Common Behaviour of NMR Parameters of ^{27}Al, ^{69}Ga, ^{71}Ga, and ^{115}In in Aqueous Solutions

J. Kodweiß, D. Köhnlein, G. Kössler, O. Lutz, W. Messner, K. R. Mohn, A. Nolle*,
G. Nothaft, P. Ruppert, N. Steinhauser, D. Zepf, E. Haid, and W. Schich
Physikalisches Institut der Universität Tübingen

Z. Naturforsch. **41 a,** 471 – 477 (1986); received December 12, 1985

The behaviour of the NMR parameters linewidth, longitudinal relaxation time, and chemical shift of ^{27}Al, ^{69}Ga, ^{71}Ga, and ^{115}In has been investigated in aqueous solutions as a function of salt and concentration of added acid or base. A similar behaviour for the NMR parameters of these nuclei has been found.

Introduction

Reported inconsistencies in the behaviour of the NMR parameters chemical shift δ, line width $\Delta\nu$ (resp. T_2), and longitudinal relaxation time T_1 of ^{45}Sc as a function of concentration and acidity of aqueous solutions led us to systematic investigations of the parameters of this element [1] and of some IIIa group elements, which will be presented in this work.

In the case of scandium, an interesting behaviour of δ, $\Delta\nu$, and $1/T_1$ has been observed for the ^{45}Sc NMR signal as a function of added acid in chloride and sulphate solutions: with increasing concentration of the acid all three parameters decrease strongly, show a minimum and finally increase again. For the linewidth of ^{27}Al in highly concentrated aluminium sulphate solutions [2] and of ^{115}In in indium nitrate solutions [3] a similar dependence has been found earlier. But systematic and comparable NMR data obtained in aqueous solutions are very rare for ^{115}In and not very frequently for ^{71}Ga and ^{69}Ga, as can be verified from some review articles [4, 5, 6]. More data are available in the case of ^{27}Al [4, 5, 6].

Due to the available multi-nuclei NMR instruments, systematic investigations of δ, $\Delta\nu$, and T_1 for the isotopes ^{27}Al, ^{69}Ga, ^{71}Ga, and ^{115}In are possible. So, the behaviour of NMR properties linewidth, relaxation time, and chemical shift, has been investigated in aqueous salt solutions as a function of added acid or base for the mentioned nuclides.

Experimental

The investigations have been performed with an NMR Fourier spectrometer using a Bruker pulse console SXP 4-100, an externally ^{1}H NMR stabilized Bruker high resolution magnet system working at 2.11 T, and a B-NC 12 data unit. Some NMR parameters for the observed nuclei are given in Table 1.

The samples have been prepared by weighing salts and solvents. Cylindrical samples of 10 mm diameter were used at a temperature of (299 ± 1) K. For the variable temperature measurements, the Bruker B-ST 100/150 unit has been employed.

The T_1 measurements have been done by the Fourier transform inversion recovery method following the procedure described in [7]. The T_2 data are derived from the linewidths obtained from NMR lines with high signal-to-noise ratios. The chemical shifts are given by $\delta = (\nu_{\text{sample}} - \nu_{\text{ref}})/\nu_{\text{ref}}$. A positive value means a shift to higher frequency at a constant field. Figure 1 shows the large spread of observable NMR properties.

Results

Gallium

In Fig. 2, the linewidths of ^{71}Ga in 0.5 molal aqueous Ga(NO$_3$)$_3$ solutions as a function of added HNO$_3$ or NaOH are given.

---

* Berlin, Hünefeldzeile 5.

Reprint requests to Prof. O. Lutz, Physikalisches Institut der Universität Tübingen, Auf der Morgenstelle, D-7400 Tübingen.

0340-4811 / 86 / 0300-0471 $ 01.30/0. – Please order a reprint rather than making your own copy.

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung") beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

Table 1. NMR properties of IIIa group elements.

