Supplementary Informations

1. Calculation of the unprotonated sulphate concentration ($[SO_4^{2-}]_{eq}$)

The $[SO_4^{2-}]_{eq}$ depends on the twofold protonation of the sulphate ion and the resulting equilibria between H_2SO_4, HSO_4^- and SO_4^{2-}. The pK^0_a of sulfuric acid increases from -3 to -0.1 in the studied temperature range.[1] Thus, H_2SO_4 can be neglected under the present experimental conditions, and the SO_4^{2-} concentration is determined by the following equilibrium.

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

In order to calculate $[SO_4^{2-}]_{eq}$ the following assumptions are made:

1.) Na_2SO_4 and $NaClO_4$ are completely dissociated in aqueous solution

2.) The total sulphate concentration is described by

$$[SO_4^{2-}]_{total} = [SO_4^{2-}]_{eq} + [HSO_4^-]_{eq} \qquad \text{eq 1}$$

3.) The total proton concentration is described by

$$[H^+]_{total} = [H^+]_{eq} + [HSO_4^-]_{eq} \qquad \text{eq 2}$$

Hereby, the total proton concentration equals the amount of added perchloric acid. The protons generated from the autoprotolysis of water can be neglected under the present experimental conditions.[2] The $[SO_4^{2-}]_{eq}$ is then calculated according to equation 3.

$$[SO_4^{2-}]_{eq} = \frac{-C+\sqrt{C^2+4K'_{HSO_4^-}(T)\cdot[SO_4^{2-}]_{total}}}{2} \qquad \text{eq 3}$$

with

$$C = [H^+]_{total} - [SO_4^{2-}]_{total} + K'_{HSO_4^-}(T) \qquad \text{eq 4}$$

The values of log $K^0(HSO_4^-)(T)$ are taken from Dickson et al.[3] The conditional log $K'(HSO_4^-)(T)$ values for the different ionic strengths ($NaClO_4$) are calculated according to the SIT. For this, temperature independent ion-ion interaction coefficients are used ($\varepsilon(HSO_4^-,Na^+)$ = -0.01 ± 0.02; $\varepsilon(SO_4^{2-},Na^+)$ = -0.12 ± 0.06; $\varepsilon(H^+,ClO_4^-)$ = 0.14 ± 0.02). The so calculated free sulphate concentration at two different $[SO_4^{2-}]_{total}$ is displayed as a function of the temperature in figure 1. The results show a general decrease of $[SO_4^{2-}]_{eq}$ with increasing temperature.

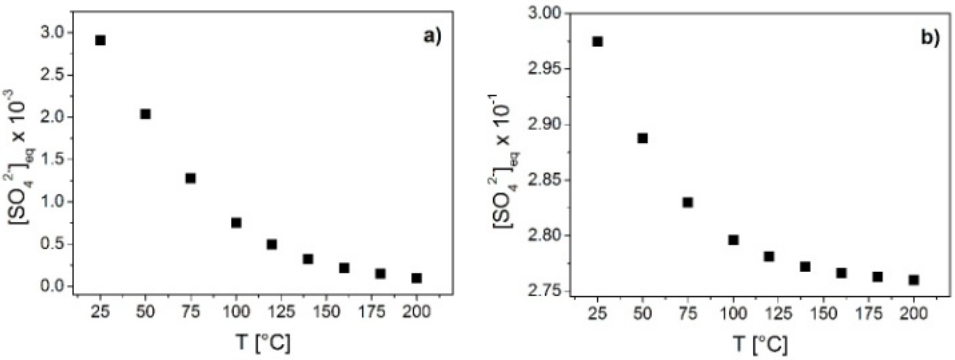

Fig. 1 $[SO_4^{2-}]_{eq}$ as a function of the temperature at a) $[SO_4^{2-}]_{total} = 5.5\cdot10^{-3}$ m and b) $[SO_4^{2-}]_{total} = 3.6\cdot10^{-1}$ m ($[HClO_4]_{total} = 8.93\cdot10^{-2}$ mol/kg H_2O)

2. Application of the specific ion interaction theory (SIT)

According to the SIT, the conditional stability constants are related to the thermodynamic log K^0_n(T) values by equation 5.

$$\log K_n^0\,(T) = \log K'_n(T) - \Delta z^2 D(T) + \Delta\varepsilon_n(T) \cdot I_m \qquad \text{eq 5}$$

