$^{25}Mg^{2+}$ Nuclear Magnetic Relaxation in Aqueous Solution

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Longitudinal nuclear magnetic relaxation rates of $^{25}Mg^{2+}$ have been measured in aqueous solutions of $MgCl_2$ and $Mg(NO_3)_2$ as a function of concentration. The value of $1/T_1$, extrapolated for infinite dilution has been compared with the "electrostatic theory" of Hertz. It turned out that the relaxation rate reflects the high cubic symmetry of the first hydration sphere of $^{25}Mg^{2+}$. Using the ^1H and $^{25}Mg^{2+}$ relaxation rates at finite salt concentration the "ion-ion contributions" to the $^{25}Mg^{2+}$ relaxation rates have been determined. They are compared with those in aqueous LiCl solutions.

A big change in the $^{25}Mg^{2+}$ relaxation rate in $MgCl_2$ solution was found when a little amount of sodium citrate was added.

Introduction

Although magnesium plays an important role in various fields of chemistry and biology only few nuclear magnetic resonance studies are known using the isotope ^{25}Mg with nuclear spin $I = 5/2$ and a natural abundance of 10.13% (Ref. [1–6]). It was found that the chemical shifts of ^{25}Mg in aqueous magnesium salt solutions amount only to a few ppm [1, 4, 5] and that the linewidths increase from a few Hz to some ten Hz with increasing concentration [4, 5]. The broadening of $^{25}Mg^{2+}$ NMR lines has been used for some complexation studies [2, 3], but there exists only an exploratory study of the longitudinal relaxation rate $1/T_1$ in two magnesium chloride solutions [6]. The reason for the rare NMR experiments with ^{25}Mg is certainly the low receptivity of this nucleus, which is only $2.2 \cdot 10^{-6}$ in a 1 molal aqueous solution compared with that of the proton.

In the following we report on measurements of $1/T_1$ of ^{25}Mg in aqueous magnesium salt solutions. One of the aims was to proceed to concentrations as low as possible for comparing the value for $(1/T_1)^0_{\text{obs}}$ at infinite dilution with the quadrupolar relaxation rate obtained by the theory of Hertz [7]. The concentration dependence of $1/T_1$ at higher salt concentrations will be used to determine relaxation contributions due to the ionic charges in the neighbourhood of the relaxing $^{25}Mg^{2+}$ nucleus.

Furthermore some measurements of $1/T_1$ were done in aqueous magnesium chloride solutions containing various amounts of the complexing sodium citrate.

Experimental

^{25}Mg is the only naturally occuring magnesium isotope with a nuclear spin and a nuclear magnetic moment. In a magnetic field of 2.114 T the Larmor-frequency of ^{25}Mg is about 5.51 MHz. The NMR signal of ^{25}Mg has been observed with a Bruker multinuclei NMR apparatus consisting of a high resolution magnetic system B-E 38 with a NMR stabilization B-SN 15, a pulsed spectrometer SXP 4-100 and a B-NC 12 computer. The temperature was (298 ± 2) K.

The magnesium salts $MgCl_2 \cdot 6\,H_2O$ and $Mg(NO_3)_2 \cdot 6\,H_2O$ were delivered by E. Merck AG, Darmstadt and were of analytical grade. The water had a conductivity of less than $10^{-4}\,\Omega^{-1}\,m^{-1}$. The concentrations of the solutions were determined by weighing salt and solvent.

The measurements of the $^{25}Mg^{2+}$ longitudinal relaxation rate $1/T_1$ were performed with the Fourier transform inversion recovery method $(180°, \text{HS}, \tau, 90°, \text{WT})_n$, see e.g. Ref. [8, 9]: First a 180° pulse is applied to the sample, immediately followed by a homospoil pulse HS. This HS pulse destroys a possible transverse magnetization after the 180° pulse; it was obtained from a homebuilt pulse generator and applied to the y-gradient shim

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coils. A variable time τ after the 180° pulse we measured the free induction decay due to the z-magnetization which is following the 90° pulse. A waiting time WT of about $5\,T_1$ is necessary for the spin system to reach equilibrium magnetization before the experiment can be repeated n times.

