Fourier Transform NMR Investigations of ^{77}Se in Aqueous Solutions

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In solutions of H_2SeO_3 , Na_2SeO_3 , NaHSeO_3 and Na_2SeO_4 in H_2O NMR signals of ^{77}Se have been observed. In these solutions chemical shifts were determined. In a 4 molal solution of Na_2SeO_3 the ratio of Larmor frequencies $\nu(^{77}\text{Se})/\nu(^1\text{H})$ has been measured with a high-resolution probe. A value of the magnetic moment of ^{77}Se in Na_2SeO_3 at infinite dilution in H_2O is given: $|\mu(^{77}\text{Se})| = 0.5332996(7)\mu_N$. Relaxation times T_1 have been measured by the inversion-recovery method. In a 4 molal solution of Na_2SeO_3 in H_2O a NOE enhancement of 0.4(1) could be observed.

Introduction

At least one isotope of the stable chalcogenide elements is accessible to NMR-studies. Of these ^{17}O and ^{33}S are quadrupolar nuclei, whereas ^{77}Se , ^{123}Te and ^{125}Te are nuclei with the favourable nuclear spin 1/2. In liquids NMR studies of ^{17}O are well known [1], whereas for ^{33}S [2, 3] and ^{123}Te , ^{125}Te [4, 5] only few data have been reported. In the last time, the interest in NMR-studies of ^{77}Se grows up [6–18], since selenium has been found to play an important role in biochemistry [11–18].

^{77}Se has a natural abundance of 7.6%, a spin $I = 1/2$ and a Larmor frequency of 17.2 MHz in a magnetic field of 2.11 T. The receptivity is three times stronger than that of ^{13}C in the same magnetic field. The range of chemical shifts in organic compounds is large, about 1500 ppm [7]. ^{77}Se - ^1H spin-spin coupling constants of about 47 Hz have been reported [13]. Investigations at low concentrations may be limited by long relaxation times, only some data have recently been given [7, 17]. Since the magnetic moment of ^{77}Se is positive an enhancement of signals due to a nuclear Overhauser effect (NOE) might be possible between ^{77}Se and ^1H .

In the following we describe ^{77}Se NMR experiments in inorganic selenium salt solutions. Since very few data are available in this area [6, 7], the ratio of the Larmor frequency of ^{77}Se to a reference nucleus, the magnetic moment of ^{77}Se , chemical shifts as a function of concentration, spin-lattice relaxation times T_1 and NOE-enhancement will be reported.

Experimental

For the NMR measurements of ^1H , ^{23}Na and ^{77}Se we used a Bruker pulse spectrometer SXP 4-100 at a magnetic field of 2.114 T. With a B-NC 12 computer the free induction decays were accumulated and Fourier transformed.

For the measurements of the ratio of the Larmor frequencies $\nu(^{77}\text{Se})/\nu(^1\text{H})$ and of the chemical shifts of ^{77}Se , a high resolution probe with internal ^1H stabilization (B-SN 20 with ^1H extension unit) was used. The measurements of the spin-lattice relaxation times T_1 were performed with a high-power probe and external ^1H stabilization B-SN 15. Typical signals of an inversion-recovery experiment are shown in Figure 1. For proton decoupling in NOE experiments we used the decoupler and power unit B-SV 3 BP and a high-resolution probe with external ^2H stabilization B-SN 20.

All measurements were performed with cylindrical sample tubes with 10 mm outer diameter. The temperature was (298 ± 2) K. The Na_2SeO_3 and H_2SeO_3 were delivered from Merck, Darmstadt, the NaHSeO_3 from Serva, Heidelberg and the Na_2SeO_4 from ICN Pharmaceuticals INC., Plainview, N.Y. All samples were used without further purification.

According to Reference [19] the chemical shift is given as

$$\delta(^{77}\text{Se}) = [(\nu_{\text{sample}} - \nu_{\text{ref.}})/\nu_{\text{ref.}}] \cdot 10^6,$$

where $\nu_{\text{ref.}}$ is the Larmor frequency of ^{77}Se in an infinitely diluted solution of Na_2SeO_3 in H_2O .

Results and Discussion

a) Ratios of the Larmor Frequencies

The ratio of the Larmor frequencies of ^{77}Se and ^1H was measured in a 4 molal solution of Na_2SeO_3 in H_2O , by using a high-resolution probe with ^1H

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Fig. 1. Absorption signals of ^{77}Se at 17.188 MHz in a 4 molal solution of H_2SeO_3 in D_2O , measured by the inversion-recovery Fourier method [24] $(180^\circ - \tau_i - 90^\circ - T)_{\text{NS}}$.

