Magnetic and Quadrupole Relaxation in Aqueous BeF_2-Solutions

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In aqueous BeF_2-solutions of different concentrations and therefore different viscosities the magnetic relaxation time T_1 was measured as a function of the viscosity over a wide range by pulsed NMR-technique. For small viscosities a linear dependence of T_1 on the viscosity was observed as predicted by theoretical calculations. Since the ground state spin of ^{19}F is $I = 1/2$, the quadrupole moment vanishes. For observing quadrupole relaxation of the F-nuclei, one has to use an excited level. With the time differential perturbed angular distribution method (TDPAD) we observed the quadrupole relaxation time T_{Rel} of ^{19}F in aqueous BeF_2-solutions.

Introduction

For aqueous solutions of different fluorides there are measurements of the proton-relaxation time T_1, done by pulsed NMR-technique. These measurements are mostly restricted to low concentrations and therefore low viscosities. We extended such investigations to aqueous BeF_2-solutions for the following reasons: i) BeF_2 is readily soluble in water, therefore solutions over a wide range of concentrations and viscosities are available, ii) with the time differential perturbed angular distribution method using the second excited $5/2^+$ level in ^{19}F it is possible at least for solutions of high viscosity, to observe quadrupole relaxations of the ^{19}F-nuclei.

Magnetic Relaxation

For the magnetic relaxation rate $1/T_1$ of an aqueous solution of BeF_2 the following general formulas are valid (for $I = 1/2$) (Ref. [1]):

$$\frac{1}{T_1} = c_1 \left[\frac{\tau_c}{1+\omega_p^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_p^2\tau_c^2}\right] + c_2\left[\frac{\tau_c}{1+\omega_p^2\tau_c^2} + \frac{4\tau_c}{1+(\omega_p+\omega_F)^2\tau_c^2}\right] \qquad (1)$$

$$c_1 = \frac{3}{10}\gamma_p^4\hbar^2\cdot\frac{1}{r_{pp}^6}\,; \quad c_2 = \frac{3}{10}\gamma_p^2\gamma_F^2\hbar^2\cdot\frac{1}{r_{pF}^6}$$

with $\gamma_{p,F}$ = gyromagnetic ratio of the proton or of the fluorine nucleus; τ_c = correlation time; ω_p, ω_F = Larmor frequencies of the proton and the fluorine nucleus, respectively. r_{pp} = distance between two protons; r_{pF} = distance between proton and fluorine nucleus.

With certain assumptions the correlation time τ_c can be written as [1]:

$$(\tau_c)_{\mathrm{Rot}} = \frac{4\pi a^3}{3kT}\eta\,, \qquad (2)$$

a = molecular radius, η = viscosity.

For small viscosities the conditions $\omega_p^2\tau_c^2 \ll 1$ and $(\omega_p+\omega_F)^2\tau_c^2 \ll 1$ hold and therefore (1) reduces to

$$\frac{1}{T_1} = 5\tau_c(c_1+c_2) = 5(c_1+c_2)\cdot\frac{4\pi a^3}{3kT}\eta\,. \qquad (3)$$

The temperature dependence of the correlation time τ_c in fluids can be described by an Arrhenius relation

$$\tau_c = \tau_0 \exp[E_a/kT]\,, \qquad (4)$$

where E_a is the activation energy of the diffusion process which is mainly responsible for the relaxation rate. Therefore one gets from (3) and (4) for the relaxation time T_1

$$T_1 = \frac{1}{5(c_1+c_2)}\cdot\tau_0^{-1}\cdot\exp[-E_a/kT]\,. \qquad (5)$$

The measurements have been done using a pulsed NMR-spectrometer working at 60 MHz. T_1 was determined by the well known 180°-τ-90° pulse-sequence-method. The principle experimental arrangement is shown in Figure 1. First, measurements of the proton relaxation rate $1/T_1$ as a function of the viscosity of different aqueous BeF_2 solutions have been done.

In Fig. 2 these results are shown together with those using the fluorine resonance. The viscosity of the samples was determined by a viscosimeter of the Hagen-Poiseuille type. For more viscous probes

