Electronic Supplementary Information

Spectroscopic characterisation of weak interactions in acidic titanyl sulfate – iron(II) sulfate solutions

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Table S1 Experimental and calculated data for determination of stoichiometries and stability constants of titanyl chloride complexes.

	Experiment A	**Experiment B**
System	$TiO^{2+} + Cl^{-} + H^{+}$	$TiO^{2+} + Cl^{-} + H^{+} + SO_4^{2-}$
Solution Composition[a]	$[TiO^{2+}] = 0.05$ mol dm^{-3} $[NO_3^{-}] = 3.10$ mol dm^{-3} $[Cl^{-}] = (0.00 - 0.50)$ mol dm^{-3} $[H^{+}] = 2.00$ mol dm^{-3} $[Na^{+}] = (1.00 - 1.50)$ mol dm^{-3}	$[TiO^{2+}] = 0.06$ mol dm^{-3} $[NO_3^{-}] = 4.00$ mol dm^{-3} $[Cl^{-}] = (0.00 - 0.50)$ mol dm^{-3} $[H^{+}] = 2.00$ mol dm^{-3} $[Na^{+}] = (2.00 - 2.50)$ mol dm^{-3} $[SO_4^{2-}] = 0.06$ mol dm^{-3}
	$I = 3.5$ mol dm^{-3}	$I = 4.5$ mol dm^{-3}
Experimental Method	UV–Vis spectrophotometry	UV–Vis spectrophotometry
Temperature	(25 ± 1) °C	(25 ± 1) °C
Wavelength range	(320 – 450) nm	(320 – 450) nm
Number of Fitted Points[b]	594 (66·9)	1056 (66·16)
Method of Calculation[c]	PSEQUAD program	PSEQUAD program
logβ_2 [d] **$TiO^{2+} + 2\ Cl^{-} = TiOCl_2^{o}$**	**1.11 (0.03)**	**1.12 (0.03)**

[a] Total concentrations are given for each components. [b] Number of datum points per experiments times by the number of replicate determination. [c] L. Zékány, I. Nagypál, in *Computational Methods for the Determination of Formation Constants*; ed. D. J. Leggett, Plenum Press, New York, 1985; [d] The standard deviations are given in parenthesis.

Table S2 Experimental and calculated data for determination of stoichiometries and stability constants of titanyl sulfate complexes.

System	$TiO^{2+} + SO_4^{2-} + H^+$
Solution Composition[a]	$[TiO^{2+}] = 0.08$ mol dm^{-3} $[NO_3^-] = 3.16$ mol dm^{-3} $[H^+] = 2.00$ mol dm^{-3} $[Na^+] = (1.00 – 1.70)$ mol dm^{-3} $[SO_4^{2-}] = (0.00 – 0.35)$ mol dm^{-3} $I = 3.8$ mol dm^{-3}
Experimental Method	UV–Vis spectrophotometry
Temperature	(25 ± 1) °C
Wavelength range	(310 – 410) nm
Number of Fitted Points[b]	561 (51·11)
Method of Calculation[c]	PSEQUAD program
log$\boldsymbol{\beta}$[d] **$TiO^{2+} + SO_4^{2-} = TiOSO_4^{o}$**	**1.64 (0.06)**

[a] Total concentrations are given for each components. [b] Number of datum points per experiments times by the number of replicate determination. [c] L. Zékány, I. Nagypál, in *Computational Methods for the Determination of Formation Constants*; ed. D. J. Leggett, Plenum Press, New York, 1985; [d] The standard deviations are given in parenthesis.

Table S3 Experimental and calculated data for determination of stoichiometries and stability constants of ferrous sulfate complexes.

