

NUCLEAR MAGNETIC RELAXATION BY INTERMOLECULAR QUADRUPOLE INTERACTION,
DETERMINATION OF THE CORRELATION TIME

A. GEIGER AND H. G. HERTZ

Institut für physikalische Chemie und Elektrochemie der Universität
Karlsruhe (W. Germany)

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ABSTRACT

Expressions for the correlation times corresponding to various models are presented which have been proposed in the literature. Experimental results for the ^7Li magnetic relaxation rate solutions of LiCl in glycerol and glycerol- d_8 as a function of the temperature are reported. In all cases a maximum for the relaxation rate is observed and is compared with the maximum for the proton relaxation rate in the same solution. As both maxima occur at the same temperature it is concluded that the electrostatic model provides a realistic description of the relaxation process. Similar experiments have been performed for solutions of Cs^+ in glycerol and of ^7Li and ^{133}Cs dissolved in water. In all cases the electrostatic model was found to be satisfactory.

INTRODUCTION

Let us assume that by some means we have produced a perturbation of the nuclear magnetization M in a static magnetic field such that M_z , the component of M in the direction of the static magnetic field, differs from the equilibrium value M_z^0 . Then the nuclear magnetization moves back towards the equilibrium value, and under suitable conditions the motion of the longitudinal component obeys the differential equation [1]

$$\frac{dM_z}{dt} = -\frac{1}{T_1} (M_z^0 - M_z) \quad (1)$$

T_1 is the longitudinal relaxation time and $1/T_1$ is called the longitudinal

relaxation rate. Nuclei with a spin $I > 1/2$ have an electric quadrupole moment Q . This has the consequence that in most cases for nuclei with $I > 1/2$ the nuclear magnetic relaxation mechanism which leads to an equation of type Eqn. (1) is caused by the interaction of the nuclear electric quadrupole moment with the electric field gradient at the nuclear site. This electric field gradient is produced by the distribution of other nuclei and of the electrons in the environment. One important feature of the electric field gradient is that in order to be effective in inducing nuclear spin transitions, and thereby magnetic relaxation, it fluctuates with time. Of course, such fluctuations with time are due to the molecular motion. The electrical field gradient is a tensor quantity, and the quantities of importance are the components of this tensor in the laboratory coordinate system, the z axis of which is the direction of the static magnetic field. Thus it is easy to imagine that the tensor components in the laboratory system vary with time when the molecules perform rotational Brownian motions. In fact, the theory of nuclear magnetic relaxation caused by intramolecular quadrupole interaction and based on fluctuations of the field gradient components due to rotational molecular motion is well established [1]. However, the situation becomes more difficult when we consider a nucleus which resides in the centre of an ion with a noble gas structure. Now, as the ion is of spherical symmetry, the concept of a rotation of the ion as a means of varying the electric field gradient at the nucleus at its centre is meaningless. Obviously, then the electric field gradient must in some way be produced by intermolecular effects.

In the literature essentially two mechanisms have been proposed in order to account for the observed intermolecular relaxation rate by quadrupole interaction. The first mechanism we may call an electronic mechanism because, primarily, distortions of the ion electron cloud are involved. There are two subversions of this hypothesis:

- i) The ion collides with the surrounding solvent molecules. During the collision the spherical symmetry of the ion is lost and consequently an electric field gradient arises at the centre of the ion. This mechanism was proposed by Deverel [2,3].
- ii) The other version which is due to Mishustin and Kessler is suitable only for the relaxation of small and highly charged ions. One example is Li^+ , the nucleus of which is the subject of the present study. According to these authors Li^+ ions have highly symmetric, presumably tetrahedral solvation shells. In such surroundings of tetrahedral symmetry - like

spherical symmetry - the electric field gradient vanishes. Thus, if it exists, the field gradient at the nuclear site arises from distortions of the common electronic system of Li^+ and the first solvation shell. The maximum distortion (and the maximum field gradient) corresponds to the breakage of one Li^+ -solvent molecule bond; the "freed" molecule most probably is leaving the first solvation shell. In this case the relaxation rate is determined by exchange of molecules i.e. by the residence time of solvent molecules in the solvation shell.

The second attempt to explain this quadrupolar relaxation rate of ion nuclei is based on an electrostatic model. The electric field gradient at the nuclear site is caused by the electric point dipoles of the surrounding solvent molecules and the point charges of other ions present in solution. This model was derived by Valiev and coworkers [5-8] and by Hertz [9]. The electronic distortion is taken into account not as a specific effect but as a universal multiplication factor, the antishielding or Sternheimer factor [10-11]. Later an improved version of this model was applied to a number of systems, including aqueous and non-aqueous electrolyte solutions [12-20]. On the whole, so far the experimental data could be satisfactorily interpreted in terms of the electrostatic theory.