Nucleus	Natural abundance (%)	Larmor frequency at 2.11 T (MHz)	Nuclear spin	Nuclear quadrupole moment* (10^{-28} m^2)	Receptivity (^{1}H = 1)
^{27}Al	100	23.45	5/2	0.15	0.21
^{69}Ga	60.4	21.60	3/2	0.19	$4.2 \cdot 10^{-2}$
^{71}Ga	39.6	27.45	3/2	0.12	$5.6 \cdot 10^{-2}$
^{115}In	95.7	19.72	9/2	0.83	0.33

* G. H. Fuller, J. Phys. Chem. Ref. Data **5,** 835 (1976).

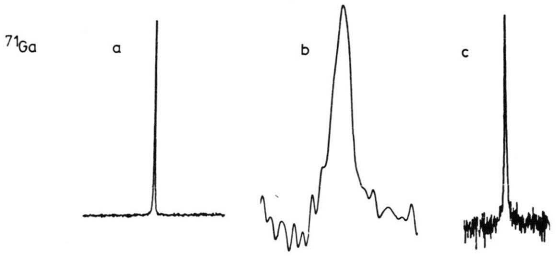

Fig. 1. Typical ^{71}Ga NMR signals of 0.5-molal solutions of $Ga(NO_3)_3$ in: a) 1 molal HNO_3; b) 1.5 molal NaOH; c) 1.8 molal NaOH. The Larmor frequencies are about: a) 27.447 MHz; b) 27.447 MHz; c) 27.454 MHz. Linewidths: a) 73 Hz; b) 1180 Hz; c) 152 Hz. Number of free induction decays: a) 50; b) 115000; c) 20000. Measuring time: a) 10 s; b) 384 min; c) 134 min.

With decreasing amount of added HNO_3 the linewidth decreases, shows a minimum and increases strongly for small amounts of acid. In the region of the minimum the dominating species in the solution must have a high symmetry, otherwise a rather strong quadrupolar broadening would occur, which means that mainly the octahedral hexa-aquo-complex $Ga(H_2O)_6^{3+}$ is present. With higher concentrations of acid the viscosity increases and may broaden the line but also a broadening occurs due to exchange processes with gallium containing species with lower symmetry. The same, but to a stronger extent, is the case for the less acid solutions. It is not easy to say which species are present in this region. Some remarks are given for instance by Tarasov et al. [8] and Akitt et al. [9]. The linewidth increases very strongly by adding small amounts of NaOH. Further the signal intensity is very small (see Figure 1). The chemical shift of the observed signal (see Figure 2) is practically independent of the added HNO_3 or NaOH until a concentration of about 1.5 molal NaOH. For higher concentrations of the base a tremendous decrease of the linewidth is found accompanied by a change of the chemical shift of $(+223 \pm 1)$ ppm, but again the signal strength is small (Figure 1). Obviously in the basic region only parts of the gallium can be detected. The shift is also constant with increasing concentration of NaOH, and the linewidth, which is somewhat larger than in the acidic minimum, increases again. The species which is observed in this region must also have a high symmetry and is supposed to be $Ga(OH)_4^-$. The chemical shift between $Ga(OH_4^-$ and $Ga(H_2O)_6^{3+}$, which is $+(223 \pm 1)$ ppm, can be compared with the results for ^{45}Sc: + 115.7 ppm [1] and ^{27}Al: + 80 ppm [2, 5].

In Fig. 3 the linewidths for solutions of 0.25 molal $Ga_2(SO_4)_3$ in sulfuric acid are given. Again the typical broadening has been found. But the lines are broader and especially at the minimum of the linewidth, where the main species is assumed to be $Ga(H_2O)_6^{3+}$, the ^{71}Ga linewidth in sulphate solutions is larger than in the nitrate solutions. This gives some indications that other species must contribute to the observed linewidth.

Indeed, in the solutions showing narrow lines a second small, and from the strong signal not wholly resolved line is observed which is situated 10 ppm towards lower frequencies. This is in analogy to the second signal (at − 3.4 ppm) in the case of ^{27}Al in acidified $Al_2(SO_4)_3$-solutions [10].