	Experiment A	**Experiment B**
System	$Fe^{2+} + SO_4^{2-} + H^+$	$Fe^{2+} + SO_4^{2-} + H^+$
Solution Composition[a]	$[Fe^{2+}]$ = 0.01 mol dm^{-3} $[SO_4^{2-}]$ = 1.28 mol dm^{-3} $[H^+]$ = (0.51 – 2.53) mol dm^{-3} $[Na^+]$ = (2.02 – 0.00) mol dm^{-3}	$[Fe^{2+}]$ = 0.10 mol dm^{-3} $[SO_4^{2-}]$ = 0.10 mol dm^{-3} $[H^+]$ = (0.24 – 2.19) mol dm^{-3} $[Na^+]$ = (1.95 – 0.00) mol dm^{-3} $[ClO_4^-]$ = 2.19 mol dm^{-3}
	I = 3.8 mol dm^{-3}	I = 2.6 mol dm^{-3}
Experimental Method	UV–Vis spectrophotometry	UV–Vis spectrophotometry
Temperature	(25 ± 1) °C	(25 ± 1) °C
Wavelength range	(260 – 420) nm	(260 – 420) nm
Number of Fitted Points[b]	474 (79·6)	474 (79·6)
Method of Calculation[c]	PSEQUAD program	PSEQUAD program
logβ_1 [d] **$Fe^{2+} + SO_4^{2-} = FeSO_4^o$**	**1.52 (0.06)**	

[a] Total concentrations are given for each components. [b] Number of datum points per experiments times by the number of replicate determination. [c] L. Zékány, I. Nagypál, in *Computational Methods for the Determination of Formation Constants*; ed. D. J. Leggett, Plenum Press, New York, 1985; [d] The standard deviations are given in parenthesis.

Table S4 Experimental and calculated data for determination of stoichiometries and stability constants of ferric sulfate complexes.

System	$Fe^{3+} + SO_4^{2-} + H^+$
Solution Composition[a]	$[Fe^{3+}] = 0.01$ mol dm^{-3} $[H^+] = (0.51 - 2.53)$ mol dm^{-3} $[Na^+] = (2.02 - 0.00)$ mol dm^{-3} $[SO_4^{2-}] = 1.28$ mol dm^{-3} $I = 3.9$ mol dm^{-3}
Experimental Method	UV–Vis spectrophotometry
Temperature	(25 ± 1) °C
Wavelength range	(350 – 444) nm
Number of Fitted Points[b]	276 (46·6)
Method of Calculation[c]	PSEQUAD program
logβ_1 [d] **$Fe^{3+} + SO_4^{2-} = Fe(SO_4)^+$**	**2.00 (0.10)**
logβ_2 [d] **$Fe^{3+} + 2\ SO_4^{2-} = Fe(SO_4)_2^-$**	**2.49 (0.08)**

[a] Total concentrations are given for each components. [b] Number of datum points per experiments times by the number of replicate determination. [c] L. Zékány, I. Nagypál, in *Computational Methods for the Determination of Formation Constants*; ed. D. J. Leggett, Plenum Press, New York, 1985; [d] The standard deviations are given in parenthesis.

Table S5 Experimental and calculated data for determination of stoichiometries and stability constants of species formed in the TiO^{2+} – Fe^{2+} – SO_4^{2-} – H^+ quaternary system.