It is the purpose of the present paper to report results of a number of experiments which were performed in order to decide which of the proposed three models is the most realistic. The basic principle underlying these experiments is the direct measurement of the time constant, which determines the fluctuation of the electric field gradient. This microscopic time constant is usually termed the correlation time. As will be shown, the different models lead to different predictions of the correlation time and thus the measurement of this time will be useful. In the next section we shall present the quantitative expressions which are to be used in the experimental section.

The system we have studied are solutions of Li^+ (^7Li) and Cs^+ (^{133}Cs) in glycerol, since the molecular motions are slow enough for a nmr study to be feasible. In a rather short section some results for aqueous solutions of some Li and Cs salts are added.

BASIC FORMULAS

RELAXATION RATES AND CORRELATION FUNCTIONS

We shall study the relaxation behaviour of the two nuclei ^7Li and ^{133}Cs in the ions Li^+ and Cs^+ . One difficult feature of these nuclei is

that both have a spin $I > 1$, and, as the theory shows, for such nuclei, in general, a relaxation time T_1 is not strictly defined [1, 21]. Thus, if $M_z = 0$ at $t = 0$ the regrowth of the longitudinal magnetization M_z relative to the equilibrium value

$$\frac{M_z^0 - M_z}{M_z^0} = f(t)$$

is not an exponential function as it should be according to eqn. (1). Rather, it is a superposition of a number of exponentials [21]. The case of ${}^7\text{Li}$ with $I = 3/2$ is comparatively simple. Hubbard has derived the formula [21]

$$\frac{M_z^0 - M_z}{M_z^0} = \frac{4}{5} \exp(-a_1 t) + \frac{1}{5} \exp(-a_2 t) \quad (2)$$

${}^{133}\text{Cs}$ has the spin $I = 7/2$, and the motion of its magnetization towards equilibrium is more complicated; therefore Cs^+ results will only be discussed on a qualitative level. In eqn. (2) the constants a_1 and a_2 are given by the relations

$$a_1 = \frac{1}{6} \frac{eQ}{\hbar}^2 J_{-22}(2\omega) \quad (3)$$

$$a_2 = \frac{1}{6} \frac{eQ}{\hbar}^2 J_{-11}(\omega) \quad (4)$$

where $J_{\lambda k}$ is the Fourier transform of the time correlation function

$$G_{-kk}(t) = \overline{V^k(0)V^{-k}(t)} \quad k = 1, 2$$

of the electric field gradient:

$$J_{-kk}(\omega) = \int_{-\infty}^{+\infty} G_{-kk}(t) \exp(-i\omega t) dt \quad (5)$$

with

$$V^0 = \frac{2}{\sqrt{6}} V_{zz}$$

$$V^{\pm 1} = V_{xz} \pm i V_{xy} \quad (6)$$

$$V^{\pm 2} = \frac{1}{2} (V_{xx} - V_{yy}) \pm i V_{xy}$$

V_{xx} V_{xy} are the components of the field gradient tensor. The liquid is an isotropic system; in such a system $G_{-11} = G_{-22}$ and we may drop the subscripts of $G(t)$. $G(t)$ approaches 0 as the time goes on; in general $V^k(0)^2 \neq 0$. If the molecular motion is fast, then the time constant for the decay of the time correlation function is short; otherwise it is long. The time dependence of $G(t)$ is dependent on the model we are postulating.

Experiments show that the deviation of eqn. (2) from an exponential is very small. In all the measurements to be reported here we were never able to detect a deviation from a simple exponential behaviour. Therefore we simulated the exponential function by a computer as an approximation to eqn. (2). Thus we replaced eqn. (2) by a law of time dependence

$$\frac{M_z^0 - M_z}{M_z^0} = \exp \left[-\frac{1}{(T_1)_{\text{eff}}} t \right] \quad (7)$$

and we may write for $(1/T_1)_{\text{eff}}$

$$\left(\frac{1}{T_1}\right)_{\text{eff}} = x_1 \frac{4}{5} a_1 + x_2 \frac{1}{5} a_2 \quad (8)$$

$$= \frac{1}{30} \frac{eQ}{\hbar}^2 [4 x_1 J_{-22}(2\omega) + x_2 J_{-11}(\omega)] \quad (9)$$

ω is the nuclear magnetic resonance frequency at the magnetic field we are applying. The quantities x_1 , x_2 are numerically unknown to us because the fitting of eqn. (7) to the real behaviour according to eqn. (2) is done by a least mean square procedure of the computer. As will be shown below, x_1 , and x_2 should not differ very much from unity. If the spin were $I = 1$, then we would have exactly [1]

$$\frac{1}{T_1} = \frac{1}{8} \frac{eQ}{\hbar}^2 [4 J_{-22}(2\omega) + J_{-11}(\omega)]$$

i.e. here $x_1 = x_2 = 1$. In the following we drop the subscript "eff" from $(1/T_1)_{\text{eff}}$ and simply write $1/T_1$; we also do this in those cases where a

rigorous $1/T_1$ is not defined.