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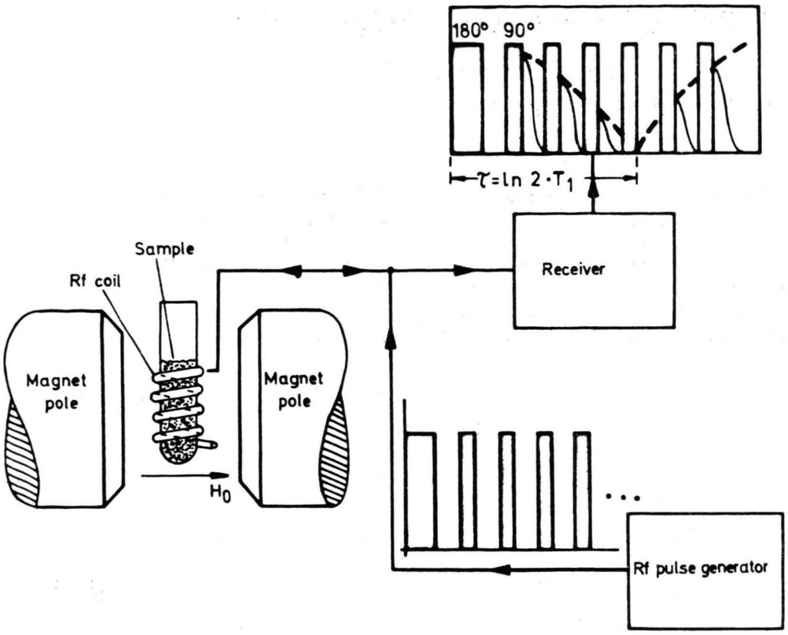

Fig. 1. Principle experimental arrangement for measuring T_1.

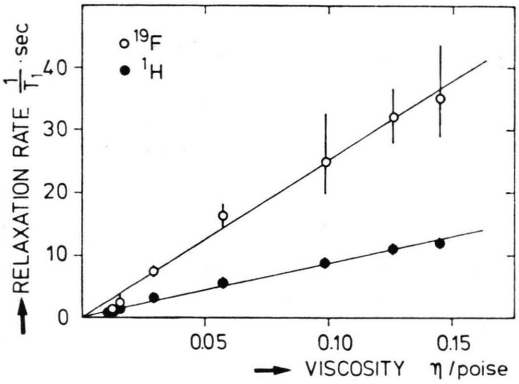

Fig. 2. $1/T_1$ as a function of viscosity ($\eta \leqq 0.15$ poise).

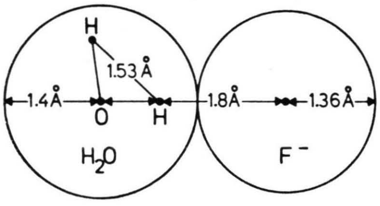

Fig. 3. Model of the $[F(H_2O)_n]^-$ complex.

Stokes' law has been used including corrections to special experimental conditions [2]. From Fig. 2 it is obvious that the relaxation rate $1/T_1$ is proportional to the viscosity η for values $\eta < 0.15$ poise within the experimental errors for the protons as well as for the fluorine nuclei. This is in good agreement with (3), but the slopes of both curves are different. To discuss these differences one has to discuss the structure of the BeF_2 solution. A very simple assumption for small concentrations of BeF_2 is, that there exist free water molecules and water molecules bound by hydration to the F-ion. Since the g-factor of the Be-nucleus in its ground state is very low compared to those of ^1H and ^{19}F, Be must not be taken into account. For the structure of the $[F(H_2O)_n]^-$ complex a simple model is suggested (Ref. [3, 4]) (Figure 3).

For the proton resonance one has to consider the next proton inside the water molecule at a distance of $r_{pp} = 1.53$ Å. But for the molecular radius a, entering in (2) one has to use a weighted averaged value between the radius of the H_2O molecule and the $[F(H_2O)_n]^-$ complex, which is not known. For the fluorine resonance only the $[F(H_2O)_n]^-$ complex is essential within this rough estimate. Therefore the radius a will become larger. But now we have up to $n = 4 \ldots 6$ next protons at a distance $r = 1.8$ Å. Thus it is not surprising that the slopes of the curves in Fig. 2 differ that much.

T_1 for the protons and the fluorine nuclei in a BeF_2 solution was also measured up to higher values of the viscosity η. The results are shown in a double logarithmic scale in Figure 4. For larger viscosities, from (1) one expects a minimum of the relaxation time at a certain viscosity, as shown in Figure 4.

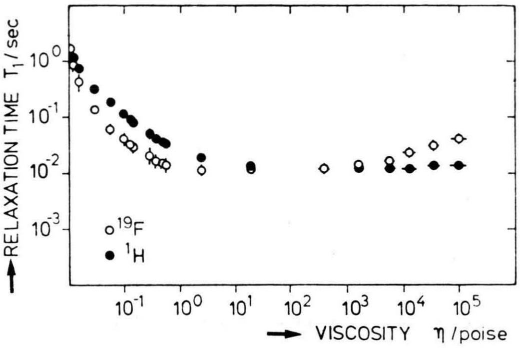

Fig. 4. T_1 for protons and ^{19}F as a function of the viscosity.