The question now arises if the relaxation processes in the case of the nitrate solutions at the linewidth minimum are governed mainly by the quadrupole interaction. To get more insight, measurements of the temperature dependence of the linewidth and of the ratio of T_1 for ^{69}Ga and ^{71}Ga were performed: The temperature dependence of the Larmor frequency and the linewidth of ^{71}Ga has been studied for the 0.5 molal solution of $Ga(NO_3)_3$

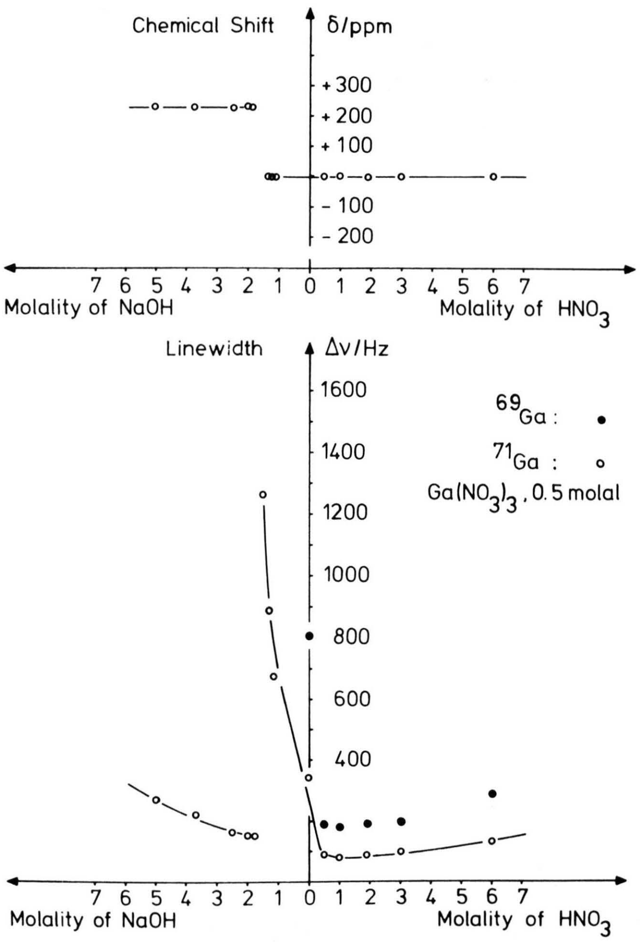

Fig. 2. Linewidth and chemical shift of ^{71}Ga (and ^{69}Ga) in 0.5 molal solutions of $Ga(NO_3)_3$ as a function of the concentration of HNO_3 and NaOH. Reference sample: 0.5 molal $Ga(NO_3)_3$ in 1 molal HNO_3.