Now the simplest assumption regarding the time correlation function is an exponential

$$G(t) = \overline{V(0)^2} \exp(-t/\tau_c)$$

τ_c is the correlation time, the quantity we wish to know. The Fourier transform of an exponential is the Lorentz function, that is

$$J(\omega) = \frac{\overline{V(0)^2}}{1 + \omega^2 \tau_c^2} \quad (11)$$

and consequently, with eqn. (9)

$$\frac{1}{T_1} = \frac{1}{15} \left(\frac{eQ}{\hbar} \right)^2 \overline{V(0)^2} \left[4 x_1 \frac{\tau_c}{1 + 4\omega^2 \tau_c^2} + x_2 \frac{\tau_c}{1 + \omega^2 \tau_c^2} \right] \quad (12)$$

If we consider the expression in the square brackets of eqn. (12) as a function of the correlation time τ_c at a given frequency (and for the moment with $x_1 = x_2 = 1$) then we find that this function has a maximum if

$$\omega \tau_c = 0.62 \quad (13)$$

With our computer approximation for $1/T_1$ we found the maximum of the effective $1/T_1$ to be

$$\omega \tau_c = 0.55 \pm 0.02 \quad (14)$$

Thus we see that x_1 and x_2 do not differ very much from unity (the weight of the double resonance frequency term is slightly greater than that of the resonance frequency term).

In the experimental procedure τ_c is varied by the variation of the temperature. The maximum of the relaxation rate is determined. As the resonance frequency is known at the temperature of maximum relaxation rate, τ_c can be determined from eqn. (14).

The nuclear magnetic resonance frequencies of typical nuclei to be considered here are about 10^7 Hz, thus $\omega \approx 10^8 \text{ sec}^{-1}$ and at the relaxation

maximum $\tau_c \approx 10^{-8}$ s. We shall see that this order of magnitude of the correlation time implies that ordinary electrolyte solutions must be considered; only rather concentrated solutions of LiCl, LiBr and LiI can be investigated and probably also some concentrated solutions of magnesium salts. The study of aqueous solutions of lithium halides is presented here. An organic solvent with which the desired study can be made at room temperature is glycerol. Thus, the majority of experiments to be described use solutions of Li and Cs halides in glycerol. temperature is glycerol. Thus, the majority of experiments to be described use solutions of Li and Cs halides in glycerol.

CORRELATION FUNCTIONS FOR THE VARIOUS MODELS

We turn now to the discussion of the correlation times which are to be expected for the various models described briefly above.

DISTORTION OF THE ELECTRON CLOUD OF THE ION DUE TO COLLISIONS WITH SOLVENT MOLECULES

The following expression for the correlation function has been derived previously [12a]:

$$G(t) = \frac{3}{10} \frac{\rho_a}{\rho_b} V_{ra}^2 \exp \left[- \left(\frac{1}{\tau_a} + \frac{1}{\tau_b} + \frac{1}{\tau_c^*} \right) t \right] \quad (15)$$

$$\frac{\rho_a}{\rho_b} = \frac{\tau_a}{\tau_b}, \quad \rho_a + \rho_b = 1 \quad (16)$$

p_a is the probability that a solvent molecule, during a collision, approaches the ion so closely that the electron cloud is distorted. V_{ra} is the electric field gradient in this state of distortion; the subscript a means state a and the subscript r that the force is repulsive. In the state b the ion is no longer distorted; the field gradient vanishes. In both states a and b the solvent molecule is a member of the first solvation shell; p_b is the probability of finding the solvent molecule in state b; τ_a and τ_b are the residence times in state a and b, respectively; $p_b \gg p_a$. τ_c^* is the rotational correlation time of the vector connecting the ionic nucleus with the collision partner.