	Experiment A	**Experiment B**	**Experiment C**
System	$TiO^{2+} + Fe^{2+} + SO_4^{2-} + H^+$	$TiO^{2+} + Fe^{2+} + SO_4^{2-} + H^+$	$TiO^{2+} + Fe^{2+} + SO_4^{2-} + H^+$
Solution Composition[a]	$[TiO^{2+}]$ = (0.00 – 0.10) mol dm^{-3} $[Fe^{2+}]$ = 0.10 mol dm^{-3} $[SO_4^{2-}]$ = 1.21 mol dm^{-3} $[H^+]$ = 2.02 mol dm^{-3} $[Na^+]$ = (0.20 – 0.00) mol dm^{-3} I = 3.8 mol dm^{-3}	$[TiO^{2+}]$ = 0.10 mol dm^{-3} $[Fe^{2+}]$ = (0.00 – 0.10) mol dm^{-3} $[SO_4^{2-}]$ = 1.21 mol dm^{-3} $[H^+]$ = 2.02 mol dm^{-3} $[Na^+]$ = (0.20 – 0.00) mol dm^{-3} I = 3.8 mol dm^{-3}	$[TiO^{2+}]$ = 0.10 mol dm^{-3} $[Fe^{2+}]$ = 0.10 mol dm^{-3} $[SO_4^{2-}]$ = (0.20 – 1.00) mol dm^{-3} $[H^+]$ = 0.97 mol dm^{-3} $[Na^+]$ = 0.80 – 1.60 mol dm^{-3} $[ClO_4^-]$ = (1.77 – 0.97) mol dm^{-3} I = 3.4 mol dm^{-3}
Experimental Method	UV–Vis spectrophotometry	UV–Vis spectrophotometry	UV–Vis spectrophotometry
Temperature	(25 ± 1) °C	(25 ± 1) °C	(25 ± 1) °C
Wavelength range	(404 – 540) nm	(404 – 540) nm	(404 – 540) nm
Number of Fitted Points[b]	414 (69·6)	414 (69·6)	414 (69·6)
Method of Calculation[c]	PSEQUAD program	PSEQUAD program	PSEQUAD program
logβ[d] **$TiO^{2+} + Fe^{2+} + 3\ SO_4^{2-} = FeTiO(SO_4)_3^{2-}$**		**7.13 (0.10)**	

[a] Total concentrations are given for each components. [b] Number of datum points per experiments times by the number of replicate determination. [c] L. Zékány, I. Nagypál, in *Computational Methods for the Determination of Formation Constants*; ed. D. J. Leggett, Plenum Press, New York, 1985; [d] The standard deviations are given in parenthesis.