After having determined the optimum experimental parameters, the whole relaxation rate measurement can be performed automatically by the T_1 Program/II for Bruker machines, which was written by Cooper [9]. The free induction decays were stored on a disk and the Fourier transformation and other calculations were done after the whole experiment had been finished with various values of τ.

For a 0.5 molal magnesium chloride solution 1500 scans for each value of τ were accumulated to get a reasonable signal-to-noise ratio. Figure 1 gives a stacked plot of the T_1-measurement of ^{25}Mg of this sample together with experimental parameters.

For determining the T_1 values either the integrated intensities of the signals or the peak intensities have been used. The T_1 calculation was not performed with the Bruker program but with a two-parameter least-squares fit procedure, which was written in Basic and could also be run on the B-NC 12 computer.

In order to be able to evaluate the $Mg(NO_3)_2$ data we measured also water proton T_1 values as a function of salt concentration c^*. These measurements were performed on a home-built pulsed NMR spectrometer at 20 MHz using the common 90°–τ–90° pulse sequence, without Fourier transformation. The samples were freed from oxygen by five freeze-pump-thaw cycles.

Experimental Results

For ^{25}Mg only a few $1/T_1$ data seem to have been published [6], but some studies of the linewidths of

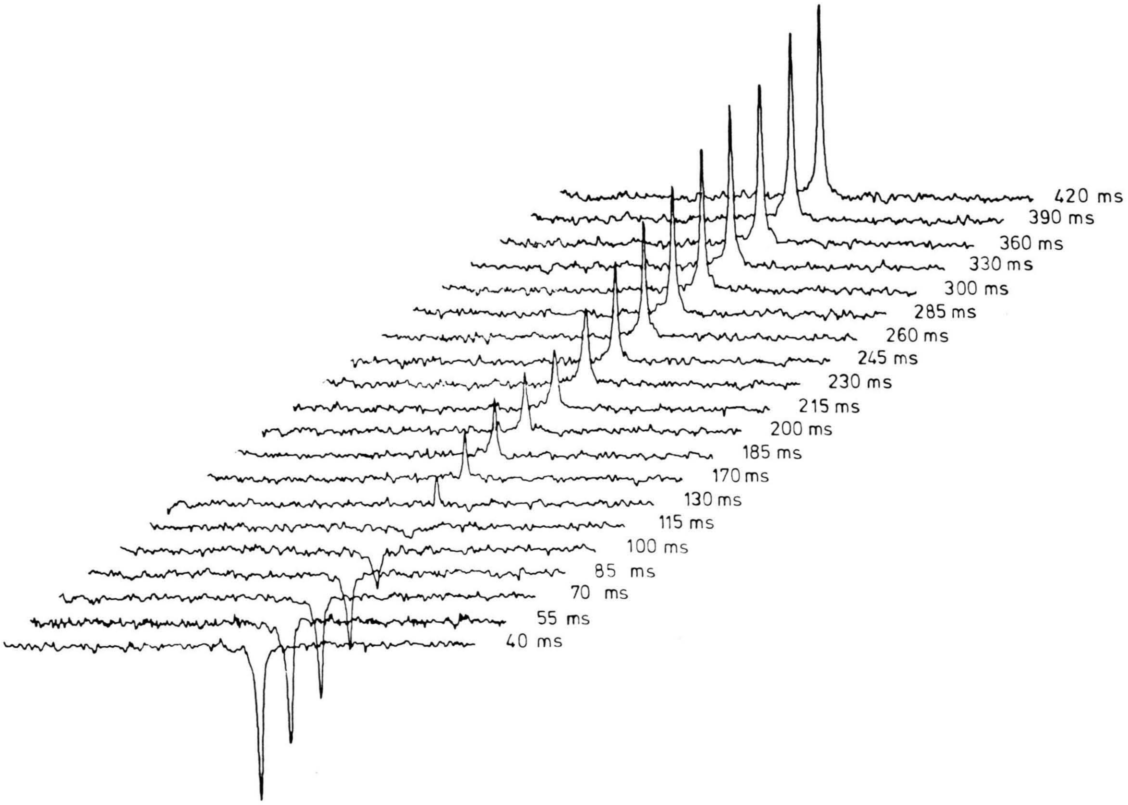

Fig. 1. Absorption signals of ^{25}Mg at 5.510 MHz in a 0.5 molal solution of $MgCl_2$ in H_2O, measured by the inversion recovery Fourier method [8]. In the figure the different waiting times between the 180° and 90° pulse are given. The recovery time was for all measurements $T = 1.5$ s. For each τ-value 1500 scans were accumulated, yielding a total measuring time of about 18.5 h. The resulting relaxation rate is $1/T_1 = (5.1 \pm 0.3)\ s^{-1}$. The plotted spectrum width is 470 Hz. The signals have been observed in a nonrotating sample tube with 10 mm outer diameter.