Now each collision of the ion with a solvent molecule produces a state

a. If Z_1 is the number of collisions per unit time, then $\tau_a \approx Z_1^{-1}$. At room temperature in liquid glycerol the number of collisions between Li^+ and glycerol molecules is approximately $7 \times 10^{11} \text{ s}^{-1}$, that is τ_a should be of the order of 10^{-11} s . The temperature dependence is given by $\tau_a T^{-1/2}$. τ_c^* is of the order of 10^{-8} s ; consequently $1/\tau_a \gg 1/\tau_b, 1/\tau_c^*$. From these values one sees that within the temperature range $400^\circ\text{K} > T > 200^\circ\text{K}$ it should not be possible to find a relaxation maximum corresponding to $\omega\tau_c = 1$ if the collision model is correct.

MODEL USING THE DISTORTION OF THE COMMON ELECTRONIC SYSTEM OF Li^+ AND THE FIRST SOLVATION SHELL

Again, in principle, eqn. (15), (16) may be applied:

$$G(t) = \frac{3}{10} \frac{\rho_b}{\rho_b} V_{sa}^2 \exp \left[- \left(\frac{1}{\tau_a} + \frac{1}{\tau_b} + \frac{1}{\tau_c^*} \right) t \right] \quad (17)$$

however, now the state a is such that one of the solvent molecules has left its tetrahedral position. V_{sa} is the field gradient in this state of distortion. In most cases, when the solvation sphere is in this activated state a, a solvent molecule exchange takes place. Then

$$\tau_a \approx \frac{d}{\bar{v}}$$

where d is the diameter of the solvent molecule and \bar{v} is the mean thermal velocity of the solvent molecule. With $d \approx 5 \text{ \AA}$ we find for glycerol $\tau_c \approx 2 \times 10^{-12} \text{ s}$. This again much shorter than τ_b which is at least of the order of 10^{-8} s at 25°C . We see that, if such a very short-lived distorted state of the solvation sphere were the source of the relaxation process, then in the temperature range $400^\circ\text{K} > T > 200^\circ\text{K}$ a maximum relaxation rate could not occur. We may also rewrite eqn. (17) in the form

$$G(t) = \frac{3}{10} \frac{\rho_b}{\rho_b} V_{sa}^2 \exp \left[- \left[\frac{1}{\tau_b} \left(1 + \frac{\rho_b}{\rho_a} \right) + \frac{1}{\tau_c^*} \right] t \right] \quad (17a)$$

If during the solvent exchange the replacement is slow, that is of diffusive character, then $\rho_a \approx \rho_b$ and the total effective correlation time

$$\frac{1}{\tau_c} = \frac{2}{\tau_b} + \frac{1}{\tau_c^*} \quad (18)$$

is the fact of the order of 10^{-8} s. Of course such a situation can occur only in the event of rather weak solvation. In this case we should expect that the maximum of the relaxation rate can be obtained in the temperature range to be considered here.

THE ELECTROSTATIC MODEL

For ions such as Li^+ the correlation function consists of two parts, G_1 and G_2 . G_1 is due to the first coordination sphere of the ion; G_2 is caused by the remainder of the solution. As has been shown elsewhere [12a] we have

$$G_1 = n_s \frac{2}{15} \left[\frac{9m(1 + \gamma_\infty)P}{r_o^4} \right]^2 \exp(-t/\tau_{s1}) [1 - \exp(-6\lambda)] \quad (19)$$

$$G_2 = \frac{24\pi}{5} \frac{[m(1 + \gamma_\infty)P]^2}{r_*^5} C'_{\text{solv}} \exp(-t/\tau_{s2}) \quad (20)$$

$$\frac{1}{\tau_{s1}} = \frac{1}{\tau_{r1}} + \frac{1}{\tau_{c1}^*} ; \quad \frac{1}{\tau_{s2}} = \frac{1}{\tau_r} + \frac{1}{\tau_{c2}^*} \quad (21)$$

where n_s is the first solvation number of the ion; m the electric dipole moment of the solvent molecule; γ_∞ the Sternheimer factor [10,11]; P the polarization factor [12a]; r_o the distance between relaxing nucleus and point dipole of solvent molecule in the first solvation sphere; r_* the closest distance of approach of solvent dipole towards the central ion outside the first solvation sphere; C'_{solv} the solvent molecule concentration (particles cm^{-3}); λ the parameter describing the degree of distortion of first solvation sphere from cubic symmetry, $\lambda > 0$ (for $\lambda = 0$ we have total quenching of field gradient due to exact symmetry); τ_{r1} the reorientation time of the solvent molecule relative to the vector r_o in the first solvation sphere; τ_{c1}^* the rotational correlation time of the vector r_o connecting the ion with the solvent molecule in the first solvation sphere; τ_r the reorientation time of the solvent molecule relative to the vector r_* outside the first solvation sphere; and τ_{c2}^* the rotational correlation

