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Electronic Supplementary Information

Spectroscopic evidence for selenium(IV) dimerization in aqueous solution

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The Supplementary Information comprises 5 pages, 1 Table and 2 Figures.

Former evidences

Several former studies already reported selenium(IV) dimerization in solutions. Early works on conductimetry and cryometry of Se concluded the probable existence of selenious acid dimers $(H_2SeO_3)_2$ in high concentrated solutions (higher than 0.005 M and up to 2 M).[1-4]

Later on, Sabbah and Carpeni[5] and Barcza and Sillén[6] performed potentiometric titrations of selenite solutions at concentrations ranging from 0.02 M to 3 M at high ionic strength (0.3 to 3 M) using different background electrolyte media. From both studies, the presence of mononuclear species $HSeO_3^-$ and H_2SeO_3 and binuclear ones, namely $H_4(SeO_3)_2$, $H_3(SeO_3)_2^-$, $H_2(SeO_3)_2^{2-}$ and $H(SeO_3)_2^{3-}$, was derived. From calorimetric studies, these findings were confirmed at high ionic strengths (1 and 3 M).[7] The extent of dimerization was found to be at a maximum at $-\log[H^+] < 2$, of high importance between $-\log[H^+]$ 2 and 10 and almost inexistent at $-\log[H^+] > 10$.[6] Barcza and Sillén[6] (0.02 to 3 M) predicted the $H_2(SeO_3)_2^{2-}$ species to be dominant between $-\log[H^+]$ from 3 to 8. Ganelina et al.[8] performed similar studies by combining potentiometric and spectrophotometric methods, but without background electrolyte and confirmed the Se(IV) polymerization. Such conclusions were, however, in contradiction with those of Ozeki et al.[9] who did not point out the formation of binuclear species since their titration curves were independent from selenium concentration (0.01 to 0.035 M).

Kinetic studies dealing with the oxidation of selenium(IV) by Np(VII), by Co(III), by chloramine-T (CAT), by N-bromosuccinimide (NBS) and by periodate in perchlorate or chloride medium confirmed the occurrence of Se(IV) dimers.[10-13] Indeed, authors needed to consider the presence of dimeric species to establish rate law describing their experimental observations. As highlighted by Dikshitulu and Ram Babu,[14] the selenium(IV) dimers exhibited a significant higher reactivity than the monomeric ones.[10-13, 15]

More recently, Lee et al.[16] evidenced by Scanning Electron Microscopy, X-ray diffraction (XRD), Fourier transform Infrared (FT-IR) and Raman spectroscopy the intercalation of selenite dimers into the gallery space of powdered or thin films Mg-Al Layer Double Hydroxide (LDH) after exchange with carbonate ions. The high observed basal spacing led authors to state that the dimers were vertically oriented to the horizontal axes of LDH. In addition, a faster overall exchange reaction with increasing H_2SeO_3 concentrations was observed, confirming former kinetics observations (see above). This association of two $HSeO_3^-$ monomers has also been proposed in the solid state of $NaHSeO_3$.[17-20]

Table S1. Stability constants used for speciation calculations using PHREEQC[21] (with log *K* corrected to *I* = 0).

Aqueous Species	**log *K*** (NEA-TDB)[22]	**log *K*** (Torres et al.)[23]
$H^+ + SeO_3^{2-} \rightleftharpoons HSeO_3^-$	8.36	8.60
$2H^+ + SeO_3^{2-} \rightleftharpoons H_2SeO_3$	11.00	11.33
$H^+ + 2\ SeO_3^{2-} \rightleftharpoons HSe_2O_6^{3-}$ ($\equiv H(SeO_3)_2^{3-}$)	–	9.55
$2\ H^+ + 2\ SeO_3^{2-} \rightleftharpoons H_2Se_2O_6^{2-}$ ($\equiv H_2(SeO_3)_2^{2-}$)	–	18.77
$3\ H^+ + 2\ SeO_3^{2-} \rightleftharpoons H_3Se_2O_6^-$ ($\equiv H_3(SeO_3)_2^-$)	–	22.57
$4\ H^+ + 2\ SeO_3^{2-} \rightleftharpoons H_4Se_2O_6$ ($\equiv H_4(SeO_3)_2$)	–	25.02
$5\ H^+ + 2\ SeO_3^{2-} \rightleftharpoons H_5Se_2O_6^+$ ($\equiv H_5(SeO_3)_2^+$)	–	27.80