In the figure different waiting times τ_i between the 180° and 90° pulse are given. The recovery time was for all measurements $T = 5$ s. For each τ_i , NS = 100 scans were accumulated, yielding a total measuring time of about 4 h. The resulting relaxation time is $T_1 = 1.4(1)$ s. The plotted spectrum width of a single spectrum is 260 Hz. The signals were observed with a high-power probe and external ^1H -lock using 10 mm nonrotating cylindrical sample tubes.

internal stabilization. The ^1H lock-frequency is given in Table 1. The result of these measurements, which were performed at several days, is:

$$\nu(^{77}\text{Se})/\nu(^1\text{H}) = 0.190957382(6).$$

To verify this result, in an other experiment ^{23}Na was used as a reference nucleus. The Larmor frequencies of ^{23}Na and ^{77}Se were measured in the same solution with a high-power probe with external ^1H stabilization B-SN 15:

$$\nu(^{77}\text{Se})/\nu(^{23}\text{Na}) = 0.7220172(2).$$

The given errors are the standard deviation.

b) Chemical Shifts

The Larmor frequency of ^{77}Se was observed in a series of inorganic compounds in aqueous solution: Na_2SeO_3 , Na_2SeO_4 , NaHSeO_3 and H_2SeO_3 . The solutions were all acid, with p_{H} values between 1 and 4. The results of the chemical shift are given in Table 1. The Larmor frequencies of ^{77}Se in the Na_2SeO_3 , NaHSeO_3 , Na_2SeO_4 and H_2SeO_3 solutions are rather different. The dependence of the Larmor

Table 1. ^{77}Se chemical shifts referred to Na_2SeO_3 at infinite dilution and spin-lattice relaxation times T_1 . The chemical shifts were measured with the high-resolution probe with ^1H internal stabilization and corrected for the chemical shifts of the ^1H signal, which was determined in a separate measurement. The Larmor frequency of ^{77}Se in Na_2SeO_3 at infinite dilution was 17 189 707(9) Hz and the ^1H -lock-frequency was 90 018 750 Hz.

Sample	Concentration (molal in H_2O)	Chemical shift δ	Relaxation time T_1/s
Na_2SeO_4	0.5	-227.9 ± 0.5	10.2 ± 0.8
	1.0	-227.6 ± 0.6	—
	1.6	-227.3 ± 0.6	—
Na_2SeO_3	0.5	0.8 ± 0.5	—
	1.0	1.5 ± 0.5	10.7 ± 0.6
	2.0	1.9 ± 0.5	—
	3.0	2.3 ± 0.5	—
	4.0	2.7 ± 0.5	5.0 ± 0.5
H_2SeO_3	0.4	28.7 ± 0.5	—
	1.0	28.5 ± 0.5	—
	1.9	28.5 ± 0.5	—
	3.0	28.7 ± 0.5	—
	4.0	28.9 ± 0.5	1.1 ± 0.1
	5.2	29.3 ± 0.5	—
	4.0 in D_2O	—	1.4 ± 0.1
NaHSeO_3	0.5	46.4 ± 0.6	—
	1.0	47.2 ± 0.6	—
	2.0	48.4 ± 0.6	—
	3.0	49.3 ± 0.5	—
	4.0	50.7 ± 0.5	0.34 ± 0.05
	5.0	51.2 ± 0.5	—

frequency on the concentration of the solutions is very small. This behaviour has already been observed in other oxyanions e.g. for ^{33}S in SO_4^{2-} [3] and for ^{125}Te in TeO_3^{2-} [5]. According to Birchall *et al.* [7] the selenium (VI) compounds have lower Larmor frequencies than the selenium (IV) compounds, this is also true for the ^{77}Se signal in the NaHSeO_3 solutions, which is shifted about 50 ppm to higher frequency than the Na_2SeO_3 signal.