time of the vector r_* connecting, the ion with a solvent molecule outside the first solvation sphere.* The total correlation function

$$G = G_1 + G_2 \quad (20a)$$

is a sum of two exponentials. Indeed, any time dependence given so far represents only an approximation. Thus, if we introduce one correlation time as an effective quantity in eqn. (11) or eqn. (12) this means that actually this is a suitable average of the time constants given in eqn. (21):

$$\tau_c = \xi_1 \tau_{s1} + \xi_2 \tau_{s2} \quad (22)$$

$$\xi_1 + \xi_2 = 1$$

In the case of very weak solvation we may drop G_1 in eqn. (20a). Now we have to replace r_* in eqn. (20) by r_o . Then a comparison of eqn. (18) and (21) shows that the two correlation time τ_c and τ_{s2} will be of the same order, i.e. approximately 10^{-8} s. Thus, in this particular situation using our present method one cannot distinguish formally between the model of distorted common electronic state of solvation sphere and the electrostatic model. But in the electrostatic theory the absolute value of the relaxation rate can be calculated, whereas in the electrostatic theory the quantity V_{sa} is unknown.

CORRELATION TIME CONNECTED WITH MAGNETIC DIPOLE-DIPOLE INTERACTION

By the statement that the correlation times τ_c and τ_{s2} are about equal we have already postulated that $\tau_c \approx 10^{-8}$ s. However, we wish to confirm this estimate experimentally; so measured the proton relaxation rate of the solvent using the same solution for which the ^7Li relaxation was measured.

The proton relaxation rate is given by the formula [1]:

$$\frac{1}{T_1} = \frac{3}{2} \gamma_I^2 \hbar^2 I(I+1) [J(\omega) + 4J(2\omega)] \quad (23)$$

*) If we write "rotational correlation time" this means "correlation time of spherical harmonics of order two". "The reorientation time" is identical with the correlation time of the spherical harmonics of first order.

Here the spectral density $J(\omega)$ is the Fourier transform of the time correlation function for the magnetic dipole-dipole interaction $g(t)$:

$$J(\omega) = \int_{-\infty}^{+\infty} g(t) \exp(-i\omega t) dt \quad (24)$$

The time correlation function $g(t)$ contains a contribution due to the intramolecular magnetic dipole-dipole interaction and a contribution due to the intermolecular dipole-dipole interaction. For glycerol in the temperature and frequency region of main interest, the intramolecular contribution is about twice as large as the intermolecular one [22a]. The effective correlation time characterizing the decay of the intermolecular correlation function is of the same order of magnitude, but it is longer than that of the intramolecular part. Let us denote the rotational correlation time of the glycerol molecule by τ_2 . In fact τ_2 is not very well defined because the glycerol molecule is not rigid [22,23]. Together with the intermolecular contribution we get an effective correlation time

$$\tau_{2*}' = \tau_2(1 + \epsilon)$$

where ϵ is a quantity of order unity. τ_2 may be expressed in terms of the correlation time of the vector connecting the solvent molecule with the cation and the reorientation time of the solvent molecule relative to this vector. For a solvent molecule residing in the first coordination sphere of the cation we obtain

$$\frac{1}{\tau_{2*}'(1)} = \frac{1}{\tau_{c1}^*} + \frac{1}{\tau_r} (1 + \epsilon)^{-1} \quad (25a)$$

and with eqn. (21)

$$\frac{1}{\tau_{2*}'(2)} = \frac{1}{\tau_{s1}} (1 + \epsilon)^{-1} \quad (25)$$

For a molecule residing in the second coordination sphere we have

$$\frac{1}{\tau_{2*}'(2)} = \left(\frac{1}{\tau_{c2}^*} + \frac{3}{\tau_r} \right) (1 + \epsilon)^{-1} \quad (26a)$$

and with eqn. (21)

$$\frac{1}{\tau_{c*}} (2) = \left(\frac{1}{\tau_{s2}} + \frac{2}{\tau_r} \right) (1 + \epsilon)^{-1} \quad (26)$$

and, finally, for the bulk of the liquid including the surroundings of the anions

$$\frac{1}{\tau_{2*}} (3) = \frac{3}{\tau_r} (1 + \epsilon)^{-1} \quad (27)$$

The quantity $3(1/\tau_r)$ in eqns. (26a) and (27) appears because τ_r and τ_2 are for first-order and second-order spherical harmonics, respectively [4,24a]. In the first solvation sphere, when fast (jumplike) solvent replacement occurs, the factor 3 is absent [1,24a]. The observed dipolar correlation time τ_d is the average of the three correlation times given in eqns. (25), (26), (27):