Hereby, I_m is the molal ionic strength and D(T) is the temperature dependent Debye-Hückel term: $D(T) = A(T)(I_m)^{0.5}/\left(1 + Ba_j(T) \cdot (I_m)^{0.5}\right)$. The Debye-Hückel parameters A(T) and Ba_j(T) are given in the NEA-TDB as a function of the temperature.[4] For the formation of the $[Cm(SO_4)_n]^{3-2n}$ (n = 1, 2, 3) complexes the values of Δz^2 are Δz^2 = -12 for n = 1, Δz^2 = -4 for n = 2 and Δz^2 = -4 for 3. The thermodynamic log K^0_n(T) and $\Delta\varepsilon_n$(T) values are obtained from the conditional log K'_n(T) values at I_m = 1.0 – 4.0 m by linear regression according to equation 5. For each temperature log K'_n(T)−Δz^2·D(T) is plotted versus I_m (SIT plots).

3. Experimentally determined speciations of the studied samples

3.1 Samples at constant ionic strength

	$[SO_4^{2-}]_{total} = 6 \cdot 10^{-3}$ mol/kg H_2O, $I_m = 2.0$ ($NaClO_4$)			
T [°C]	$\chi\ Cm^{3+}$	$\chi\ Cm(SO_4)^{+}$	$\chi\ Cm(SO_4)_2^{-}$	$\chi\ Cm(SO_4)_3^{3-}$
25	0.939	0.068	0.005	0.002
50	0.939	0.054	0.001	0.006
75	0.895	0.101	0.007	0.002
100	0.881	0.114	0.006	0.001
120	0.855	0.146	0.007	0.003
140	0.830	0.148	0.013	0.005
160	0.818	0.163	0.013	0.004
180	0.795	0.174	0.012	0.005
200	0.800	0.169	0.024	0.004

	$[SO_4^{2-}]_{total} = 1.5 \cdot 10^{-2}$ mol/kg H_2O, $I_m = 2.0$ ($NaClO_4$)			
T [°C]	$\chi\ Cm^{3+}$	$\chi\ Cm(SO_4)^{+}$	$\chi\ Cm(SO_4)_2^{-}$	$\chi\ Cm(SO_4)_3^{3-}$
25	0.868	0.130	0.008	0.002
50	0.899	0.091	0.002	0.000
75	0.771	0.221	0.012	0.000
100	0.696	0.295	0.015	0.000
120	0.637	0.357	0.011	0.003
140	0.529	0.416	0.065	0.005
160	0.502	0.464	0.043	0.004
180	0.478	0.475	0.005	0.005
200	0.448	0.484	0.079	0.007

	$[SO_4^{2-}]_{total} = 3.1 \cdot 10^{-2}$ mol/kg H_2O, $I_m = 2.0$ ($NaClO_4$)			
T [°C]	$\chi\ Cm^{3+}$	$\chi\ Cm(SO_4)^{+}$	$\chi\ Cm(SO_4)_2^{-}$	$\chi\ Cm(SO_4)_3^{3-}$
25	0.826	0.186	0.018	0.002
50	0.753	0.191	0.020	0.016
75	0.660	0.248	0.074	0.016
100	0.561	0.327	0.094	0.016
120	0.443	0.438	0.094	0.016
140	0.291	0.541	0.136	0.016
160	0.268	0.541	0.173	0.016
180	0.268	0.499	0.172	0.011
200	0.225	0.509	0.188	0.044

	$[SO_4^{2-}]_{total} = 1.16 \cdot 10^{-1}$ mol/kg H_2O, $I_m = 2.0$ ($NaClO_4$)			
T [°C]	$\chi\ Cm^{3+}$	$\chi\ Cm(SO_4)^{+}$	$\chi\ Cm(SO_4)_2^{-}$	$\chi\ Cm(SO_4)_3^{3-}$
25	0.519	0.390	0.120	0.002
50	0.359	0.398	0.144	0.054
75	0.114	0.592	0.288	0.016
100	0.007	0.508	0.439	0.048
120	0.000	0.432	0.524	0.048
140	0.000	0.227	0.728	0.096
160	0.000	0.145	0.654	0.250
180	0.000	0.050	0.532	0.414
200	0.000	0.025	0.558	0.456