The chemical shift of ^1H in the 4 molal Na_2SeO_3 solution in H_2O relative to a solution with vanishing concentration of Na_2SeO_3 is $\delta(^1\text{H}) = 0.5 \pm 0.1$ and that of ^{23}Na : $\delta(^{23}\text{Na}) = 2.3 \pm 0.2$.

c) Larmor Frequencies at Vanishing Concentration and Magnetic Moment

The ratio of the Larmor frequencies $\nu(^{77}\text{Se})/\nu(^1\text{H})$ of a 4 molal Na_2SeO_3 solution can be extrapolated for a solution with infinite dilution: With the chemical shift data we get:

$$\nu(^{77}\text{Se})/\nu(^1\text{H})|_{\text{extrapol.}} = 0.19095696(10).$$

For ^{23}Na as reference nucleus the result is:

$$\nu(^{77}\text{Se})/\nu(^{23}\text{Na})|_{\text{extrapol.}} = 0.721\,906\,2(4).$$

With the ratio $\nu(^{23}\text{Na})/\nu(^2\text{H}) = 1.723\,1746(4)$ of Lutz [20] and $\nu(^2\text{H})/\nu(^1\text{H}) = 0.153\,506\,086(6)$ of Nolle [21] we get:

$$\nu(^{77}\text{Se})/\nu(^1\text{H})|_{\text{extrapol.}} = 0.190\,957\,0(2),$$

which is in good agreement with the upper value.

From the ratio $\nu(^{77}\text{Se})/\nu(^1\text{H})|_{\text{extrapol.}}$ and the magnetic moment of the proton in water, $\mu_{\text{P}} = 2.792\,744\,0(11) \cdot \mu_{\text{N}}$ (Reference [22]) we derive for the magnetic moment of ^{77}Se in SeO_3^{2-} at vanishing concentration in H_2O :

$$|\mu(^{77}\text{Se})| = 0.533\,299\,6(7) \mu_{\text{N}}.$$

The result is not corrected for diamagnetism. There is a good agreement with former measurements of Weaver [6]:

$$\mu(^{77}\text{Se}) = +0.533\,26(5) \mu_{\text{N}}.$$

Because of the limited accuracy of this value of the magnetic moment, the chemical shift between the H_2SeO_3 solution with added paramagnetic catalysts of Weaver [6] and the SeO_3^{2-} ion at vanishing concentration of the present work, is not obvious. The sign of the magnetic moment of ^{77}Se is positive [6].

d) Spin-lattice Relaxation Times and Nuclear Overhauser Effect

^{77}Se spin-lattice relaxation in selenium oxyanions may arise from a variety of mechanisms: spin-rotation interaction, intramolecular and intermolecular dipole-dipole coupling, chemical shift anisotropy, scalar spin-spin coupling or chemical exchange. These different mechanisms can be separated by performing various experiments. In a first approximation we have measured in a few samples, which have been used for the chemical shift measurements, spin-lattice relaxation times of ^{77}Se with the inversion recovery method and a NOE enhancement. The results of the relaxation measurement are given in Table 1. For ^{77}Se in the SeO_4^{2-} and SeO_3^{2-} ions at low concentration relaxation times of 10 s occur, with increasing concentration the relaxation times of SeO_3^{2-} diminish to the half of

this value. In HSeO_3^- very short relaxation times have been found. For this solution with the high-resolution probe relatively broad signals of about 10 Hz have been measured. For ^{77}Se in a 4 molal solution of selenic acid in H_2O a value of T_1 of 1.1 s has been determined. Using D_2O as solvent for a selenic acid solution of the same concentration only a slight change is found. Wehrli reported for a non specified D_2SeO_3 solution a value $T_1 = 3.5$ s at 301 K [23]. Probably he used a less concentrated solution for his measurements.

Our NOE measurements indicate, that in aqueous solutions of selenium oxyanions the intermolecular dipole-dipole contribution to the relaxation times is small. In the 4 molal solutions of H_2SeO_3 and NaHSeO_3 and in the 1.6 molal solution of Na_2SeO_4 we found no NOE enhancement within an error limit of 10%. But for the 4 molal solution of Na_2SeO_3 in H_2O , an enhancement of 0.4(1) could be observed. For ^{77}Se a NOE enhancement up to 2.6 is possible. Because in H_2SeO_3 and NaHSeO_3 solutions no NOE was observed, even in these solutions the dipole-dipole contribution to spin-lattice relaxation is negligible.

These measurements show, that for the observed selenium compounds the dipole-dipole contribution to the spin-lattice relaxation plays only a minor role. This has also been observed by Dawson *et al.* [17] in organoselenic compounds, where no significant NOE could be observed as far as we know. Although long relaxation times and not the maximum nuclear Overhauser enhancement have been observed ^{77}Se NMR investigations will certainly find their way into various applications, since also at low concentrations which may occur in biochemical samples a reasonable signal intensity can be obtained as was shown for a 10 millimolar solution of Na_2SO_3 in H_2O . For about 1 ml in a 10 mm non-rotating cylindrical tube a signal-to-noise ratio of 4 was found within 26 hours.

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