^{27}Al Nuclear Magnetic Resonance Studies in Solutions of Light and Heavy Water and the Ratio of the Larmor-Frequencies of ^{27}Al and ^{2}H

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Very few studies of ^{27}Al NMR have been reported, especially with respect to Al^{3+} ions interacting with non aqueous solvents [1–5].

The best value for the ratio of the Larmor frequency of the ^{27}Al nucleus to a reference nucleus has been determined by Lindström [6, 7]: $\nu_{^{27}\mathrm{Al}}/\nu_{^{1}\mathrm{H}} = 0{,}260\,5694(10)$ He measured the frequencies of the two nuclei in different probes.

The absolute chemical shift of a hydrated ion can be evaluated [8, 9] by obtaining the magnetic moment of the corresponding nucleus using two different, highly accurate methods.

1. A magnetic moment influenced by the diamagnetic shielding of the electrons of the ion or the atom is obtained when either atomic beam or optical pumping methods are employed.

2. When dilute aqueous solutions are investigated by the nuclear magnetic resonance method, the resulting magnetic moment is not only dependent upon the diamagnetic shielding of the ionic electrons but also upon the interaction of the water molecules with the ion.

By comparing the magnetic moments determined under these two conditions, the effect of the water molecules, i. e. the absolute chemical shift of the ion in dilute aqueous solution, can be calculated. For Rb^+ and Cs^+ this has been done in Ref. [8] and [9].

We have measured the ratio of the Larmor frequencies of ^{27}Al and ^{2}H with high accuracy, and we have calculated the magnetic moment for ^{27}Al in the species Al^{3+} hydrated by heavy water. An investigation of the dependence of the NMR signals of ^{27}Al and ^{2}H from the concentration of some aluminium salts in light and heavy water solutions was made.

Our NMR spectrometer [9] is able to detect the nuclei ^{2}H and ^{27}Al at a field of 18.07 kOe merely by changing the radio-frequency from 11.81 MHz to 20.05 MHz. The magnetic field was held constant with the aid of a ^{7}Li NMR-probe [10]. The measurement was made with tested spherical probes [11]. No susceptibility correction has to be made. All the solutions are acidified with the corresponding acid. Concentrations are given in

$$f = \frac{\text{number of soluted Al}^{3+}\text{ ions}}{\text{number of solvent molecules}}\,.$$

The chemical shifts $\delta_{\mathrm{Al}} = \nu_{\mathrm{probe}} - \nu_0$ are referred to the Larmor frequency of the Al^{3+} ion in infinite dilution ν_0, that means for the species $Al(H_2O)_6{}^{3+}$, which has been stated by Schuster and Fratiello [12].

The shifts for the deuterium resonance are referred to pure D_2O. The temperature was (26 ± 1) °C.

^{27}Aluminium Resonance

a) *$AlCl_3$ in light water:* There is no shift detectable in the concentration range from $f = 0.002$ to $f = 0.053$ for the ten solutions studied, which are in this range. The uncertainty is ± 1 Hz. The line width is very small, in contrary to Ref. [2], and increases from 3 Hz for $f = 0.002$ to 13 Hz for $f = 0.053$.

b) *$Al(NO_3)_3$ in light water:* The ten solutions studied in the range from $f = 0.003$ to $f = 0.055$ show a shift, which depends nearly linearly on the concentration of the solutions; the lines are displaced toward higher frequencies with increasing concentration:

$$\delta_{\mathrm{Al}} = (5 \pm 1)\ \mathrm{Hz} \quad \text{for} \quad f = 0.055.$$

The Larmor frequency for small concentrations is the same as in solutions of $AlCl_3$ in H_2O. The line width increases with increasing concentration: From about 2 Hz for $f = 0.003$ to 8 Hz for $f = 0.055$.

c) *$Al_2(SO_4)_3$ in light water:* We have also observed two ^{27}Al resonance lines, as has Flanagan [13]; The spacing is about 68 Hz. This phenomenon will be studied in detail.

d) *$AlCl_3$ and $Al(NO_3)_3$ in heavy water:* There is a small but remarkable difference in the Larmor frequencies of ^{27}Al in solutions of light and heavy water: For 5 solutions of each salt in each solvent, we found in the concentration range from $f = 0.002$ to $f = 0.005$:

$$\nu(H_2O) - \nu(D_2O) = (5 \pm 1)\ \mathrm{Hz}\,.$$

That means, there is a difference in the shielding of the ^{27}Al nucleus in the Al^{3+} ion by light and heavy water of

$$\sigma_{H_2O} - \sigma_{D_2O} = -(0.25 \pm 0.05)\ \mathrm{ppm}.$$

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Such a solvent isotope effect on the chemical shift of ions in aqueous solutions has also been found recently by the investigation of the NMR of alkali and halide ions [8, 14–17].

Deuterium Resonance

The position of the deuterium line also depends on the concentration of the aluminium salts. The resonance frequency increases with increasing concentration nearly linearly. The shift for the solution of $AlCl_3$ with $f = 0.00837$ is $\delta_{^2\mathrm{H}} = (3.9 \pm 0.7)$ Hz, the linewidth is about 2 Hz. The linewidth increases with increasing concentration.

The Ratio of the Larmor Frequencies

In a definite solution of $AlCl_3$ in acidified heavy water, the Larmor frequencies of ^{2}H and ^{27}Al have been measured alternately in the same probe at constant field, by varying the radio-frequency. The concentration of the probe was $f = 0.00837$. The solvent consisted of 92.7 mol-% D_2O, 6.5 mol-% H_2O and 0.8 mol-% HCl. The line widths are small, 2 Hz for the deuterium line and 3 Hz for the aluminium line. The result is:

$$\nu_{^{27}\mathrm{Al}}/\nu_{^2\mathrm{H}} = 1.697\,440\,40 \quad (4) .$$

The error is three times the RMS error.

In very diluted solutions, the Al nucleus is shielded only by its own electrons and by the water molecules, which interact with the Al^{3+} ion. Therefore, an extrapolation to vanishing concentration of the salts for ^{2}H and ^{27}Al yields the Larmor frequency for such an Al nucleus, relative to the Larmor frequency of ^{2}H in pure heavy water. We obtained:

$$[\nu_{^{27}\mathrm{Al}}/\nu_{^2\mathrm{H}}]_{\mathrm{extrapol}} = 1.697\,440\,96 \quad (30) .$$

The error arises from the uncertainties in the extrapolation to zero concentration.

Using the $\nu_{^2\mathrm{H}}/\nu_{^1\mathrm{H}} = 0.153\,506\,083$ (60) of Smaller [18] and the uncorrected moment of the proton in water $\mu_\mathrm{p} = 2.79268(2)\ \mu_\mathrm{N}$ of Cohen and DuMond [19], the magnetic moment of ^{27}Al is calculated for the species Al^{3+}, which is hydrated by heavy water:

$$[\mu_{^{27}\mathrm{Al}}]_{\mathrm{uncorr}} = +3.638\,4084 \quad (15)\ \mu_\mathrm{N} .$$

The value is not corrected for the diamagnetism of the electrons. The error results from the value of Smaller [18]. The moment is naturally affected by the uncertainty in the magnetic moment of the proton, which is $\pm 7 \cdot 10^{-6}$.

If there were a magnetic moment of the ^{27}Al, which is measured by an other method on free ions or atoms with the necessary accuracy, the absolute shielding of the ^{27}Al nucleus in Al^{3+} by water molecules would be evaluable.

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