$$\begin{aligned} \tau_d &= X_1 \tau_{2*}(1) + X_2 \tau_{2*}(2) + X_3 \tau_{2*}(3) \\ &= (1 + \epsilon) \left(X_1 \tau_{s1} + X_2 \frac{\tau_{s2} \tau_r}{\tau_r + 2\tau_{s2}} + X_3 \frac{\tau_r}{3} \right) \\ & \quad X_1 + X_2 + X_3 = 1 \end{aligned} \quad (28)$$

where the X_i are the mole fractions of solvent molecules occurring in the i th region around the central cation. The observed dipolar correlation time according to eqn. (28) has to be compared with the observed quadrupolar correlation time as given in eqn. (22). It will be seen that τ_c and τ_d are not exactly the same but $\tau_c/\tau_d \approx 1$ is to be expected.

The time constant τ_d determines the correlation function [1]

$$g(t) = \left(\frac{2}{15} b^6 \right) \exp(-t/\tau_d) \quad (29)$$

which gives the Fourier transform

$$J_d(\omega) = \frac{4\tau_d}{15b^6} \frac{1}{1 + \omega^2 \tau_d^2} \quad (30)$$

b is the representative intramolecular proton-proton separation in the

glycerol molecule.

Then again, the determination of the maximum of $1/T_1$ when τ_d is varied by temperature change yields τ_d via the relation

$$\omega\tau_d = 0.62 \quad (14a)$$

In this way the effective correlation time of the dipol-dipole interaction can be compared directly with the effective correlation time of the quadrupole interaction.

EXPERIMENTAL SECTION

All measurements were carried out on a pulse spectrometer consisting of a home-made rf-transmitter and receiver. This set of instruments (and two other pulse spectrometers) were connected to a process control computer (Mincal 523, Dietz, Mulheim, F.R.G.). The organization of the computer system is as follows [24b]. A re-entrant steering routine communicates with three teletypes, one for each spectrometer, and assembles the input in a multitasking mode in several control strings which describe the pulse sampling sequences that are necessary for the desired measurements and which are executed by a real time-operating system. The pulse distances within the pulse sequences are generated by the executive by means of a home-built program-controlled clock with a precision of $\pm 1\mu\text{s}$. The pulse lengths are produced via a 12-bit counter with a clock frequency of 10 MHz. The analog signals were read in by an analog-digital converter having a clock frequency of 100 MHz. Not only is improvement of the signal-to-noise ratio accomplished by signal accumulation, but also at the same time improvement has been achieved by integration over certain ranges of the signals recorded. All proton relaxation measurements were standardized so as to give $T_1 = 3.60$ s for pure water at $t = 25^\circ\text{C}$. Correspondingly the ${}^7\text{Li}$ and ${}^{133}\text{Cs}$ relaxation times were compared with experimental results obtained previously in this laboratory. All the reported measurements are given as a function of the temperature. The temperature was controlled by a gas stream through a Dewar probe head which contained the sample. If needed, the gas was cooled by passing through a cooling coil immersed in liquid nitrogen. Within the Dewar probe head the gas was heated to the desired temperature by variation of the electric heating power. The actual temperature was measured in the gas stream by aid of the thermocouple

directly in front of the sample. Temperature constancy achieved was $\pm 0.3^\circ\text{C}$ during the total measuring time. As a check, the temperature was also measured directly behind the sample. With low gas flow rates we observed a temperature difference of up to 3°C between the two measuring points which corresponds to a temperature gradient of 1°cm^{-1} along the sample. As the "temperature of the sample" we took the mean value of these temperatures on the assumption that the temperature varies linearly along the sample. Of course, all samples were carefully freed from oxygen in the usual way.

All salts were of highest purity commercially available (LiCl, LiBr, CsCl, CsBr, suprapur, $\text{LiI}\cdot 2\text{H}_2\text{O}$, Merck AG Darmstadt). The salts were dried at about 120°C before use. The solutions in glycerol were prepared by weighting in the glove box under a dry N_2 atmosphere and in the presence of P_2O_5 [22a]. Normal glycerol, according to the producer (Fluka, Basel), had a water content less than 0.1 wt. %. The fully deuterated glycerol- d_8 was purchased from Merck, Sharp and Dohme, Canada; the producer quotes a deuteron content of better than 97 %. The water content in the glycerol solutions was checked by titration. When the water content was greater than 0.2 %, the sample was heated to 100°C and dry N_2 was bubbled through the liquid for about three hours [22a,b]; then the sample was sealed off. For the solutions in D_2O , $\text{LiI}\cdot 2\text{H}_2\text{O}$ was dissolved in D_2O (99.9 % D_2O content, Merck) and most of the protons were removed by a repeated solvent evaporation and dissolution procedure. The salt concentration was determined by titration.