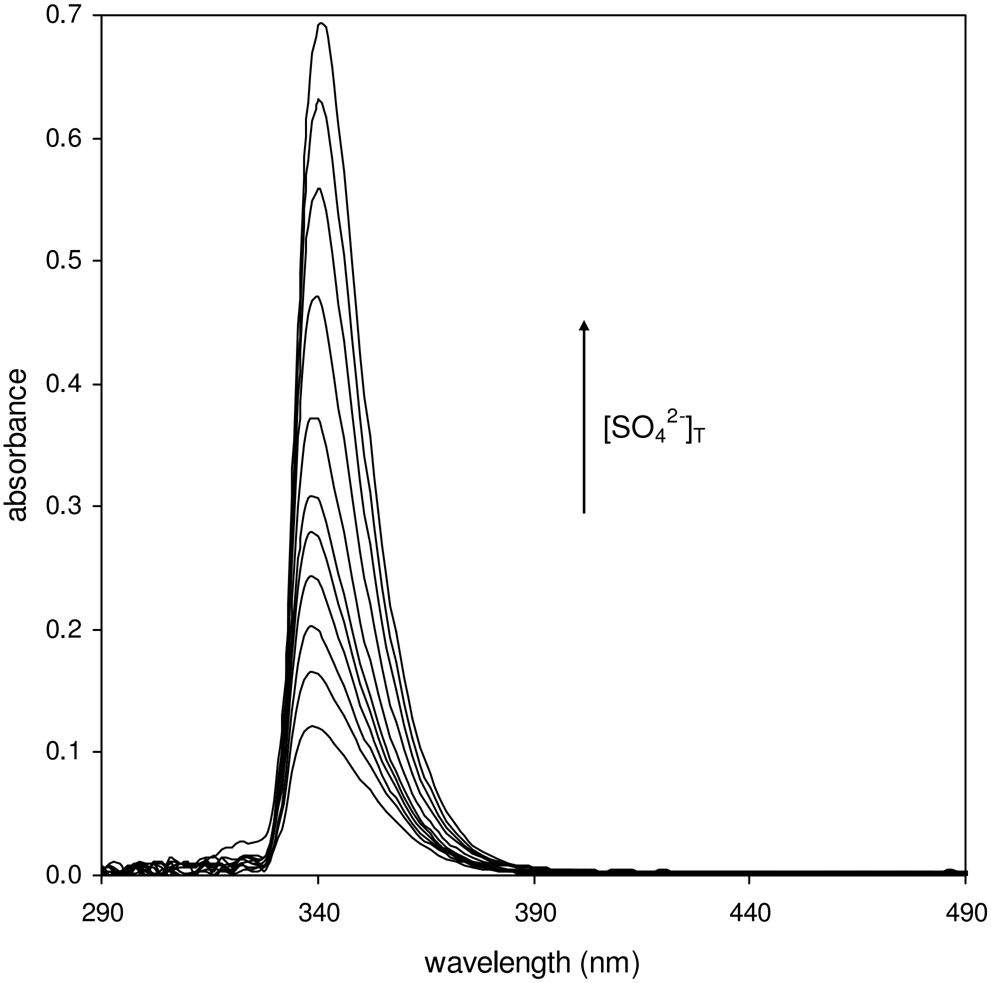

Fig. S1 UV–Vis spectra of $TiOSO_4$ solutions at different total sulfate concentrations under acidic conditions ($[TiO^{2+}]_T = 0.08$ mol dm^{-3}; $[HNO_3]_T = 2.00$ mol dm^{-3}; $[SO_4^{2-}]_T = (0.00 - 0.35)$ mol dm^{-3}; $[NaNO_3]_T = 1.00$ mol dm^{-3}). The starting titanyl nitrate solution was used as blank for these measurements.