^{25}Mg NMR signals are known [4, 5], from which values of $1/T_1$ could be estimated under the assumption that for $^{25}Mg^{2+}$ in aqueous solutions $T_1 = T_2$ and that the observed linewidths are natural linewidths. In recent years, obviously due to better homogeneities of the magnetic field, the linewidths of $^{25}Mg^{2+}$ (Ref. [10]) were found to be smaller, indicating that instrumental broadening had influenced the linewidths. Therefore in the present work systematic measurements of the more reliable relaxation rates $1/T_1$ of $^{25}Mg^{2+}$ in aqueous solutions of $MgCl_2$ and $Mg(NO_3)_2$ with different concentrations at (298 ± 2) K are reported. The results are given in Table 1.

As already known from the linewidths, the relaxation rates strongly decrease with decreasing concentration and the $1/T_1$ values are rather different for $MgCl_2$ and $Mg(NO_3)_2$ solutions. From Fig. 2 the relaxation rate at infinitely dilute aqueous solution $(1/T_1)^0_{\text{obs}} = (4.5 \pm 0.2)\ \text{s}^{-1}$ was found by extrapolation. This value is still smaller than the value extrapolated from linewidths of Simeral and Maciel [5] and the estimated value of Lindman et al. [6]. For two samples of $MgCl_2$ in highly deuterium enriched water the relaxation rates $1/T_1$ are higher than for analogous solutions in H_2O.

Table 1. $^{25}Mg^{2+}$ NMR relaxation rates in aqueous solutions. The measurements were performed at 5.510 MHz at (298 ± 2) K. The values of $1/T_1$ have been measured by the inversion recovery method.

Salt	Concentration c^* [molal]	Solvent	$1/T_1$ [s^{-1}]
$Mg(NO_3)_2$	0.1	H_2O	4.8 ± 0.3
	0.5	H_2O	5.9 ± 0.3
	1.0	H_2O	7.8 ± 0.4
	2.0	H_2O	13.9 ± 0.7
	3.0	H_2O	25.3 ± 1.3
	4.0	H_2O	44.6 ± 2.2
$MgCl_2$	0.1	H_2O	4.9 ± 0.4
	0.5	H_2O	5.1 ± 0.3
	1.0	H_2O	5.6 ± 0.3
	2.0	H_2O	7.8 ± 0.4
	3.0	H_2O	11.2 ± 0.6
	4.0	H_2O	17.8 ± 0.9
	5.0	H_2O	33.0 ± 1.6
	5.5	H_2O	46.5 ± 2.3
	0.5	D_2O (94.6%)	5.7 ± 0.3
	1.0	D_2O (89.3%)	6.3 ± 0.3
$MgCl_2$	1.0	0.005 molal NaCi*	9.2 ± 0.5
	1.0	0.01 molal NaCi*	13.8 ± 0.7
	1.0	0.05 molal NaCi*	49.3 ± 2.5
	1.0	0.1 molal NaCi*	94.3 ± 7.8

* The solvent was H_2O with the given concentration of sodium-citrate.

