Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Structural Characterization of Metal Complexes in Aqueous Solutions: A XAS study of stannous fluoride

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Estimation of structural parameters of stannous fluoride complexes from EXAFS spectra

Lets start by writing the EXAFS spectrum of a given stannous fluoride solution, $\chi_i(k)$, following the formal description of the photoelectron scattering phenomena:[?]

$$\chi_i(k) = \frac{S_0 N_i f(k) e^{-2k\sigma_i^2} e^{-2R_i/\lambda(k)}}{kR_i^2} sin[2kR_i + \delta(k)] \tag{1}$$

Where S_0 corresponds to the amplitude reduction factor, N_i and R_i are the coordination number and bond distance of the coordination shell, respectively, $f(k)$ and $\delta(k)$ are scattering properties of the neighboring atoms, $\lambda(k)$ is the inelastic free mean path of the photoelectron, and σ_i^2 is the mean-square displacement in bond distance, also known as the Debye-Waller factor. Here we assume that the EXAFS spectrum can be approximated by single scattering of a single coordination shell, which is sufficient for simple coordination complexes. Note that the scattering properties and the inelastic free mean path are dependent on the photoelectron wavenumber k and the identity of the neighboring atoms.

We can also express $\chi_i(k)$ as a linear combination of the EXAFS spectra of stannous complexes $\hat{\chi}_j(k)$:

$$\chi_i(k) = \sum_{j=1}^{n} \alpha_{jk} \hat{\chi}_j(k), \qquad i \leq m \tag{2}$$

$$\sum_{j=1}^{n} \alpha_{ij} = 1 \tag{3}$$

Where α_{ij} corresponds to the proportion of the j-th species for the measured solution i. Naturally the proportion of species for a given solution must add to one, since we consider completeness of our ensemble of species.

Replacing equation 1 in both sides of equation 2 and removing duplicated terms in both

sides yields the following:

$$\frac{N_i e^{-2k\sigma_i^2} e^{-2R_i/\lambda(k)}}{R_i^2} sin[2kR_i + \delta(k)] = \sum_{j=1}^{n} \alpha_{ij} \frac{\hat{N}_j e^{-2k\sigma_j^2} e^{-2\hat{R}_j/\lambda(k)}}{\hat{R}_j^2} sin[2k\hat{R}_j + \delta(k)] \quad (4)$$

The previous equation can be simplified by assuming similarity between the Debye-Waller factor of the measured solution and the stannous complexes, as well as similarity for the photoelectron mean free path:

$$e^{-2k\sigma_i^2} \approx e^{2k\sigma_j^2} \quad ; \quad e^{R_i/\lambda(k)} \approx e^{\hat{R}_j/\lambda(k)} \quad (5)$$

$$\frac{N_i}{R_i^2} sin[2kR_i + \delta(k)] = \sum_{j=1}^{n} \alpha_{ij} \frac{\hat{N}_j}{\hat{R}_j^2} sin[2k\hat{R}_j + \delta(k)] \quad (6)$$

A small angle approximation can be performed for the sinusoidal part of the equation by arbitrarily selecting a wavenumber (k_0) that enforces a null value. We can therefore perturb the equation around k_0 and perform the approximation via Taylor expansion:

$$sin[2k_0R_i + \delta(k_0)] = 0 \quad (7)$$

$$sin[2(k_0 + \Delta k)R_i + \delta(k_0 + \Delta k)] \approx sin[2\Delta kR_i] \quad (8)$$

$$\approx 2\Delta kR_i - \frac{(2\Delta kR_i)^3}{3!} \quad (9)$$

Rewriting equation 6 in terms of the small angle approximation and separating the expanded terms yields the following equations:

$$N_i = \sum_{j=1}^{n} \alpha_{ij} \hat{N}_j \frac{R_i}{\hat{R}_j} \tag{10}$$

$$R_i = \frac{\sum_{j=1}^{n} \alpha_{ij} \hat{N}_j \hat{R}_j}{N_i} \tag{11}$$

Finally, assuming similarity between the estimated bond distance of the measured solution and the bond distance of the stannous complexes yields the following expressions for N_i and R_i:

$$R_i \approx \hat{R}_j \tag{12}$$

$$N_i = \sum_{j=1}^{n} \alpha_{ij} \hat{N}_j \tag{13}$$

$$R_i = \frac{\sum_{j=1}^{n} \alpha_{ij} \hat{N}_j \hat{R}_j}{\sum_{j=1}^{n} \alpha_{ij} \hat{N}_j} \tag{14}$$

Example of input file for PHREEQC calculations

```
DATABASE ../../phreeqc.dat
INCLUDE$ ../../sn_database
TITLE Speciation of solution with 0.2 m SnF2 + NaF

SOLUTION 1
    units       mol/kgw
    pH          7.00   charge
    temp        25.0
    -water      1.00     # kg
    Sn          0.20
    Na          <x>
    F           <y>

EQUILIBRIUM_PHASES
    SnO(s)          0.0     0.0
    Sn(OH)2(s)      0.0     0.0

SELECTED_OUTPUT
    -file snf2-naf.sel
    -reset false
    -pH true
    -molalities SnF3- SnF2 SnF+ Sn+2
    -totals Sn
END
```