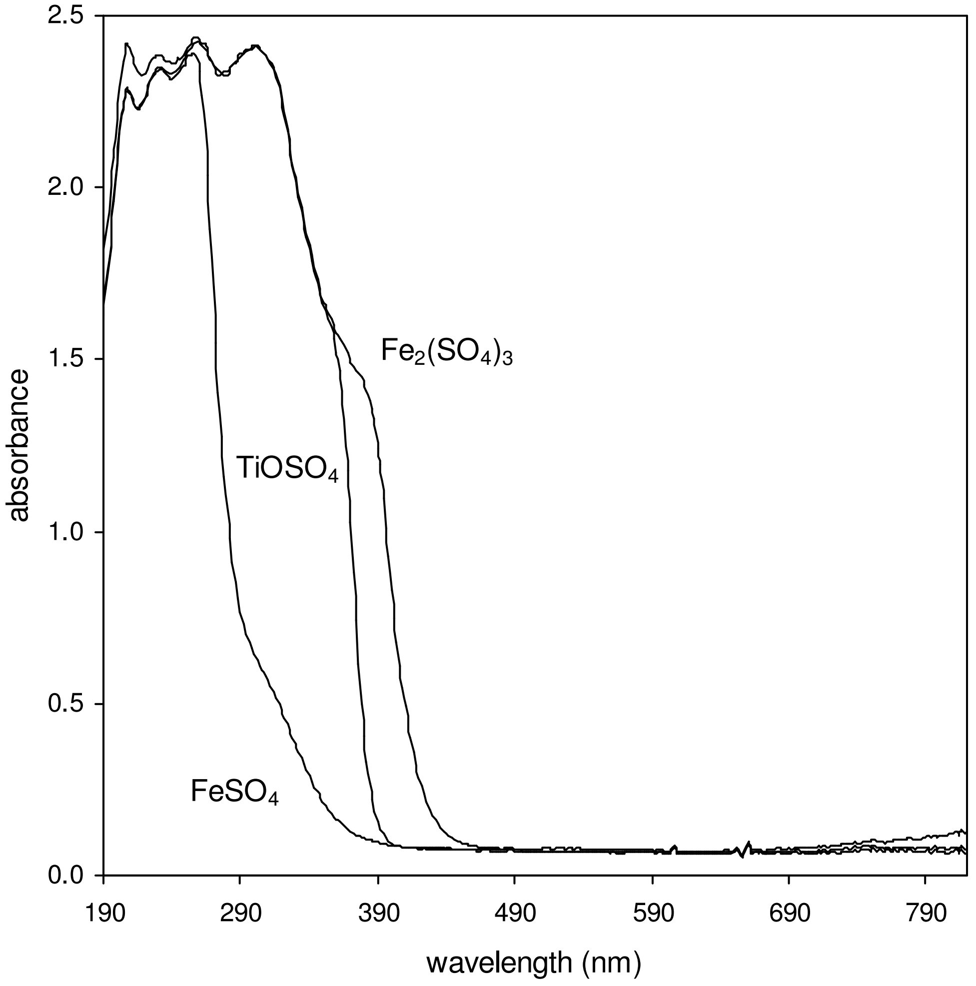

Fig. S2 UV–Vis spectra of $FeSO_4$, $TiOSO_4$ and $Fe_2(SO_4)_3$ in aqueous acidic solution ($[Fe^{2+}] = [TiO^{2+}] = [Fe^{3+}] = 0.10$ mol dm^{-3}; $[HClO_4] = 2.20$ mol dm^{-3}).

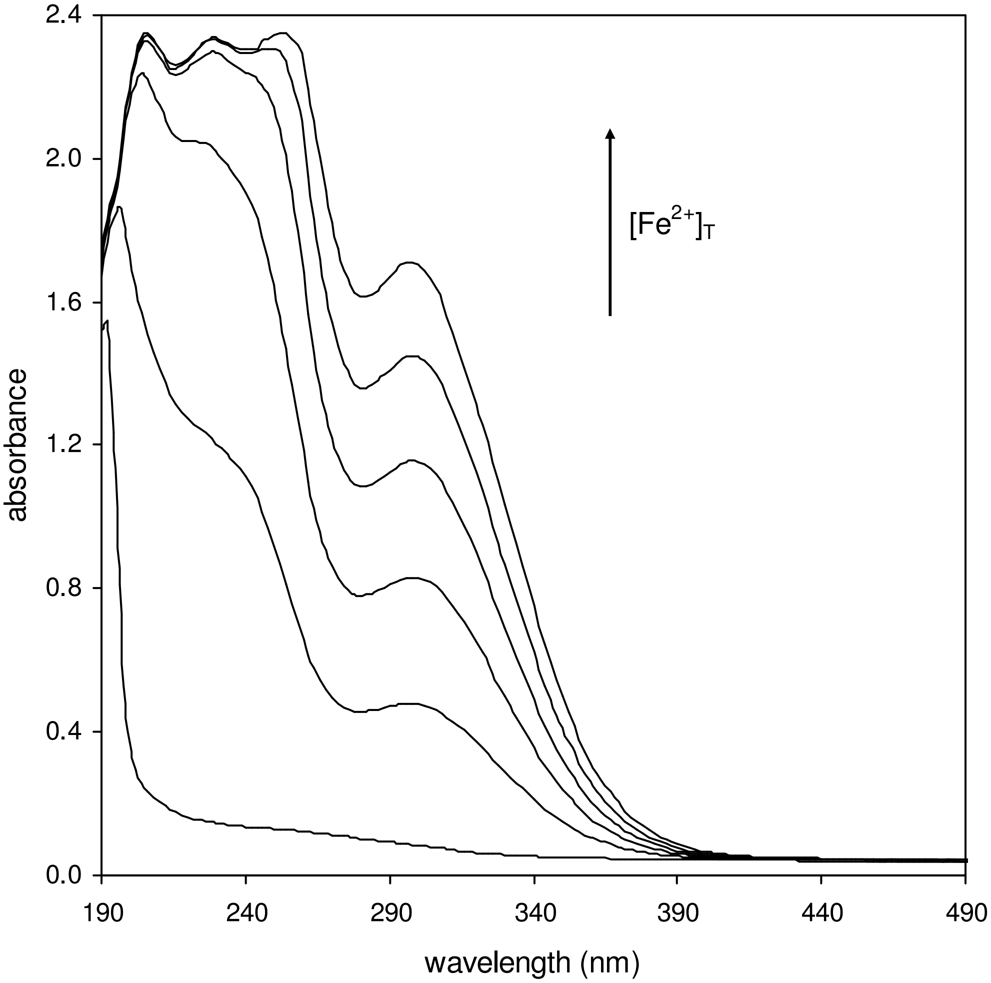

Fig. S3 UV–Vis spectra of acidic ferrous sulfate solutions at constant total proton and sulfate concentrations but at different total iron(II) concentration ($[Fe^{2+}]_T$ = (0.00 – 0.10) mol dm^{-3}; $[H_2SO_4]_T$ = 1.00 mol dm^{-3}; $[SO_4^{2-}]_T$ = 1.10 mol dm^{-3}).