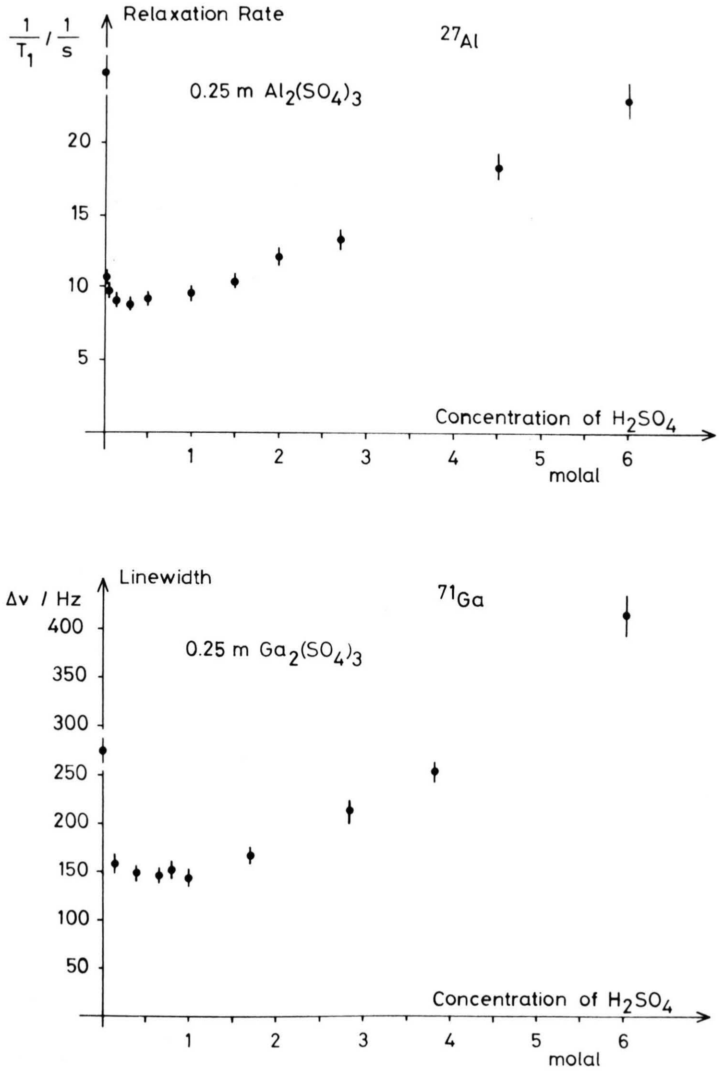

Fig. 3. Longitudinal relaxation rate $1/T_1$ of ^{27}Al in 0.25 molal solutions of $Al_2(SO_4)_3$ as a function of H_2SO_4 and linewidth $\Delta\nu = 1/\pi T_2$ for ^{71}Ga in 0.25 molal solutions of $Ga_2(SO_4)_3$ as a function of H_2SO_4.

in 1 molal HNO_3 (Figure 4). The temperature has been varied between 274 K and 324 K. The effect on the Larmor frequency is small, the frequency decreases by about 1 ppm for the range of 50 K. The decrease of the linewidth as a function of temperature is presented in Figure 4. The typical behaviour for a quadrupolar broadened signal is found. The narrowing effect is rather strong, the linewidth decreases by a factor of 2 in the given temperature range. Such a strong change in linewidth with temperature has also been found in the case of the IIIb-nuclide ^{139}La in lanthanum nitrate and chloride solutions [11].

If the relaxation process is mainly governed by the quadrupole interaction, the ratio of the quadrupole moments of two isotopes can be derived from the ratio of the longitudinal relaxation times [12, 13]: In the case of identical nuclear spins, e.g. for ^{69}Ga and ^{71}Ga, the following relation is obtained:

$$(Q(^{69}\mathrm{Ga})/Q(^{71}\mathrm{Ga}))^2 = T_1(^{71}\mathrm{Ga})/T_1(^{69}\mathrm{Ga})\,.$$

With the longitudinal relaxation times $T_1(^{69}\mathrm{Ga}) = (5.1 \pm 0.2)$ ms and $T_1(^{71}\mathrm{Ga}) = (2.0 \pm 0.1)$ ms, which have been measured by the inversion recovery method for both ^{69}Ga and ^{71}Ga in the 0.5 molal solution of $Ga(NO_3)_3$ in 1 molal HNO_3, the following ratio is found:

$$Q(^{69}\mathrm{Ga})/Q(^{71}\mathrm{Ga}) = 1.60 \pm 0.08\,.$$

This can be compared with the ratio measured by NQR-investigations by Dehmelt [14]:

$$Q(^{69}\mathrm{Ga})/Q(^{71}\mathrm{Ga}) = 1.5867\,.$$

It is obvious that mainly quadrupole relaxation for gallium must be assumed in the given solution.

^{115}Indium

Only little information is available on ^{115}In NMR signals in aqueous solutions [4, 5, 6]. In the early work of Cannon and Richards [3], some data are given for the linewidth in a 0.33 molal solution of indium nitrate as a function of the concentration of nitric acid. In our work, the NMR linewidths of ^{115}In in 0.1 molal aqueous solutions of $In(NO_3)_3$ have been measured as a function of concentration of HNO_3. Since the linewidth increases strongly with the indium nitrate concentration, a low salt concentration has been choosen.

