[45]Scandium NMR Investigations in Aqueous Solutions

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[45]Sc NMR chemical shifts, linewidths, and longitudinal relaxation rates have been measured in aqueous solutions of scandium chloride and sulphate as a function of the appropriate acid. A common typical behaviour of these parameters without sudden changes has been observed. Also signals in the basic range have been obtained. $H_2O - D_2O$ solvent isotope effects on Larmor frequency and relaxation rates are presented.

Introduction

An investigation of common NMR parameters such as chemical shifts, linewidths, and longitudinal relaxation rates in aqueous solutions for III a and III b elements revealed [1] that for [45]Sc inconsistent NMR data can be found in literature as also has been remarked earlier in some review articles [2−4]. The relatively few [45]Sc NMR data [5−9] are partly obscured by incompletely reported data or very short communications.

In the following we report data recently obtained with a Fourier spectrometer as well as data which have been measured about a dozen years ago with a CW-spectrometer and which have been published at that time in a more general form only [5].

Experimental

The early measurements have been performed at 1.81 T by a multi nuclei frequency-swept CW-spectrometer which was described in [10]. The recent investigations have been done with a Fourier spectrometer using a Bruker pulse spectrometer SXP 4-100 and an externally stabilized Bruker magnet system working at 2.11 T. The free induction decays near the Larmor frequency of 21.87 MHz were accumulated and Fourier transformed by the B-NC 12 data unit. The scandium salts are from Auer-Remy, Hamburg. The samples have been prepared from the scandium salts with known water content by weighing salt and solvents.

Cylindrical samples with 10 mm diameter were used at a temperature of (299 ± 1) K. The chemical shifts ar e given by $\delta(^{45}Sc) = (v_{sample} - v_{ref.})/v_{ref.}$. The usual reference sample was a 0.11 molal solution of $ScCl_3$ in 1 molal HCl.

The T_1 measurements were performed by the Fourier transform inversion recovery method [11, 12]. For the evaluation of T_1 the peak intensities were used for a two-parameter least-squares fit procedure [13]. For measuring short relaxation times, the standard T_1 program version [12] was replaced by a special time saving half-automatically T_1-procedure. A typical signal is given in Figure 1.
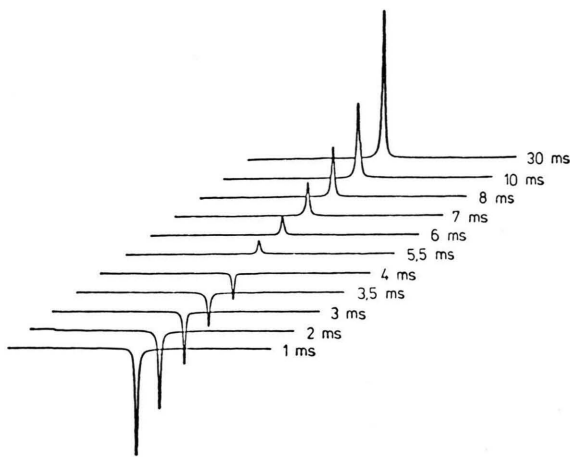

Fig. 1. Stagged plot of a T_1-measurement of [45]Sc in 0.11 molal $ScCl_3$ in 0.05 molal HCl: $T_1 = (7.2 \pm 0.3)$ ms. Each line was obtained by 200 free induction decays after the 90° pulse of the FT inversion recovery sequence. The τ-values are given in the figure. The whole measuring time was 30 min.

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Results

⁴⁵Sc in Acidic Scandiumchloride Solutions

The results are presented in Figure 2:

The chemical shift of ^{45}Sc in 0.11 molal solutions of $ScCl_3$ with different HCl concentrations shows a small decrease at very low concentrations of HCl (see insert) and a strong increase with increasing HCl concentration from about 4 molal HCl. Certainly the position of the signal is the average of lines of different species present in the solutions.
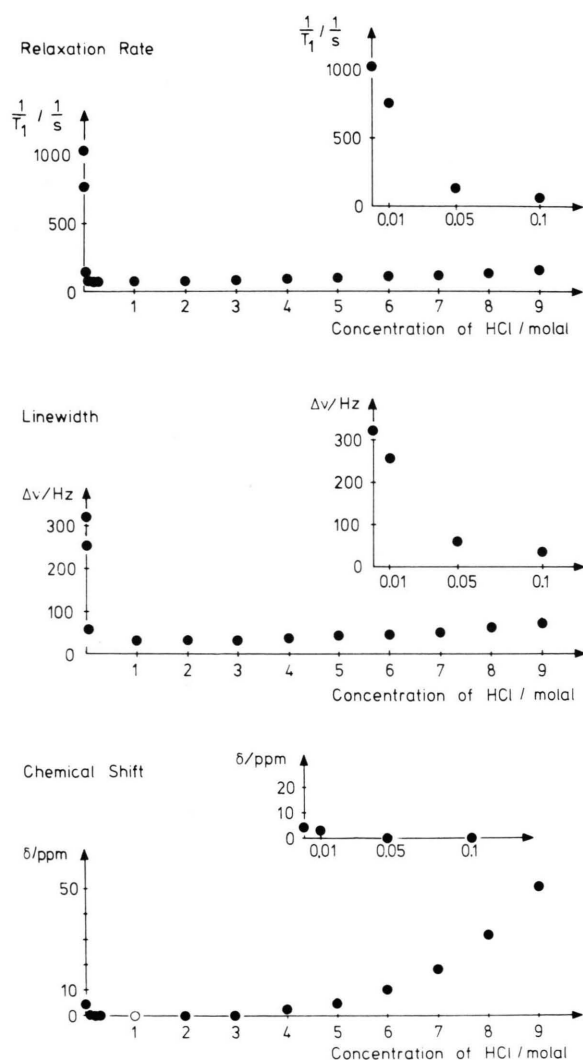

But this is not indicated by a sudden change in chemical shifts (and relaxation times) as reported in Fig. 4 of Reference 9. We find a continuous trend in the chemical shift as well as for both relaxation times, also given in Figure 2. The measured linewidths as a function of the added HCl decrease strongly from 320 Hz for the not acidified aqueous solution to 29 Hz for the reference solution. With increasing HCl concentration the line broadens to 70 Hz for the highest measured HCl concentration (9 molal). Again a flat curve without jumps is found. It should be mentioned that the errors for the linewidths are about 2−3% and much smaller than the size of the given symbols. This is due to the high signal-to-noise ratio (see Fig. 5, showing signals of much lower concentrated solutions).

The measured longitudinal relaxation rates also given in Fig. 2 show exactly the same behaviour as the linewidths, that means that T_1 and T_2 are strongly correlated. Comparing the individual values for the different HCl concentrations one finds that for very small HCl concentrattions T_1 and T_2 are equal. From about 0.05 molal HCl the longitudinal relaxation time T_1 is about 20% through 25% longer than the transversal relaxation time T_2, calculated from the measured linewidths. The line broadening due to the inhomogeneity of the magnetic field was controlled with a ^{2}H NMR signal and it amounts to about 2−3 Hz for the narrow ^{45}Sc lines. Therefore, a nearly constant difference in the two relaxation rates of 20% remains for the concentration range where HCl > 0.05 molal. This indicates that not only quadrupolar effects govern the relaxation behaviour but also exchange effects have to be taken into account.

To obtain more information, in Fig. 3 a further experiment is given: The linewidths of ^{45}Sc are presented in solutions for which the ratio of moles HCl and moles $ScCl_3$ have been changed. In the insert the different concentrations of $ScCl_3$ are given.

It is very interesting that independent of the $ScCl_3$ concentration the lines broaden when the ratio [HCl]/[$ScCl_3$] gets smaller than 0.5. It would be very speculative to assign this feature to one of the very different species which are assumed to be present in these solutions [9].

⁴⁵Sc in Acidic Scandiumsulphate Solutions

In Fig. 4, chemical shifts, linewidths, and longitudinal relaxation rates are given for solutions of

Fig. 2. Chemical shift δ, linewidth Δv, and longitudinal relaxation rate $1/T_1$ of ^{45}Sc in 0.11 molal aqueous solution of $ScCl_3$ as a function of added HCl. The low concentration range of HCl is given in expanded scale in the inserts respectively.

0.11 molal $Sc_2(SO_4)_3$ in H_2SO_4 of various concentrations.

At a first view, the behaviour is very similar as for scandium chloride. But the lines are shifted something to higher frequencies compared with the HCl-solutions.

The linewidth in the pure water solution is relatively narrow and for increasing concentration of H_2SO_4, the decrease is not as strong as in the case of HCl. The minimum is also just below 1 molal H_2SO_4 and again a broadening is observed for higher concentrations of the sulphuric acid.