	$[SO_4^{2-}]_{total} = 1.44 \cdot 10^{-1}$ mol/kg H_2O, $I_m = 2.0$ ($NaClO_4$)			
T [°C]	$\chi\ Cm^{3+}$	$\chi\ Cm(SO_4)^{+}$	$\chi\ Cm(SO_4)_2^{-}$	$\chi\ Cm(SO_4)_3^{3-}$
25	0.402	0.461	0.120	0.002
50	0.293	0.422	0.190	0.054
75	0.032	0.616	0.343	0.016
100	0.002	0.436	0.514	0.047
120	0.000	0.348	0.556	0.105
140	0.000	0.147	0.728	0.192
160	0.000	0.093	0.622	0.324
180	0.000	0.031	0.432	0.546
200	0.000	0.021	0.329	0.657

	$[SO_4^{2-}]_{total} = 2.12 \cdot 10^{-1}$ mol/kg H_2O, $I_m = 2.0$ ($NaClO_4$)			
T [°C]	$\chi\ Cm^{3+}$	$\chi\ Cm(SO_4)^{+}$	$\chi\ Cm(SO_4)_2^{-}$	$\chi\ Cm(SO_4)_3^{3-}$
25	0.359	0.437	0.194	0.002
50	0.213	0.442	0.241	0.054
75	0.012	0.534	0.451	0.032
100	0.002	0.287	0.588	0.118
120	0.000	0.218	0.623	0.151
140	0.000	0.029	0.657	0.348
160	0.000	0.056	0.542	0.422
180	0.000	0.016	0.256	0.715
200	0.000	0.013	0.175	0.815

	$[SO_4^{2-}]_{total} = 2.97 \cdot 10^{-1}$ mol/kg H_2O, $I_m = 2.0$ ($NaClO_4$)			
T [°C]	$\chi\ Cm^{3+}$	$\chi\ Cm(SO_4)^{+}$	$\chi\ Cm(SO_4)_2^{-}$	$\chi\ Cm(SO_4)_3^{3-}$
25	0.324	0.472	0.194	0.002
50	0.213	0.399	0.319	0.054
75	0.012	0.473	0.508	0.038
100	0.002	0.222	0.662	0.118
120	0.000	0.168	0.635	0.199
140	0.000	0.015	0.624	0.402
160	0.000	0.024	0.494	0.517
180	0.000	0.016	0.201	0.782
200	0.000	0.013	0.103	0.890

	$[SO_4^{2-}]_{total} = 3.65 \cdot 10^{-1}$ mol/kg H_2O, $I_m = 2.0$ ($NaClO_4$)			
T [°C]	$\chi\ Cm^{3+}$	$\chi\ Cm(SO_4)^{+}$	$\chi\ Cm(SO_4)_2^{-}$	$\chi\ Cm(SO_4)_3^{3-}$
25	0.251	0.505	0.236	0.002
50	0.182	0.407	0.349	0.054
75	0.007	0.436	0.571	0.038
100	0.002	0.207	0.680	0.131
120	0.000	0.151	0.648	0.207
140	0.000	0.014	0.575	0.466
160	0.000	0.004	0.456	0.565
180	0.009	0.008	0.154	0.830
200	0.000	0.013	0.078	0.909

3.2 Samples at constant sulphate concentration

3.2.1 $[SO_4^{2-}]_{total}$ = 0.05 mol/kg H_2O

	I_m = 0.60 ($NaClO_4$), $[SO_4^{2-}]_{total}$ = 0.05 mol/kg H_2O			
T [°C]	χ Cm^{3+}	χ $Cm(SO_4)^+$	χ $Cm(SO_4)_2^-$	χ $Cm(SO_4)_3^{3-}$
25	0.593	0.313	0.100	0.000
50	0.458	0.362	0.132	0.000
75	0.353	0.439	0.230	0.000
100	0.206	0.483	0.304	0.000
120	0.114	0.584	0.301	0.000
140	0.058	0.584	0.332	0.033
160	0.000	0.584	0.442	0.033
180	0.000	0.555	0.442	0.033
200	0.000	0.500	0.564	0.000