The lines are at least 1000 Hz broad and the typical behaviour is observed (Fig. 5): very broad lines for high concentrations of HNO_3, a minimum of the linewidth at about 0.5 molal HNO_3 and an increase of the linewidth for lower concentrations of HNO_3. At very small concentrations of HNO_3, the lines broaden so strongly that no longer a signal could be observed. The quadrupolar relaxation is very effective in the case of ^{115}In due to its large quadrupole moment (see Table 1). From an earlier investigation [15] on hyperfine structure anomalies of ^{115}In and ^{113}In informations about the ratio of the linewidths of both nuclei are available which confirm the quadrupolar origin of the linewidths.

^{27}Aluminium

Earlier unpublished data obtained in our laboratory showed [2] that the linewidths of ^{27}Al in aqueous solutions of $Al_2(SO_4)_3$ as a function of increasing amounts of added sulfuric acid first decrease, have a minimum, and then increase. At the minimum linewidth, the species $Al(H_2O)_6^{3+}$ dominates although a second ^{27}Al NMR line is observable. In the mentioned investigation, the salt concentration was relatively high, 2.5 molal, and therefore a large range of concentrations of sulphuric acid had to be investigated. Some data are also given by Zarikov and Nikiforow [16].

In Figs. 3, 5, 6 longitudinal relaxation rates $1/T_1$, which have been measured by the inversion recovery method, are given for solutions which are 0.25 molal in $Al_2(SO_4)_3$, 0.5 molal in $Al(NO_3)_3$, and 0.5 molal in $AlCl_3$ as a function of the concentration of the respective acid. Again the very typical behaviour is found for $1/T_1$. The value at the minimum is somewhat smaller than 10 ms, a value suggested from the linewidth of about 3 Hz, typically found for the species $Al(H_2O)_6^{3+}$ [10], if $T_2 = T_1$. But the relaxation rates $1/T_1$ at the minimum are different for the different anions: $(8.7 \pm 0.4)\ \mathrm{s}^{-1}$ for sulphate, $(5.7 \pm 0.3)\ \mathrm{s}^{-1}$ for nitrate, and $(7.4 \pm 0.4)\ \mathrm{s}^{-1}$ for chloride solutions. It is interesting that for perchlorate solutions Holz et al. [17] have found $1/T_1 = 5.7\ \mathrm{s}^{-1}$ and for chloride solutions Hertz et al. [18] give $1/T_1 = 7.5\ \mathrm{s}^{-1}$. Obviously the differences in $1/T_1$ are due to anionic effects and they must be taken into account. Perchlorate and nitrate anions have the smallest influence. These results for the relaxation rates indicate again that the hexaaquo

