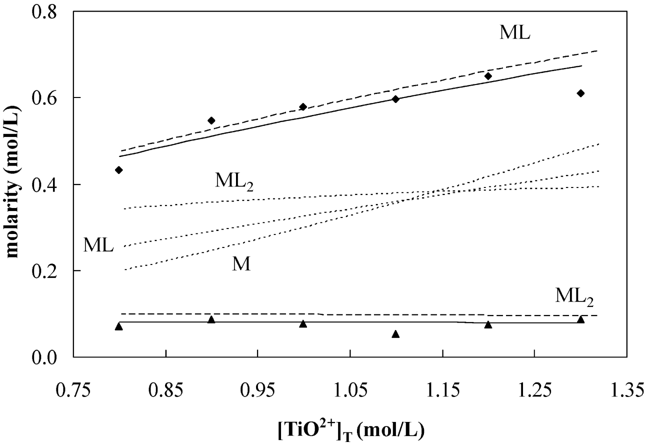

Figure 5. Measured (symbols) and calculated (lines) concentrations of the ML and ML_2 species at different total titanyl concentrations: $[H^+]_T = 1.6$ mol/L; $[SO_4^{2-}]_T = 2.1$ mol/L; $[TiO^{2+}]_T = (0.8$ to $1.3)$ mol/L. The calculations were carried out using formation constants from our first set of measurements (solid lines; $\log\beta_1 = 0.85$, $\log\beta_2 = 0.68$, $\log K_{sulfate} = 1.10$), second set (dashed lines; $\log\beta_1 = 0.99$, $\log\beta_2 = 0.97$, $\log K_{sulfate} = 1.14$) and values from ref 1b (dotted lines; $\log\beta_1 = 0.53$, $\log\beta_2 = 1.08$, $\log K_{sulfate} = 0.39$), which predict appreciable concentrations of free titanyl (M).

Baillon et al.'s stability constants,[5b] on the other hand, imply ML_2 predominates under most of the present conditions (Figure 5 and Supporting Information, Figure S6). Since Baillon's thesis[5c] does not provide more quantitative information, the reason for this strikingly different result is difficult to resolve. However, there are several unusual aspects to their results, including (a) their stability constant values ($\log\beta_1 = 0.53$, $\log\beta_2 = 1.08$) implying $K_2 > K_1$, (b) their significantly different sulfate protonation constant, which may be more suitable for pure sulfuric acid solutions,[5b,c] (c) their measured Raman peak intensities[5b] which are lowest for hydrogensulfate even though it predominates in acidic solutions, and (d) their assumption that free Ti(IV) is negligible,[5b] which is in conflict with their own equilibrium constants (Figure 5 and Supporting Information, Figure S6).

Conclusions

The results of the present study give a sound description of Ti(IV) speciation in concentrated acidic solutions used in titania production processes. Titanium(IV) forms complexes with the sulfate ion (i.e., there is no evidence of hydrogensulfate coordination). Species with 1:1 and 1:2 stochiometry have been characterized, with relatively small stability constants. The $TiOSO_4^o$ complex predominates everywhere under the present experimental conditions.

Finally, one of the great remaining challenges in solution chemistry is to develop a better understanding of medium effects in concentrated electrolyte solutions.[10] Insights regarding the weak interaction between cations and anions such as are afforded here by the Raman-active titanyl sulfate species will be fundamental to this endeavor. For example, this will underpin future thermodynamic modeling of hydrometallurgical leaching by sulfuric or hydrochloric acids.

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Supporting Information Available: Primary Raman data and evaluated equilibrium constants are given in Figures S1 to S6 and Tables S1 to S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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