	I_m = 1.10 ($NaClO_4$), $[SO_4^{2-}]_{total}$ = 0.05 mol/kg H_2O			
T [°C]	χ Cm^{3+}	χ $Cm(SO_4)^+$	χ $Cm(SO_4)_2^-$	χ $Cm(SO_4)_3^{3-}$
25	0.734	0.225	0.048	0.000
50	0.629	0.287	0.048	0.000
75	0.461	0.383	0.161	0.000
100	0.336	0.463	0.195	0.000
120	0.211	0.560	0.195	0.000
140	0.125	0.560	0.325	0.000
160	0.125	0.560	0.325	0.000
180	0.064	0.560	0.341	0.052
200	0.000	0.505	0.499	0.051

	I_m = 2.09 ($NaClO_4$), $[SO_4^{2-}]_{total}$ = 0.05 mol/kg H_2O			
T [°C]	χ Cm^{3+}	χ $Cm(SO_4)^+$	χ $Cm(SO_4)_2^-$	χ $Cm(SO_4)_3^{3-}$
25	0.753	0.171	0.086	0.000
50	0.680	0.198	0.086	0.000
75	0.552	0.302	0.143	0.000
100	0.425	0.362	0.189	0.000
120	0.344	0.434	0.208	0.000
140	0.201	0.526	0.262	0.000
160	0.171	0.526	0.317	0.000
180	0.137	0.526	0.317	0.000
200	0.088	0.552	0.317	0.080

	I_m = 3.11 ($NaClO_4$), $[SO_4^{2-}]_{total}$ = 0.05 mol/kg H_2O			
T [°C]	χ Cm^{3+}	χ $Cm(SO_4)^+$	χ $Cm(SO_4)_2^-$	χ $Cm(SO_4)_3^{3-}$
25	0.782	0.238	0.000	0.000
50	0.670	0.289	0.000	0.000
75	0.464	0.459	0.100	0.000
100	0.321	0.558	0.110	0.000
120	0.234	0.631	0.132	0.000
140	0.087	0.663	0.264	0.000
160	0.087	0.663	0.264	0.000
180	0.070	0.663	0.267	0.000
200	0.009	0.678	0.308	0.030

	I_m = 4.11 ($NaClO_4$), $[SO_4^{2-}]_{total}$ = 0.05 mol/kg H_2O			
T [°C]	χ Cm^{3+}	χ $Cm(SO_4)^+$	χ $Cm(SO_4)_2^-$	χ $Cm(SO_4)_3^{3-}$
25	0.753	0.183	0.032	0.000
50	0.682	0.238	0.028	0.000
75	0.552	0.379	0.081	0.000
100	0.420	0.471	0.105	0.000
120	0.338	0.520	0.134	0.000
140	0.260	0.540	0.250	0.000
160	0.173	0.645	0.194	0.000
180	0.125	0.653	0.212	0.000
200	0.060	0.626	0.331	0.000

3.2.2 $[SO_4^{2-}]_{total}$ = 0.20 mol/kg H_2O

	I_m = 1.01 ($NaClO_4$), $[SO_4^{2-}]_{total}$ = 0.20 mol/kg H_2O			
T [°C]	χ Cm^{3+}	χ $Cm(SO_4)^+$	χ $Cm(SO_4)_2^-$	χ $Cm(SO_4)_3^{3-}$
25	0.370	0.479	0.157	0.001
50	0.237	0.427	0.276	0.038
75	0.042	0.523	0.461	0.019
100	0.011	0.321	0.614	0.070
120	0.006	0.233	0.670	0.098
140	0.006	0.111	0.664	0.287
160	0.006	0.056	0.537	0.462
180	0.006	0.028	0.297	0.678
200	0.006	0.007	0.228	0.786

	I_m = 2.04 ($NaClO_4$), $[SO_4^{2-}]_{total}$ = 0.20 mol/kg H_2O			
T [°C]	χ Cm^{3+}	χ $Cm(SO_4)^+$	χ $Cm(SO_4)_2^-$	χ $Cm(SO_4)_3^{3-}$
25	0.359	0.437	0.194	0.002
50	0.213	0.442	0.241	0.054
75	0.012	0.534	0.451	0.032
100	0.002	0.287	0.588	0.118
120	0.000	0.218	0.623	0.151
140	0.000	0.029	0.657	0.348
160	0.000	0.056	0.542	0.422
180	0.000	0.016	0.256	0.715
200	0.000	0.013	0.175	0.815