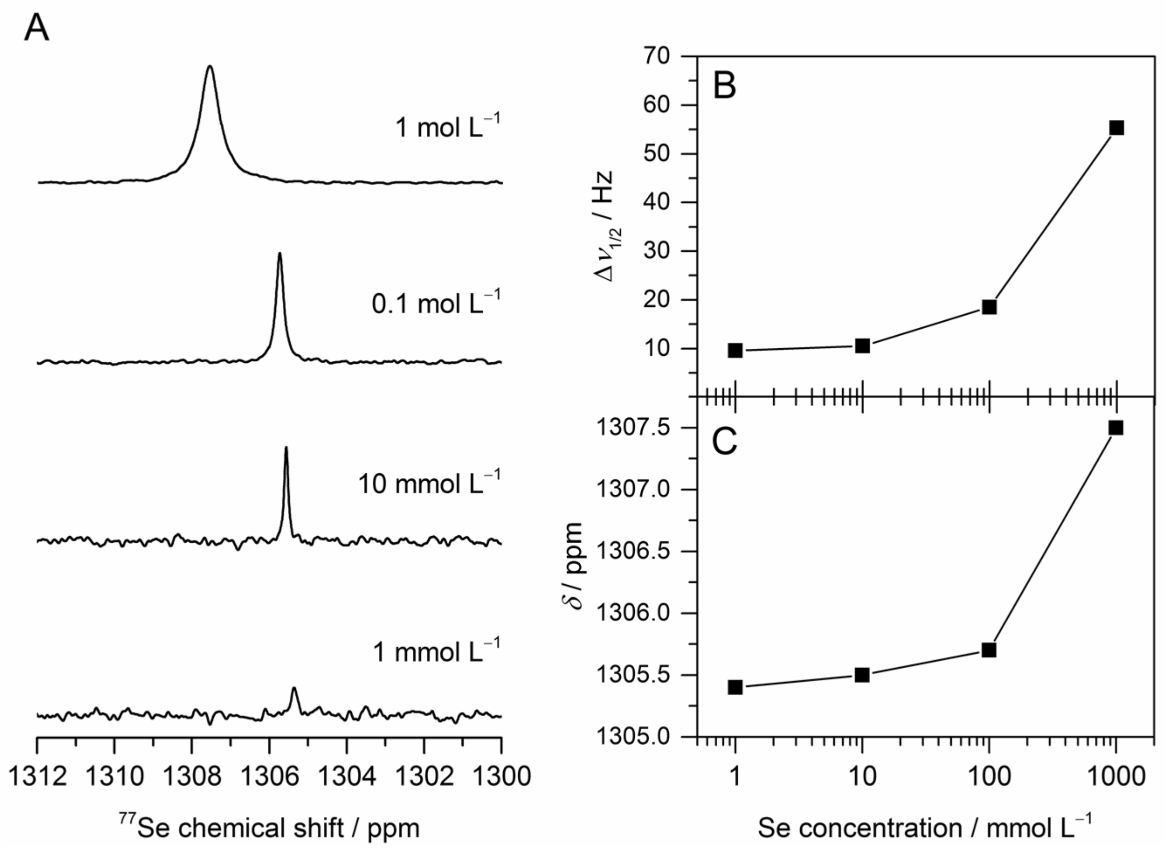

Fig. S1. ^{77}Se NMR spectra (recorded at $B_0 = 9.4$ T) of Se(IV) at pH$_c$ 5 (A) with concentrations from 1 mmol L^{-1} through 1 mol L^{-1} at constant total ionic strength (3 mol L^{-1}), together with their graphical evaluation showing the dependence of selenium concentration on line width (B) and chemical shift (C).

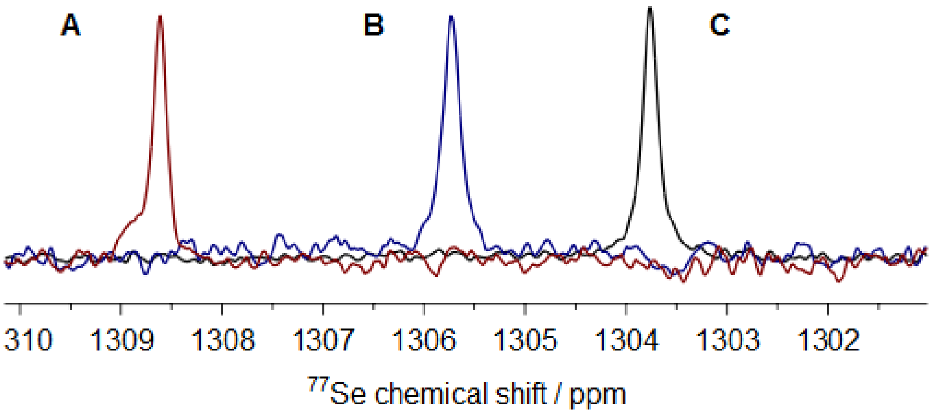

Fig. S2. Superposition of ^{77}Se NMR spectra of 0.1 mol L^{-1} Se(IV) samples at pH$_c$ 5 with variable total ionic strengths (NaCl): (A) 5.6 mol L^{-1}, (B) 3.0 mol L^{-1}, and (C) 0.3 mol L^{-1}.

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