RESULTS

THE MAGNETIC RELAXATION OF ^7Li IN GLYCEROL

CORRELATION TIMES

The electric quadrupole moment of ^7Li is comparatively small; however, the magnetic moment is relatively large. This leads to the expectation that part of the relaxation is also due to magnetic dipole-dipole interaction [4,14,25-27]. Therefore, with regard to the present problem, as the first step one has to examine what is the contribution of the magnetic dipole-dipole interaction relative to the quadrupole interaction. The procedure is straightforward. One dissolves Li^+ in the fully deuterated solvent. Then the difference of the relaxation rates in the normal compound and in the deuterated one is the relaxation part caused by

magnetic dipole-dipole interaction. The results of the corresponding experiments are shown in Figs. 1 and 2. Two facts may immediately be recognized from these drawings: (i) In both solvents, glycerol and glycerol- d_8 the relaxation rate has a maximum at a certain temperature; (ii) In the range of the maximum which is the only region of interest in this section, the relaxation rates in the two solvents differ very little. Thus the magnetic dipole-dipole contribution is small compared with the quadrupolar part and for simplicity in the present section we shall take the total ${}^7\text{Li}$ relaxation rate in the solvent glycerol as being caused by quadrupole interaction. Then we chose as a weighted average at the maximum of the total ${}^7\text{Li}$ relaxation rate

$$\omega\tau_c = 0.58 \quad (14b)$$

We shall return to the discussion of the detailed features of Figs. 1 and 2 below.

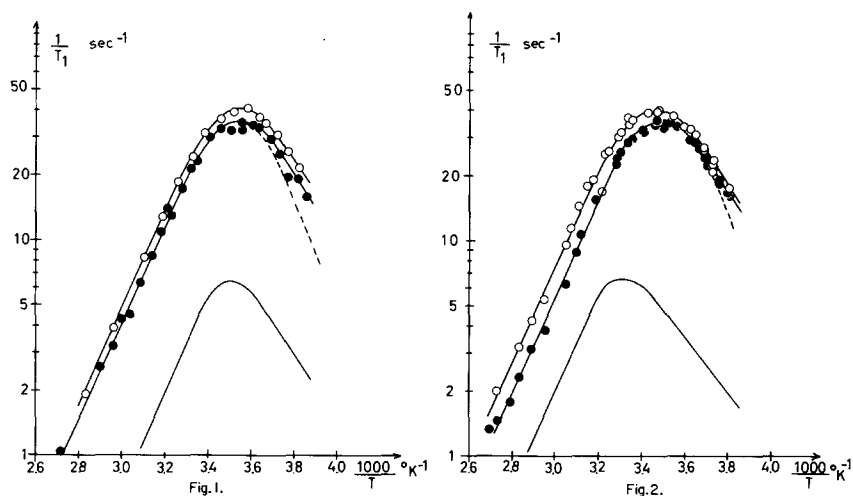


Fig. 1 ${}^7\text{Li}$ relaxation rates in $c^* = 4.9 \bar{m}$ solution of LiBr in glycerol (O) and glycerol- d_8 (●) as a function of the temperature. Concentration is given in the aquamolality scale (moles salt/55.5 moles solvent). Lower smooth curve represents difference between two upper curves.

Fig. 2 ${}^7\text{Li}$ relaxation rates in $c^* = 9.3 \bar{m}$ solutions of LiCl in glycerol (O) and glycerol- d_8 (●) as a function of the temperature. For other details see legend of Fig. 1.