	I_m = 3.16 ($NaClO_4$), $[SO_4^{2-}]_{total}$ = 0.20 mol/kg H_2O			
T [°C]	χ Cm^{3+}	χ $Cm(SO_4)^+$	χ $Cm(SO_4)_2^-$	χ $Cm(SO_4)_3^{3-}$
25	0.370	0.479	0.157	0.001
50	0.237	0.405	0.320	0.038
75	0.024	0.510	0.508	0.019
100	0.011	0.246	0.711	0.068
120	0.006	0.180	0.704	0.141
140	0.006	0.057	0.578	0.419
160	0.006	0.028	0.537	0.508
180	0.006	0.028	0.230	0.770
200	0.006	0.007	0.142	0.885

	I_m = 4.05 ($NaClO_4$), $[SO_4^{2-}]_{total}$ = 0.20 mol/kg H_2O			
T [°C]	χ Cm^{3+}	χ $Cm(SO_4)^{+}$	χ $Cm(SO_4)_2^{-}$	χ $Cm(SO_4)_3^{3-}$
25	0.404	0.428	0.209	0.001
50	0.234	0.388	0.320	0.038
75	0.024	0.460	0.550	0.019
100	0.011	0.201	0.711	0.107
120	0.006	0.150	0.685	0.163
140	0.006	0.034	0.438	0.594
160	0.006	0.014	0.367	0.646
180	0.006	0.028	0.159	0.809
200	0.006	0.007	0.093	0.903

4. $\Delta\varepsilon_n$ values for the stepwise formation of the $[Cm(SO_4)_n]^{3-2n}$ complexes (n = 1, 2, 3)

T [°C]	$\Delta\varepsilon_1$	$\Delta\varepsilon_2$	$\Delta\varepsilon_3$
25	-0.15 ± 0.04	-0.10 ± 0.06	-
50	-0.15 ± 0.04	-0.04 ± 0.07	-
75	-0.18 ± 0.05	0.04 ± 0.05	-
100	-0.17 ± 0.07	0.06 ± 0.04	-
120	-0.12 ± 0.06	0.04 ± 0.06	-0.11 ± 0.08
140	-0.11 ± 0.09	0.00 ± 0.04	-0.26 ± 0.04
160	-0.21 ± 0.10	0.06 ± 0.05	-0.14 ± 0.03
180	-0.17 ± 0.12	0.07 ± 0.03	-0.20 ± 0.05
200	-0.27 ± 0.11	0.08 ± 0.02	-0.24 ± 0.08

5. Cm(III) lifetime values

5.1 Molar fractions of the studied samples

1.03 m $NaNO_3$	Cm^{3+}	$CmNO_3^{2+}$	$Cm(NO_3)_2^{+}$
25°C	0.331	0.662	0.017
100°C	0.220	0.583	0.204
160°C	0.016	0.636	0.373
200°C	0.000	0.644	0.567

0.03 m Na_2SO_4	Cm^{3+}	$CmSO_4^{+}$	$Cm(SO_4)_2^{-}$	$Cm(SO_4)_3^{3-}$
25°C	0.826	0.186	0.018	0.002
100°C	0.561	0.327	0.094	0.016
160°C	0.268	0.541	0.173	0.016
200°C	0.225	0.509	0.188	0.044

0.20 m Na_2SO_4	Cm^{3+}	$CmSO_4^{+}$	$Cm(SO_4)_2^{-}$	$Cm(SO_4)_3^{3-}$
25°C	0.334	0.528	0.157	0.001
100°C	0.011	0.201	0.711	0.107
160°C	0.006	0.014	0.435	0.587
200°C	0.006	0.007	0.093	0.903

5.2 Experimental determined lifetimes of the samples given in 5.1

T	No ligands	$[NO_3^-]_{total}$ = 1.03m	$[SO_4^{2-}]_{total}$ = 0.03 m	$[SO_4^{2-}]_{total}$ = 0.20 m
25	68 ± 5 µs	83 ± 5 µs	74 ± 5 µs	84 ± 5 µs
100	66 ± 5 µs	77 ± 5 µs	65 ± 5 µs	82 ± 5 µs
160	52 ± 5 µs	64 ± 5 µs	59 ± 5 µs	79 ± 5 µs
200	36 ± 5 µs	10 ± 5 µs	55 ± 5 µs	85 ± 5 µs

6. References

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