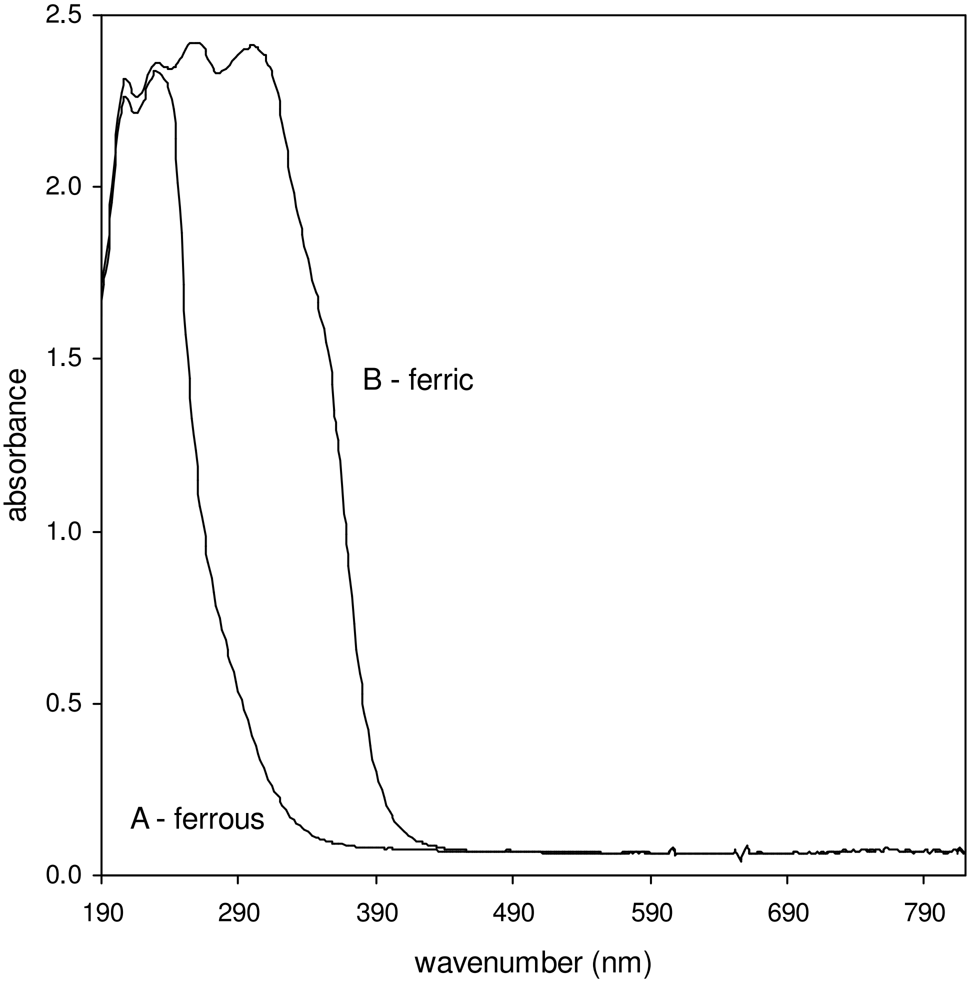

Fig. S4 UV–Vis spectra of acidic titanyl sulfate solutions containing ferrous (A) and ferric (B) ions ($[TiOSO_4]_T$ = 0.01 mol dm^{-3}; A – $[Fe^{2+}]_T$ or B – $[Fe^{3+}]_T$ = 0.01 mol dm^{-3}; $[H_2SO_4]_T$ = 1.24 mol dm^{-3}; $[SO_4^{2-}]_T$ = 1.26 mol dm^{-3}). The concentration of the $FeTiO(SO_4)_3^{2-}$ complex is too low to be detected here.