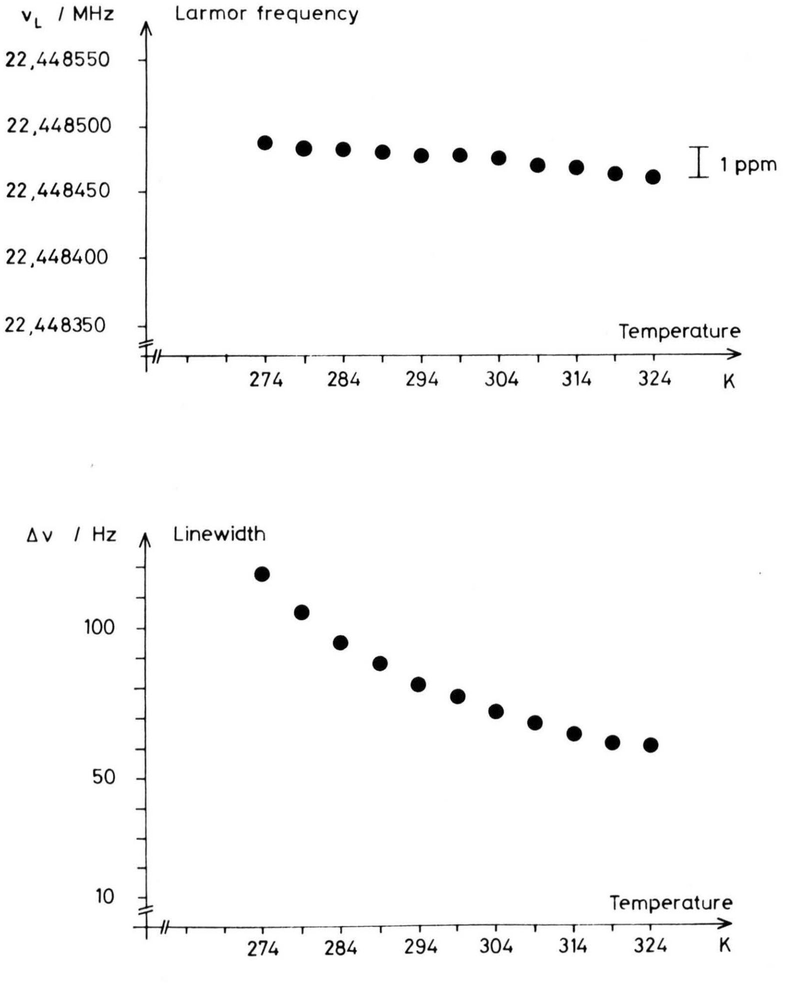

Fig. 4. Temperature dependence of the Larmor frequency and the linewidth of the ^{71}Ga NMR signal in a 0.5 molal solution of $Ga(NO_3)_3$ in 1 molal HNO_3.

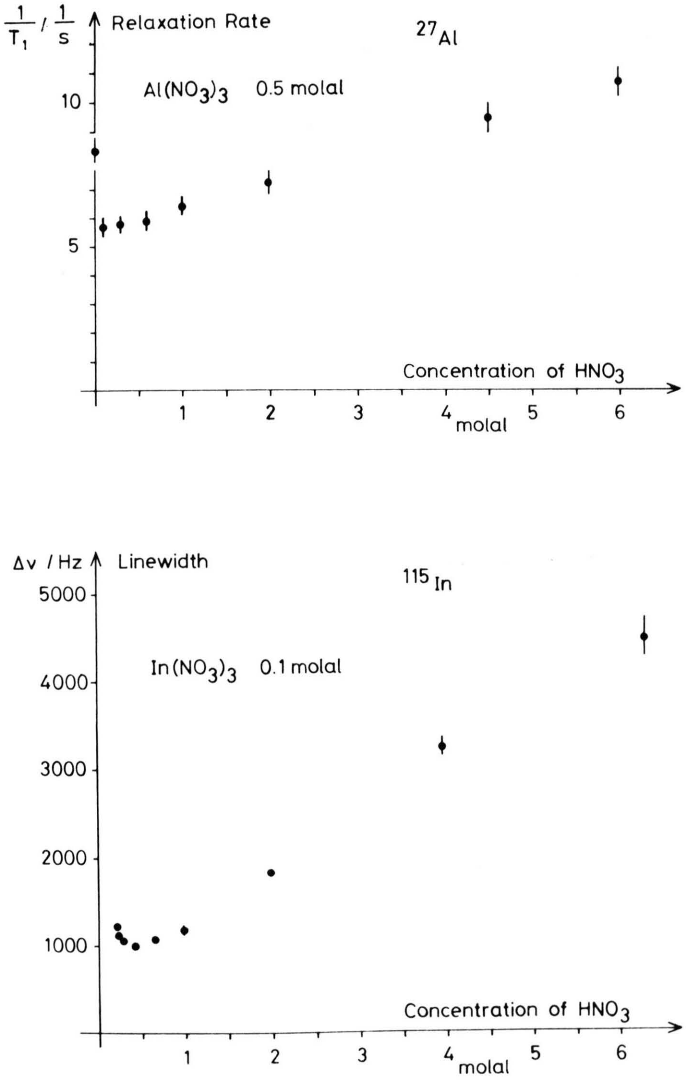

Fig. 5. Longitudinal relaxation rate $1/T_1$ of ^{27}Al in 0.5 molal solutions of $Al(NO_3)_3$ as a function of HNO_3 and linewidth of ^{115}In in 0.5 molal solutions of $In(NO_3)_3$ as a function of HNO_3.