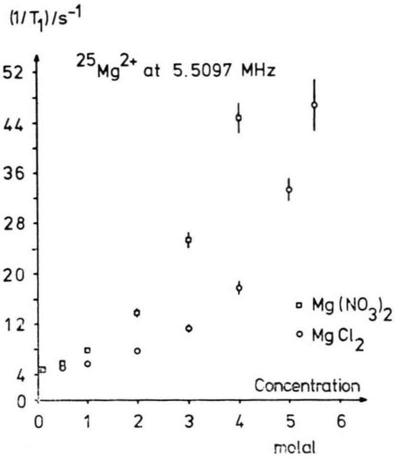

Fig. 2. Concentration dependence and extrapolation of the $^{25}Mg^{2+}$ nuclear magnetic relaxation rate $1/T_1$ in aqueous solutions of $MgCl_2$ and $Mg(NO_3)_2$ at (298 ± 2) K.

Further, the relaxation rate of $^{25}Mg^{2+}$ in solutions containing a little amount of sodium citrate increases very rapidly with the content of the complexing agent (see Table 1).

The water proton relaxation rates $(1/T_1)_{^1H}$ in aqueous solutions of $Mg(NO_3)_2$ are obtained from the R_H values in Table 2, using the relation

$$(1/T_1)_{^1H} = (1/T_1)^0_{^1H} \cdot R_H$$

with $(1/T_1)^0_{^1H} = 0.28\ \text{s}^{-1}$ the water proton relaxation rate in pure water at 298 K.

Evaluation and Discussion of $^{25}Mg^{2+}$ Relaxation Rates

a) Relaxation at Infinite Dilution

Since the ^{25}Mg nucleus possesses an electric quadrupole moment $Q = 0.22 \cdot 10^{-28}\ \text{m}^2$ [11], it relaxes by the quadrupole moment-electric field gradient (QF) interaction. For quadrupolar ionic nuclei the most frequently used theory of relaxation is the "electrostatic theory" as developed by Hertz [7, 12], and it has been successfully applied to the alkali- and halide nuclei in aqueous and non-aqueous solutions [13–15]. Also the relaxation rates of some di-valent and tri-valent ions could be explained satisfactorily [6, 7, 16, 17]. According to this theory the fluctuating electric field gradients are produced by the solvent dipoles and ionic charges in the neighbourhood of the relaxing nuclei. At infinite dilution only solvent dipoles contribute

Table 2. Ion-Ion contributions $\Delta_{a,c}$ to QF relaxation in aqueous $MgCl_2$ and $Mg(NO_3)_2$ solutions according to Equation (6). For $MgCl_2$ solutions R_H and $R_{^{35}Cl}$ are taken from Ref. [18] resp. [21]. The values of Δ_c and Δ_a in parenthesis are given for the readers convenience in units of 10^{13} g cm^{-3} s^{-1}. (* Reference [14].)

	c^* [molal]	$R_{^{25}Mg}$	$\varkappa(c^*)$ for Mg^{2+}	R_H	Δ_c in 10^{26} kg^2 A^{-2} s^{-5}	$R_{^{35}Cl}$	$\varkappa(c^*)$ for Cl^-	Δ_a in 10^{26} kg^2 A^{-2} s^{-5}	$\frac{1}{2}\Delta_a/\Delta_c$	$(\Delta_a/\Delta_c)_{LiCl}$
$MgCl_2$	0	1	5.2	1	0 (0)	1	0.9	0 (0)		
	1	1.24	4.4	1.43	0.14 (0.16)	1.5	0.92	0.02 (0.02)	0.06	—
	2	1.73	3.5	2.04	2.57 (2.88)	2.7	0.94	0.29 (0.33)	0.06	0.05 *
	3	2.5	2.7	2.93	6.99 (7.84)	4.5	0.96	0.70 (0.78)	0.05	—
	4	4.0	1.8	4.14	18.2 (20.4)	6.7	0.98	1.12 (1.26)	0.03	0.04 *
	5	7.3	1	5.79	44.2 (49.6)					
$Mg(NO_3)_2$	0	1	5.2	1	0 (0)					
	1	1.73	4.4	1.45	3.83 (4.3)					
	2	3.1	3.5	1.92	13.0 (14.6)					
	3	5.6	2.7	2.50	30.7 (34.4)					
	4	9.9	1.8	3.15	62.8 (70.4)					