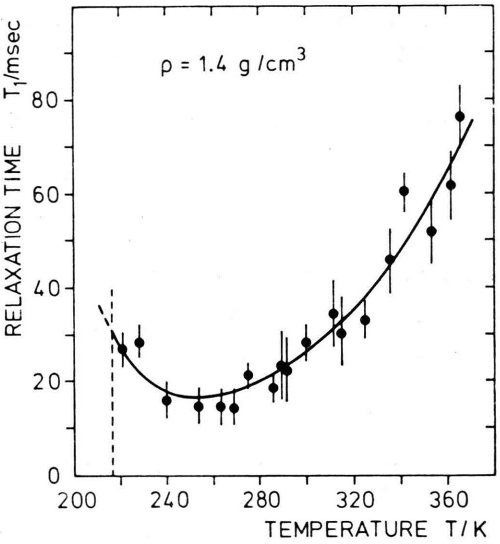

Fig. 5. T_1 of the protons as a function of temperature.

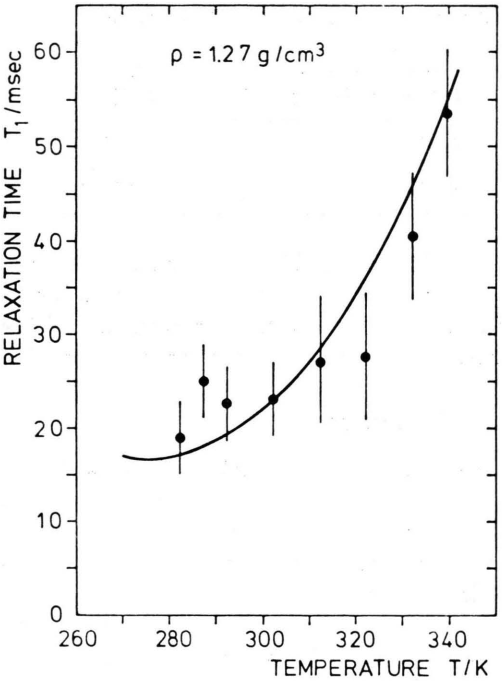

Fig. 6. T_1 of the fluorine nuclei as a function of the temperature.

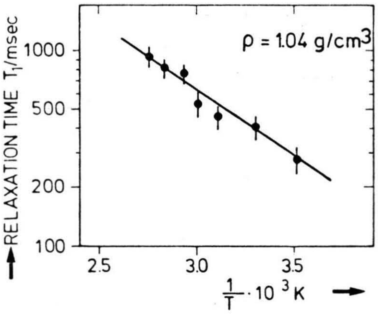

Fig. 7. T_1 is plotted in a logarithmic scale versus $1/T$.

The relaxation time T_1 for protons and the fluorine nuclei decreases up to viscosities of the order of 100 poise and then increases again. But there is no quantitative agreement with Equation (1). The minimum is broadened too much. Presumably the reason for this behaviour is the concentration dependent structure of the BeF_2 solution.

For the proton as well as for the fluorine resonance, investigations have been done on the temperature dependence of T_1 for samples with small viscosities η. As an example, in Fig. 5 T_1 of the protons is plotted versus temperature T for an aqueous solution of a density $\varrho = 1.4$ g/cm^3, which corresponds to a viscosity of $\eta = 0.75$ poise at room temperature.

In Fig. 6, the fluorine relaxation time is plotted versus temperature for $\varrho = 1.27$ g/cm^3 ($\eta = 0.1$ poise). The drawn lines are fits according to Equation (1). The values for the distances r_{pp} and r_{pF} have been chosen to $r_{pp} = 1.53$ Å and $r_{pF} = 1.8$ Å. Taking this values as fixed one has to change the molecular radius a by about 20% for the different samples. For the fluorine resonance an averaged value of $n = 3.7$ for the number of hydrated H_2O-molecules has to be assumed.

From the measurements at higher temperatures one can get the activation energy of the diffusion process involved using (5). In Fig. 7, as an example the relaxation time T_1 is plotted in a logarithmic scale versus $1/T$ for the sample with $\eta = 0.02$ poise

Table 1. Activation energies for BeF$_2$ solutions.

ϱ [g/cm^3]	Concentration [$\cdot 10^{21}$ cm^{-3}]	η [poise]	E_a [eV]
1.04	0.66	0.012 (1)	0.130 (20)
1.27	5.03	0.081 (8)	0.218 (20)
1.41	8.06	0.620 (2)	0.165 (10)

(at $T = 293$ K). In Table 1 the results for the activation energies are listed for the different measurements. The activation energies are of the same order as those reported for other systems [5].