Table 2. H_2O-D_2O solvent isotope effects on T_1 resp. $\Delta\nu$, m = molal. mr = mol-ratio: moles solute/moles solvent.

Nuclide	Sample	T_1/ms	$\Delta\nu$/Hz
^{27}Al	0.1 m $AlCl_3$ in 2.1 m NaOH in H_2O	41.9 ± 2.0	–
^{27}Al	0.1 m $AlCl_3$ in 2.1 m NaOD in D_2O	31.6 ± 1.5	–
^{27}Al	0.5 m $AlCl_3$ in 1 m HCl in H_2O	106 ± 6	–
^{27}Al	0.5 m $AlCl_3$ in 1 m DCl in D_2O	79 ± 4	–
^{27}Al	0.5 m $Al(NO_3)_3$ in 1 m HNO_3 in H_2O	157 ± 8	–
^{27}Al	0.5 m $Al(NO_3)_3$ in 1 m DNO_3 in H_2O	123 ± 6	–
^{71}Ga	0.5 m $Ga(NO_3)_3$ in 1 m HNO_3 in H_2O	5.0 ± 0.3	–
^{71}Ga	0.5 m $Ga(NO_3)_3$ in 1 m DNO_3 in D_2O	3.9 ± 0.2	–
^{71}Ga	0.4 m $Ga(NO_3)_3$ in 2.1 m NaOH in H_2O	–	144 ± 15
^{71}Ga	0.4 m $Ga(NO_3)_3$ in 2.1 m NaOD in D_2O	–	170 ± 17
^{115}In	$In(NO_3)_3$ (mr = 0.0018) in HNO_3 (mr = 0.009) in H_2O	–	980 ± 60
^{115}In	$In(NO_3)_3$ (mr = 0.0018) in DNO_3 (mr = 0.009) in D_2O	–	1330 ± 80

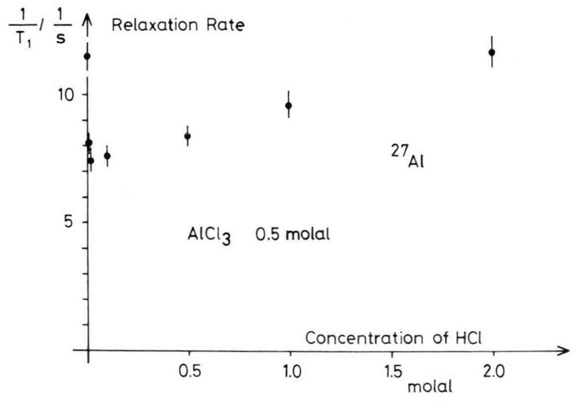

Fig. 6. Longitudinal relaxation rate $1/T_1$ of ^{27}Al in aqueous 0.5 molal $AlCl_3$ as a function of the concentration of HCl.

complex is the dominating but not the only species present in the solutions, as has been recently shown also by chemical shift measurements [19].

Concluding, for a comparison of the relaxation rates of ^{27}Al in aqueous solutions with theory, for instance the electrostatic theory of Hertz [13], T_1 data in solutions with concentrations as low as possible should be available. But this requirement for "infinite" dilution can be hardly fullfilled due to the further need of acidity of the solutions. Naturally these requirements are valid for all the IIIa- and IIIb-elements.

Solvent Isotope Effect

Due to the higher viscosity and the smaller self-diffusion coefficient of D_2O compared with those of H_2O, the quadrupolar relaxation of ionic nuclei shows a solvent isotope effect which is expected to be about 23% at infinite dilution (see e.g. [20]). In a review article by Holz [20] data are listed for a couple of elements for which this effect has been measured.