Both relaxation rates show the same dependence and here the individual values of $1/T_1$ and $1/T_2$ (from linewidths) are nearly the same, taking into account the experimental errors for both. But a tendency for $T_1 > T_2$ is observable.
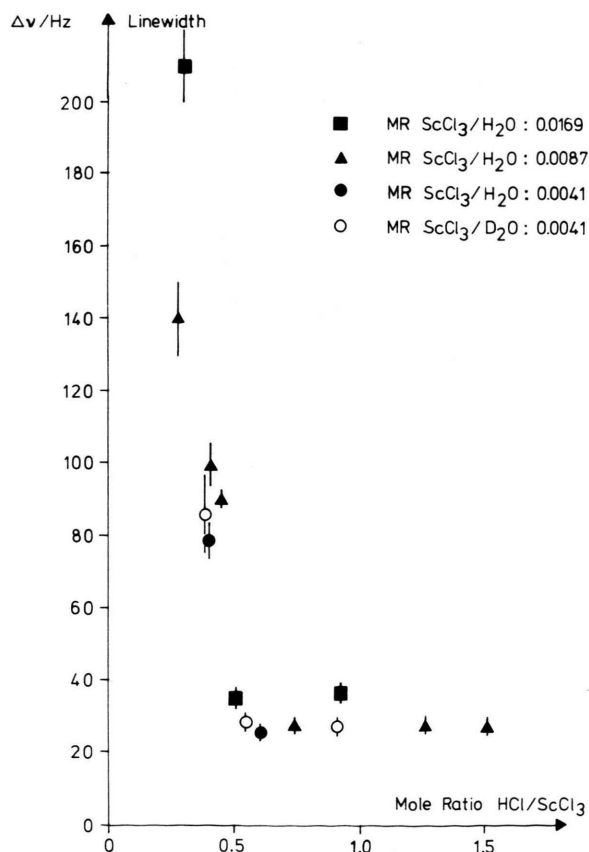

Fig. 4. Chemical shift δ, linewidth $\Delta\nu$, and longitudinal relaxation rate $1/T_1$ of ⁴⁵Sc in 0.11 molal aqueous solution of $Sc_2(SO_4)_3$ as a function of added H_2SO_4.

⁴⁵Sc in Basic Solutions of Scandium Chloride

In strongly basic aqueous solutions (> 10 molal NaOH) a very small amount of $ScCl_3$ can be dissolved. In Fig. 5 the signals of 0.005 molal solutions of $ScCl_3$ in 14 molal NaOH and in 1 molal HCl are presented. First, from the signal-to-noise ratios of these low concentrated solutions the high accuracy of the measurement for the higher concentrated solutions can be imagined. Further, a very large chemical shift of 115.7 ppm is found for the different species, where in the acidic region mainly $Sc(H_2O)_6^{3+}$ and in the basic region mainly $Sc(OH)_4^-$ are present.

For ²⁷Al and ⁷¹Ga the equivalent shifts are 80 ppm and 223 ppm [1, 14], respectively.

The linewidth of 196 Hz in the given basic solution is much broader than in the HCl-solution. This