to the relaxation. An interesting feature connected with the quadrupolar relaxation is the occurence of field-gradient quenching effects. This means that an arrangement of cubic symmetry of solvent dipoles around the ion leads to a quenching of the electric field gradient in the centre of the ion and thus to a reduction of the QF interaction. In the theory this effect is quantitatively described by a factor Λ (Ref. [15]) which is 0 for total quenching and 1 if no quenching occurs. For the small di-valent Mg^{2+} ion a relatively high symmetry of the hydration sphere is to be expected and therefore a small Λ-value.

The relaxation rate of an ionic nucleus at infinite dilution is given by

$$\left(\frac{1}{T_1}\right)^0 = \left(\frac{1}{4\pi\,\varepsilon_0}\right)^2 A\,\frac{m^2\,\tau_c\,n_s}{r_0{}^8}\,\beta + \left(\frac{1}{T_1}\right)^{\mathrm{II}} \tag{1}$$

(This formula corresponds to Eq. (24) in Ref. [15], but is here written with a factor containing ε_0, the vacuum dielectric constant, in order to be used in the SI system.)

In (1) the first term describes the relaxation rate produced by the solvent dipoles of the first coordination sphere and the second term $(1/T_1)^{\mathrm{II}}$ stands for relaxation contributions from outside the first coordination sphere. A is a constant for a given nucleus [15], m the electric dipole moment of the solvent molecule, τ_c the rotational correlation time in the first coordination sphere, n_s the first coordination number, and r_0 the closest distance of approach between the centre of the ion and the solvent point dipole. The quantity $\beta = g_Q h \Lambda$ contains the above mentioned quenching factor Λ. The exact meaning of g_Q and h is of minor importance here and may be found elsewhere [15], since for small structure-making ions as Mg^{2+} $g_Q \to 1$ and $h \to 1$, thus in our case $\beta \approx \Lambda$.

$$\left(\frac{1}{T_1}\right)^{\mathrm{II}} = \left(\frac{1}{4\pi\,\varepsilon_0}\right)^2 A\,\frac{4\pi}{9}\,\frac{m^2\,\tau_{\mathrm{solv}}\,c_{\mathrm{solv}}}{b^5} \tag{2}$$

with τ_{solv} the rotational correlation time in the pure solvent, c_{solv} the dipole concentration in particles per m^3, and b the closest distance of approach of solvent molecules outside the first solvation sphere to the centre of the ion. In the case of $^{25}Mg^{2+}$ in aqueous solution the above mentioned quantities have the following numerical values:

$$\begin{aligned}
A_{^{25}Mg} &= 4.52 \cdot 10^{-27}\,\mathrm{A}^2\,\mathrm{s}^4\,\mathrm{kg}^{-2},\\
m_{H_2O} &= 6.07 \cdot 10^{-30}\,\mathrm{Asm},\\
c_{\mathrm{solv}} &= c_{H_2O} = 3.34 \cdot 10^{28}\,\mathrm{particles/m^3},\\
\tau_{\mathrm{solv}} &= \tau_{H_2O} = 2.5\,\mathrm{ps},\\
\tau_c &= \tau_{H_2O}\,k = 13\,\mathrm{ps}, \text{ since for } Mg^{2+}\ k = 5.2\\
&\quad \text{(Ref. [18])},\\
n_s &= 6,\\
r_0 &= r_{Mg^{2+}} + r_{H_2O} = (0.65 + 1.4) \cdot 10^{-10}\,\mathrm{m}\\
&= 2.05 \cdot 10^{-10}\,\mathrm{m},\\
b &= 3.45 \cdot 10^{-10}\,\mathrm{m}.
\end{aligned}$$