Quadrupole Relaxations

Fluorine has only one stable isotope with the mass number $A = 19$. In its ground state ^{19}F as well as the proton has the nuclear spin $I = 1/2$, therefore no quadrupole moment exists. On measuring quadrupole relaxations in aqueous fluorine solutions one has to use an excited state of the ^{19}F nucleus. For the following measurements the second excited state at 197 keV in ^{19}F was used. Some relevant properties of ^{19}F are given in Figure 8. The $5/2^+$ level used for measurement was populated by the ^{19}F(p, p')^{19}F reaction using the pulsed ion beam of the Erlangen Tandem-accelerator with a proton energy of 5 MeV.

From measurements with the time differential perturbed angular distribution method (TDPAD) one can get information about the quadrupole relaxation time T_1 of the fluorine nucleus. The experimental arrangement is shown in Figure 9. Perpendicular to the plane defined by the beam axis and the direction of the observed γ-radiation an external magnetic field between 0.4 T and 2 T was applied. The γ-ray intensity observed at a time t and at an angel θ with respect to the beam axis is given by

$$I(\theta,t) = I_0 \exp(-t/\tau) \sum_{k \text{ even}} A_{kk} P_k(\cos(\theta - \omega_L t)). \quad (6)$$

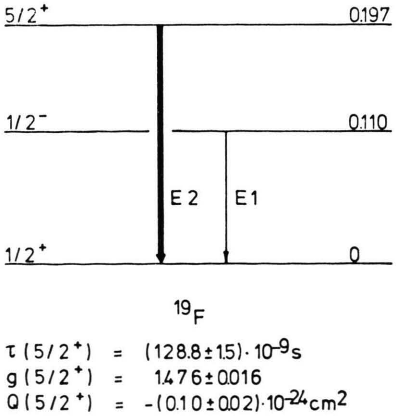

Fig. 8. Some properties of ^{19}F nucleus [7].

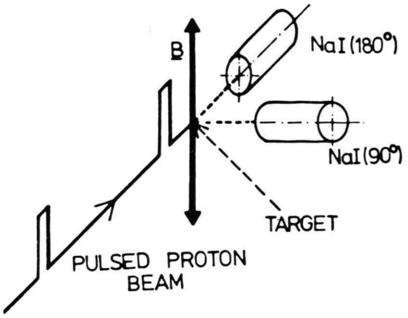

Fig. 9. Experimental arrangement for a TDPAD-measurement.

To eliminate the exponential decay one has to form the coincidence counting rate ratio $R(\theta,t)$ of counters with an angel of 90° to each other. For the case discussed here ($R\ \theta,t$) is given by

$$R(\theta,t) = \frac{N(\theta,t) - N(\theta+90°,t)}{N(\theta,t) + N(\theta+90°,t)} = \frac{3}{4} A_{22} \cos 2(\theta - \omega_L t). \quad (7)$$

$N(\theta, t)$ is the time dependent coincidence counting rate corrected for background. In the case of additional statistical fluctuating perturbations the amplitude A_{22} of Eq. (6) must be replaced by an effective A_{22}^{eff} which is related to A_{22} by

$$A_{22}^{\text{eff}} = e^{t/T_{\text{Rel}}} A_{22}. \quad (8)$$

Equation (8) describes an exponential decrease of the modulation amplitude A_{22} in the time spectrum. The relaxation rate $1/T_{\text{Rel}}$ depends on the correlation time τ_c, the quadrupole moment Q and on an effective electric field gradient $|V_{zz}|$.

$$1/T_{\text{Rel}} \approx \tau_c \cdot (eQ)^2 \cdot |V_{zz}|^2. \quad (9)$$

To avoid changes in the viscosity of the solution during the irradiation a special target arrangement has been used which is described elsewhere (Ref. [6]). The measurements have been done for different BeF$_2$-solutions. For a sample with $\eta = 0.1$ poise the time spectrum is shown in Figure 10. In this case no relaxation was observed. This is in contrast to results obtained with ^{111}InCl$_3$ solutions with different amounts of glycerin. These measurements