Fig. 3. Linewidths of aqueous solutions of $ScCl_3$ with concentrations given in the insert as a function of the ratio mole HCl/mole $ScCl_3$. These results have been obtained with the CW-spectrometer [10].
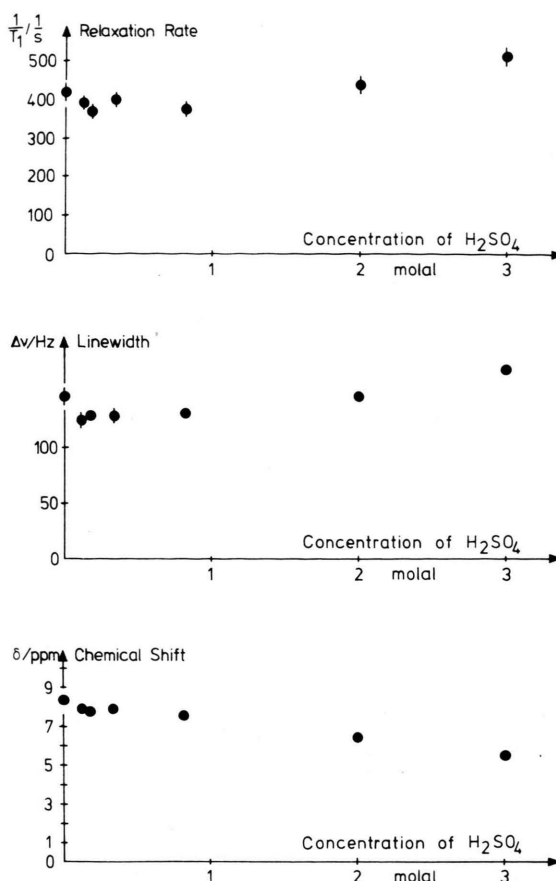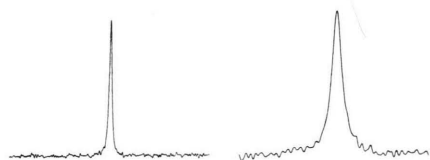
Fig. 5. ^{45}Sc NMR signals of solutions of $ScCl_3$, 0.005 molal in 1 molal HCl (left) and 14 molal NaOH (right). The line in the basic solution is 196 Hz wide, its shift to higher frequency is 115.7 (0.4) ppm. 2000 free induction decays have been accumulated within 7 min for the left and 7000 free induction decays within 12 min for the right signal.

fact has also been observed in the case of ^{27}Al and ^{71}Ga [1, 14].

Solvent Isotope Effects

A very interesting feature of the NMR signals is is the H_2O-D_2O solvent isotope effect of the III b elements. For ^{45}Sc in solutions of $ScCl_3$ in H_2O and D_2O, $\delta_{iso} = -(6.2 \pm 0.2)$ ppm has been reported [5]. Surprisingly, for ^{89}Y a smaller effect was observed by Schwenk et al. [15]. But this decrease in the III b group as a function of atomic number was confirmed with a ^{139}La investigation [16].

A remeasurement of the ^{45}Sc solvent isotope effect for solutions of relatively low concentrations, a 0.11 molal $ScCl_3$ solution in 1 molal HCl in H_2O and 1 mol DCl in D_2O yields:

$$\delta_{iso} = -(5.9 \pm 0.1) \text{ ppm} .$$

Also the relaxation times are different in these H_2O- and D_2O-solutions:

$$T_1 \text{ (in } D_2O) = (12.2 \pm 0.6) \text{ ms} \quad \text{and}$$
$$T_1 \text{ (in } H_2O) = (14.5 \pm 0.7) \text{ ms} .$$

Such an isotopic effect is found also for other heteronuclei [16, 17] and is an indication that the quadrupolar interaction governs mainly the relaxation processes since the viscosities of H_2O and D_2O solutions are different.

As stated earlier, a ^{45}Sc signal could also be found in the very basic region. Here the Larmor fre-quency of ^{45}Sc is higher in $NaOD/D_2O$- than in $NaOH/H_2O$-solutions. For some solutions with 0.005 molal $ScCl_3$ and concentrations of NaOH resp. NaOD larger than 10 molal a solvent isotope effect of $\delta_{iso} = +(1.0 \pm 0.4)$ ppm was observed.

If one proposes that in the alkaline and in acidic region mainly the tetrahydroxo complexes resp. the hexahydrat complexes are dominant, the change in the sign of the solvent isotope effect is not unreasonable.

The unusual dependence of the amount of δ_{iso} in the acidic region as a function of atomic number is unique in the different groups of the periodic table [18] at the moment and is not yet understood. Further systematic studies of all the different nuclei are in progress.

Summary

The chemical shifts, linewidths, and longitudinal relaxation rates of ^{45}Sc NMR in scandium chloride and sulphate solutions as a function of acid concentration show a very typical behaviour with a minimum for these NMR parameters. Although the signal-to-noise ratio is very high, no discontinuities for the mentioned NMR parameters were found for the used concentrations. Such steps, reported in [9], would directly indicate the change from one species to another certainly present in the solutions [9], and which are observable e.g. by line splittings in the case of ^{71}Ga [1].

This typical behaviour of the given NMR parameters is not unique for the case of scandium, but has also been observed for aqueous solutions of some III a elements: ^{27}Al in $Al_2(SO_4)_3$ [14], ^{69}Ga, ^{71}Ga in $Ga(NO_3)_3$ and $Ga_2(SO_4)_3$ [1], and ^{115}In in $In(NO_3)_3$ [1].

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