(A detailed geometrical calculation of the lowest possible b value for an octahedral coordinated ion showed us that in the special case of Mg^{2+} one has to take

$$\begin{aligned}
b &= r_{Mg^{2+}} + r_{H_2O} + 1.4 \cdot 10^{-10}\,\mathrm{m}\\
&= 3.45 \cdot 10^{-10}\,\mathrm{m}
\end{aligned}$$

rather than the values for the socalled Al^{3+} or Li^+ models used by Lindman et al. [6].) If we introduce the above values in Eq. (1) and (2) and if we set $\beta \approx \Lambda = 1$, we obtain the maximum relaxation rate for ^{25}Mg^{2+}, $(1/T_1)^{\max} = 341\ \mathrm{s}^{-1}$, which is possible within the electrostatic theory under the assumption that there is no field-gradient quenching which means absence of cubic symmetry. The measured value $(1/T_1)^0_{\mathrm{obs}} = 4.5\ \mathrm{s}^{-1}$ is very much lower, indicating the expected strong field-gradient quenching. Following the procedure which is given in Ref. [15] we calculate the β-value using the relation

$$\beta = \frac{(1/T_1)^0_{\mathrm{obs}} - (1/T_1)^{\mathrm{II}}}{(1/T_1)^{\max} - (1/T_1)^{\mathrm{II}}}\,. \tag{3}$$

With the calculated value $(1/T_1)^{\mathrm{II}} = 0.32\ \mathrm{s}^{-1}$ (according to Eq. (2)), we obtain as our final result $\beta = 0.012$. As to be expected, this result means that around the Mg^{2+} ion the water molecules are arranged on positions with such a high cubic symmetry that in the centre at the ^{25}Mg^{2+} nucleus the electric field gradient is nearly completely quenched. This β-value may be compared to the β for Li$^+$ in H_2O, since Li$^+$ has almost the same ionic radius ($r_{\mathrm{Li}^+} = 0.59 \cdot 10^{-10}$ m). For Li$^+$ in water $\beta = 0.035$ has been determined [15].

We see that the smaller β-value as determined for Mg^{2+} is quite reasonable taking into account the twofold charge of Mg^{2+} compared to Li$^+$.

b) Relaxation at Finite Salt Concentration

Due to the presence of other ions, in particular of counterions, at finite salt concentrations the QF interaction is increased [12]. This additional relaxation contribution Δ is normally called the "ion-ion contribution", but it includes also effects of higher ion-water correlations [12, 14] which may be present in special cases [19, 20].

The ionic relaxation rate as a function of the salt concentration c^* may be written as

$$(1/T_1)(c^*) = \left(\frac{1}{T_1}\right)^0 \frac{\tau_c(c^*)}{\tau_c(c^* = 0)} + \frac{4\pi}{9} A\, \Delta(c^*)\,, \tag{4}$$

where the first term describes the variation of the ion-solvent interaction by correlation time variations as a function of the salt concentration and the second term represents the concentration dependent ion-ion-term. In order to determine the ion-ion contribution Δ we have to know the quantity $\tau_c(c^*)$ which can be approximated as usually [13] using the water proton relaxation rate ratio R_{H} (as a function of salt concentration) by the relation

$$\tau_c(c^*) = \tau_c(c^* = 0)\, \varkappa\, R_{\mathrm{H}} \tag{5}$$

with $\varkappa(0) = k$ for $c^* = 0$ and $\varkappa(c) \to 1$ for $c^* \geqq 5$ molal and $R_{\mathrm{H}} = (1/T_1)_{1_{\mathrm{H}}}(c^*)/(1/T_1)^0_{1_{\mathrm{H}}}$.

From Eqs. (4) and (5) we obtain:

$$\Delta_{a,c} = \frac{9}{4\pi} A^{-1} (1/T_1)^0_{a,c} \left(R_{a,c} - R_{\mathrm{H}} \frac{\varkappa(c^*)}{\varkappa(0)} \right), \tag{6}$$

where the index a stands for anionic nuclei and c for cationic nuclei.

$$R_{a,c} = \frac{(1/T_1)_{a,c}(c^*)}{(1/T_1)^0_{a,c}}$$

is the relaxation rate ratio of the ionic nuclei.