For the nuclides investigated here, results for T_1 resp. $\Delta\nu$ are given in Table 2. Obviously, T_1 is shorter resp. $\Delta\nu$ is larger in the deuterium oxide solutions. This is the case in aluminium chloride as well as in nitrate solutions, where mainly the hexa-aquo-complex is present. Also in the basic solutions, where the tetrahydroxo-complex is dominating, the solvent isotope effect is found. In all examples the pure H_2O-D_2O effect is something obscured by the relatively high concentrations of the acids and bases which are needed for the appropriate pH-value. A solvent isotope effect is found for all elements although the values of the relaxation rates are decreasing strongly going through the row aluminium, gallium, indium.

Summary

The linewidth and longitudinal relaxation rates of the investigated IIIa group nuclei show a very typical behaviour with a minimum for these parameters as a function of the acidity. The results are very similar to those of the IIIb nucleus ^{45}Sc [1]. The linewidths resp. relaxations rates at the minimum originate mainly from the quadrupolar interaction.

As a function of the atomic number of these elements, the effects increase not only due to the increase of the quadrupole moments (see Table 1) but also due to the increase of the Sternheimer antishielding factors [13, 21]. The H_2O-D_2O solvent isotope effect of the relaxation rates is well established in the acidic and the basic range.

Acknowledgement

We thank the Deutsche Forschungsgemeinschaft for financial support, and U. Thissen for some assistance.

[1] E. Haid, D. Köhnlein, G. Kössler, O. Lutz, W. Messner, K. R. Mohn, G. Nothaft, B. van Rickelen, W. Schich, and N. Steinhauser, Z. Naturforsch. **38a,** 317 (1983).
[2] B. W. Epperlein, Diplomarbeit, Tübingen 1971, unpublished.
[3] T. H. Cannon and R. E. Richards, Trans. Faraday Soc. **62,** 1378 (1966).
[4] J. W. Akitt, in: Annual Reports on NMR Spectroscopy, E. F. Mooney (ed.), Academic Press, New York **5A,** 466 (1972).
[5] R. K. Harris and B. E. Mann, NMR and the Periodic Table, Academic Press, New York 1978.
[6] F. W. Wehrli, in: Annual Reports on NMR Spectroscopy, G. A. Webb (ed.), Academic Press, New York **9,** 126 (1979).
[7] M. Holz, S. Günther, O. Lutz, A. Nolle, and P. G. Schrade, Z. Naturforsch. **34a,** 944 (1979).
[8] V. P. Tarasov and Y. A. Buslaev, Mol. Phys. **24,** 665 (1972).
[9] J. W. Akitt, N. N. Greenwood, and A. Storr, J. Chem. Soc. 4441 (1965).
[10] B. W. Epperlein and O. Lutz, Z. Naturforsch. **23a,** 1413 (1968).
[11] O. Lutz, H. Oehler, J. Mag. Res. **37,** 261 (1980).
[12] N. Bloembergen, "Nuclear Magnetic Relaxation", pp. 118, Benjamin, New York 1961.
[13] H. G. Hertz, Ber. Bunsenges. Phys. Chem. **77,** 531 (1973).
[14] H. G. Dehmelt, Phys. Rev. **92,** 1240 (1953).
[15] O. Lutz, A. Nolle, and A. Uhl, Z. Physik **248,** 159 (1971).
[16] M. M. Zaripov and E. A. Nikiforov, Russ. J. Phys. Chem. **53,** 39 (1979).
[17] M. Holz, H. L. Friedman, and B. L. Tembe, J. Mag. Res. **47,** 454 (1982).
[18] H. G. Hertz, R. Tutsch, and H. Versmold, Ber. Bunsengesell. **75,** 1177 (1971).
[19] J. W. Akitt and B. E. Mann, J. Mag. Res. **44,** 584 (1981).
[20] M. Holz, in: Progress in NMR Spectroscopy, in press.
[21] E. A. C. Lucken, Nuclear Quadrupole Coupling Constants, Academic Press, London 1969.