Graphical results for speciation of stannous fluoride solutions

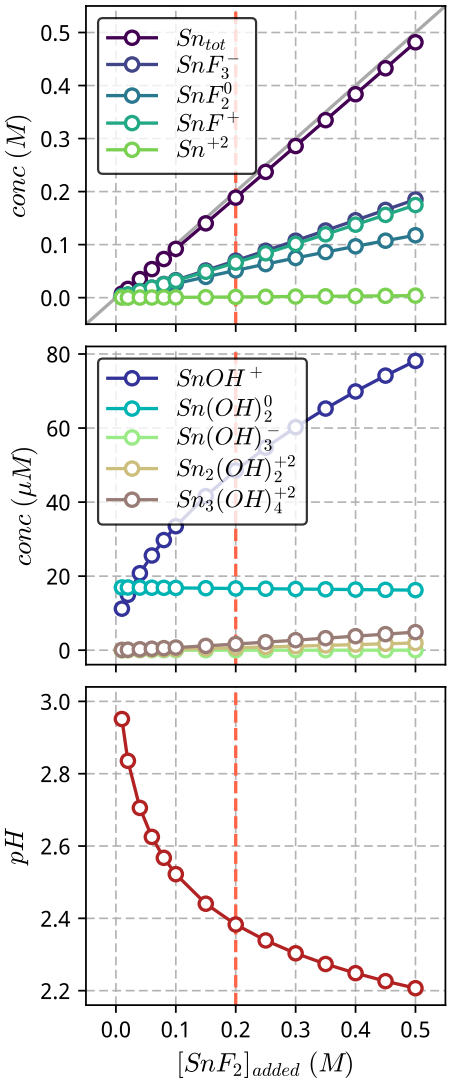

Figure S1: Distribution of stannous fluoride complexes (top), hydrolytic species (middle) and solution pH (bottom) as a function of the added amount of SnF_2in solution. The solid gray line (top) indicates the 1:1 ratio between the added concentration of SnF_2 and the observed concentration in solution. The segmented red line indicates the concentration used for XAS measurements.

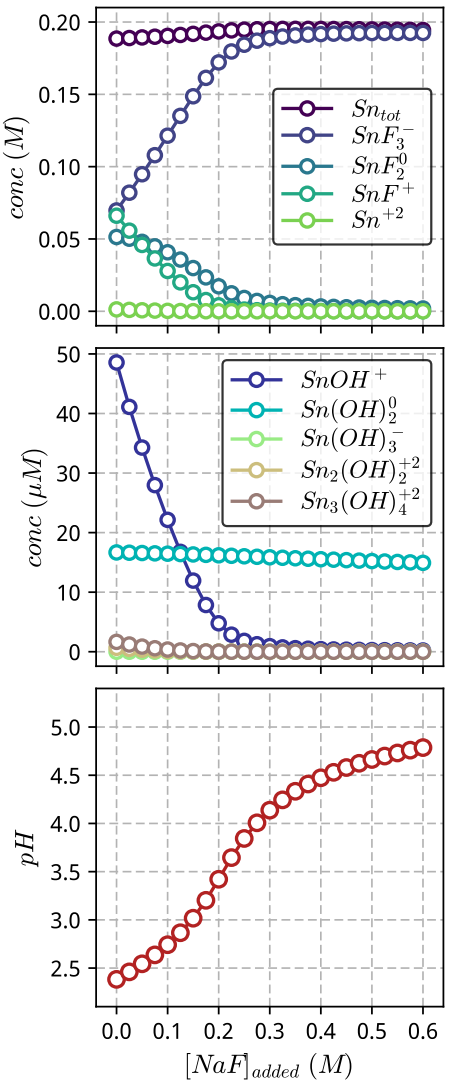

Figure S2: Distribution of stannous fluoride complexes (top), hydrolytic species (middle) and solution pH (bottom) as a function of the added amount of NaF in a solution SnF_2 0.2 M. Note that the distribution of species shifts towards predominance of SnF_3^- for concentrations of NaF exceeding 0.3 M.

Examples of input files for ORCA calculations

Example file for geometry optimization

```
1 ! RI-MP2 ZORA/RI ma-ZORA-def2-TZVPP SARC/J
2 ! TightSCF TightOpt Grid5 FinalGrid6
3 ! CPCM
4 %basis
5   newgto Sn "old-ZORA-TZVPP" end
6 end
7 %method
8   SpecialGridAtoms 50
9   SpecialGridIntAcc 7
10 end
11 %cpcm
12   smd true
13   solvent "WATER"
14   sola 1.17
15   solb 0.18
16 end
17 %geom MaxIter 500 end
18 %pal nprocs 12 end
19
20 # Geometry optimization for the SnF3^- complex
21 * xyzfile -1 1 init.xyz
```

Example file for vibrational analysis

```
1 ! RI-MP2 ZORA/RI ma-ZORA-def2-TZVPP SARC/J
2 ! TightSCF TightOpt NumFreq Grid5 FinalGrid6
3 ! CPCM MORead
4 %basis
5   newgto Sn "old-ZORA-TZVPP" end
6 end
7 %method
8   SpecialGridAtoms 50
9   SpecialGridIntAcc 7
10 end
11 %cpcm
12   smd true
13   solvent "WATER"
14   sola 1.17
15   solb 0.18
16 end
17 %moinp "init.gbw"
18 %freq
19   Increment 0.001
20 end
21 %pal nprocs 12 end
22
23 # Vibrational analysis of the SnF3^- complex
24 * xyzfile -1 1 init.xyz
```

Example file for orbital localization

```
1 ! RI-MP2 ZORA/RI ma-ZORA-def2-TZVPP SARC/J
2 ! TightSCF Grid5 FinalGrid6
3 ! CPCM MORead
4 %basis
5   newgto Sn "old-ZORA-TZVPP" end
6 end
7 %method
8   SpecialGridAtoms 50
9   SpecialGridIntAcc 7
10 end
11 %cpcm
12   smd true
13   solvent "WATER"
14   sola 1.17
15   solb 0.18
16 end
17 %moinp "init.gbw"
18 %loc
19   LocMet IAOIBO
20 end
21 %pal nprocs 12 end
22
23 # Localization of orbitals for the SnF3^- complex
24 * xyzfile -1 1 init.xyz
```