In Table 2 the Δ_c values for ^{25}Mg^{2+} as obtained from (6) are listed together with the other quantities used. Fortunately Weingärtner et al. [21] measured recently the ^{35}Cl$^-$ relaxation rates in aqueous MgCl$_2$ solutions allowing us to calculate for these solutions also the Δ_a for ^{35}Cl$^-$ (see Table 2). Thus we are able to give the characteristic ratio Δ_a/Δ_c which has been determined also for the alkali halide solutions [14] and which should be unity in the absence of short range order around the ion-ion encounter configuration. A comparison with the aqueous LiCl solution [13, 14] shows that almost the same ratio Δ_a/Δ_c for both solutions is found if one takes into account that we have to divide the MgCl$_2$ Δ_a/Δ_c ratio by a factor of two in order to be able to compare the 2–1 electrolyte with an 1–1 electrolyte. This result means that the structure of both solutions is very similar in the concentration range investigated. Why is the Δ_a/Δ_c ratio so small? One possible explanation might be that strongly hydrated cations produce relatively weak electric field gradients at the anionic nucleus, however, the presence of anions disturbs the high symmetry of the cationic hydration shell, thus producing by this water-ion correlation relatively high field gradients at the cationic nucleus.

It should be pointed out that the absolute Δ_a and Δ_c values are larger than the corresponding values in LiCl solutions, which possibly is a characteristic difference between the "symmetric" 1–1 electrolytes and the "asymmetric" 2–1 electrolytes.

For Mg(NO$_3$)$_2$ solutions we can only determine Δ_c (see Table 2). As already indicated by the strong increase of $(1/T_1)_{25\mathrm{Mg}}$ with concentration, here we find ion-ion contributions which are still distinctly greater than those in the $MgCl_2$ solutions. But this is not surprising having in mind the extraordinary strong effects of the multiatomic ions ClO_4^- and BF_4^- e.g. on the $^{23}Na^+$ and $^7Li^+$ relaxation which were recently discussed in detail by Contreras and Hertz [19, 20]. Obviously also the NO_3^- anion is strongly influencing the quadrupolar relaxation rate of the cationic $^{25}Mg^{2+}$ nucleus.

Simeral and Maciel [5] concluded from their $^{25}Mg^{2+}$ linewidth data that the concentration dependence of the $^{25}Mg^{2+}$ relaxation in aqueous $Mg(NO_3)_2$ may be completely explained by viscosity effects. Besides the fact that it is dangerous to use the macroscopic quantity viscosity as a measure for correlation times, these authors [5] used a concentration dependence of $\Delta\nu_{1/2} = 1/\pi T_2$ which is falsified by field inhomogeneity effects. A comparison of their linewidths with our T_1 data shows e.g. for $Mg(NO_3)_2$ that at low concentrations the linewidth was broadened by a factor 2, but at higher concentrations only by about 10%. Thus Simeral and Maciel [5] found a weaker increase of the relaxation rate with the salt concentration, which hid the ion-ion contributions really present. Therefore the conclusion drawn from linewidth data should be regarded with caution as also earlier examples showed [22].

The D_2O-H_2O isotope effect, characterized by the ratio of $^{25}Mg^{2+}$ relaxation in D_2O and H_2O, $(1/T_1)_{D_2O}/(1/T_1)_{H_2O}$, is found to be 1.13 in 0.5 m $MgCl_2$ and 1.15 in 1 m $MgCl_2$ solution. (The ratios are obtained from the data in Table 1, and are corrected for 100% D_2O). These are reasonable values for quadrupolar ionic nuclei showing, as to be expected [23], that the QF interaction dominates and e.g. dipole-dipole relaxation contributions from water protons are negligible as well as slow chemical exchange effects. The ratio agrees within the limits of experimental error with that of other ionic nuclei [23].

The relaxation rates in presence of sodium citrate shall not be evaluated. They have been performed in order to show the strong dependence of the relaxation rate upon complexing species and to demonstrate that T_1 measurements also of $^{25}Mg^{2+}$ may become, similar to $^{23}Na^+$ [24], a powerful tool in the study of biological systems [2].

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