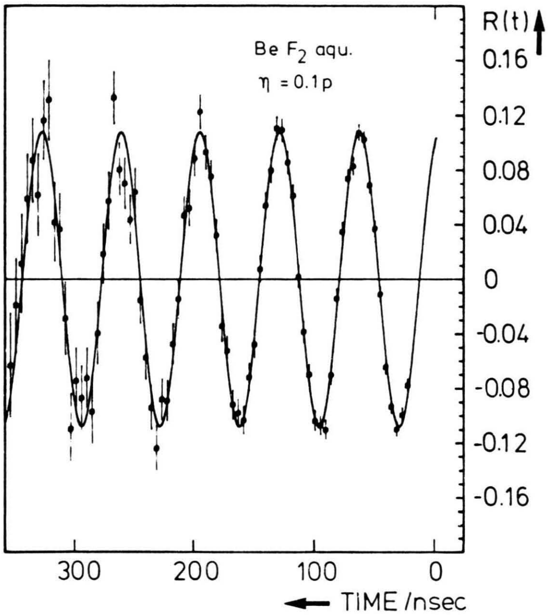

Fig. 10. Time spectrum for BeF_2 aqueous solution $\eta =$ 0.1 poise.

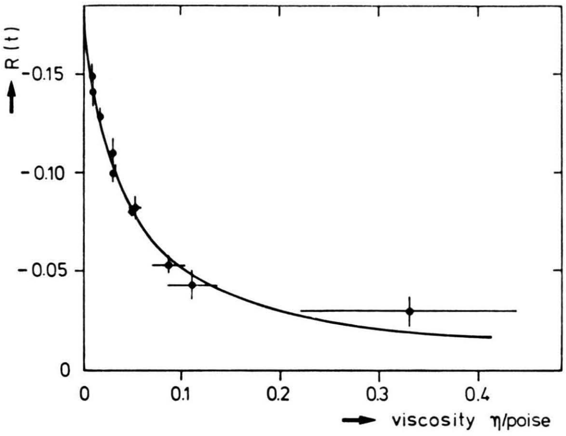

Fig. 11. Measurements of A_{22}^{eff} as function of η in $InCl_3$ solutions with different amounts of glycerin.

were performed with the perturbed angular correlation method (TDPAC). The probe nucleus was ^{111}Cd which is produced by electron capture from ^{111}In. In Fig. 11 the effective amplitude A_{22}^{eff} is plotted versus the viscosity of the solution. The difference in the quadrupole moments $Q(^{111}\text{Cd}(5/2^+))$ $= 0.77$ b) cannot explain such a different behaviour. May be the formation of the $[\text{F(H}_2\text{O})_n]^-$ complex is the essential point for the low relaxation rate of the BeF_2 solution.

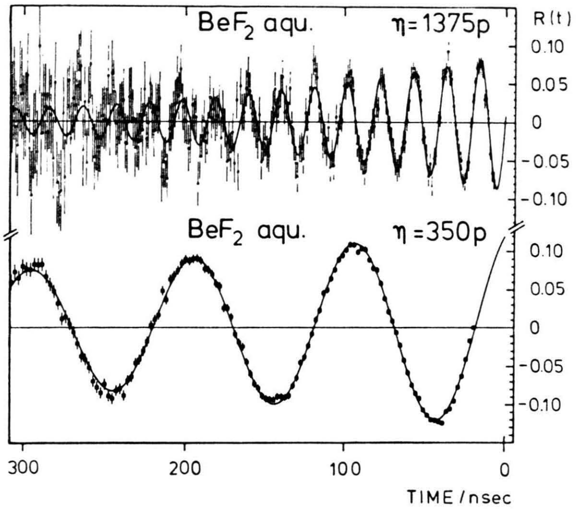

Fig. 12. Time spectra for BeF_2 solutions for high viscosities.

Table 2. Values for the quadrupole relaxation in BeF_2 solutions.

ϱ [g/cm^3]	Concentration [$\cdot 10^{21}$ cm^{-3}]	η [poise]	T_{Rel} [sec]
1.24	4.5	0.060 (6)	$>10^{-5}$
1.28	5.4	0.10 (1)	$>10^{-5}$
1.36	7.1	0.30 (3)	$>10^{-5}$
1.57	12.3	350 (100)	579 (33) $\cdot 10^{-9}$
1.59	12.6	1375 (100)	192 (19) $\cdot 10^{-9}$

Going to much higher viscosities of the BeF_2 solutions quadrupole relaxation can be seen. In the time spectra (Fig. 12) the decreasing of the modulation amplitude with time is very obvious. This is due to quadrupole relaxation processes. The drawn lines are fits according to the formulas (6) through (8). The resulting values from the fit procedures are given in Table 2. To get relaxation times which are in a proper time scale for measurement one has to choose very high viscosities. As seen from the NMR investigations, at these high viscosities the structure of the BeF_2 solution is not known. Therefore no model calculations can be made for discussing the observed quadrupole relaxation.

Acknowledgement

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