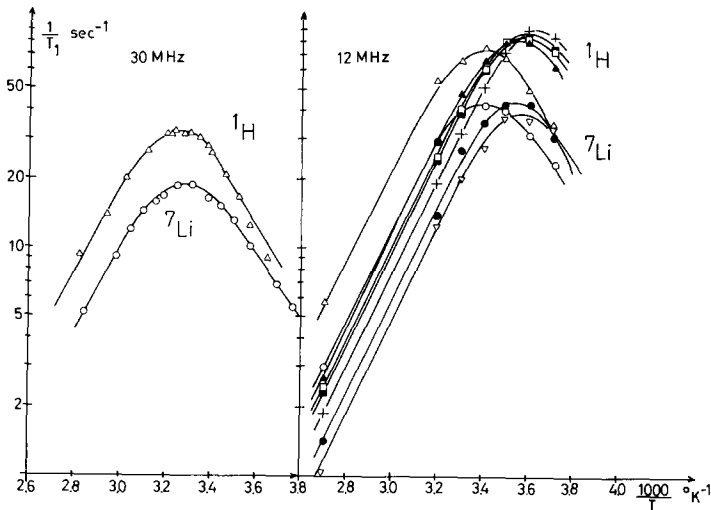


Fig. 3 ${}^7\text{Li}$ relaxation rates (○, $16.4 \bar{m}$; ●, $6.8 \bar{m}$; ▽, $2.9 \bar{m}$) and proton relaxation rates (△, $16.4 \bar{m}$; ▲, $6.8 \bar{m}$; □, $4.9 \bar{m}$; ■, $2.9 \bar{m}$; +, $1 \bar{m}$) of various Li bromide solutions in glycerol as a function of the temperature.

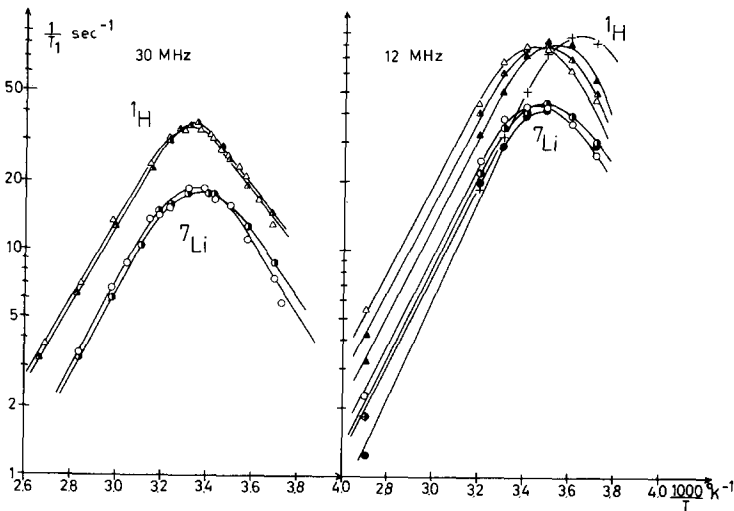


Fig. 4 ${}^7\text{Li}$ relaxation rates (○: $11 \bar{m}$ ○: $9.3 \bar{m}$, ●: $2.9 \bar{m}$) and proton relaxation rates (△: $11 \bar{m}$, ▲: $9.3 \bar{m}$, ▲: $6.9 \bar{m}$ +: $1 \bar{m}$) of various Li chloride solutions in glycerol as a function of the temperature.

In Figs. 3 and 4 we present further ${}^7\text{Li}$ relaxation results together with proton relaxation rates in the same LiCl and LiBr solutions, as a function of the temperature for various concentrations and frequencies. It may be shown that at the maximum the relaxation rates at different frequencies should satisfy the relation

$$\frac{(1/T_1)_{\max}}{(1/T_1)'_{\max}} = \frac{\omega'}{\omega}$$

In our case $\omega'/\omega = 2.5$ and the ratios $(1/T_1)_{\max} / (1/T_1)'_{\max}$ lie between 2.25 and 2.54 which shows the quality of our measurements.

The most important feature of these figures is the observation that in all cases the maxima of the ${}^7\text{Li}$ relaxation and the proton relaxation are very close to each other. At these maxima the correlation times as derived from eqns. (14a), (14b) are

$$\tau_c = 7.7 \times 10^{-9} \text{ s for } {}^7\text{Li}$$

$$\tau_d = 8.2 \times 10^{-9} \text{ s for } {}^1\text{H}$$

when the frequency was $\nu = 12$ MHz, and

$$\tau_c = 3.1 \times 10^{-9} \text{ s for } {}^7\text{Li}$$

$$\tau_d = 3.3 \times 10^{-9} \text{ s for } {}^1\text{H}$$

when the frequency was $\nu = 30$ MHz.

In Fig. 5 we give temperatures at which the relaxation maximum occurs (which is also the temperature at which τ_c and τ_d , respectively, have the values as given above) as a function of the salt concentration. As may be seen from Fig. 5 at all concentrations the temperatures corresponding to a given correlation time are almost the same when the correlation time represents a quadrupolar or a dipolar mechanism. Thus, reversely, at a given temperature, the correlation time of the quadrupole interaction and that of the dipole interaction are very close to each other.

In order to present this result in a yet more distinct way we wish to transform all our correlation times to one single temperature. This can

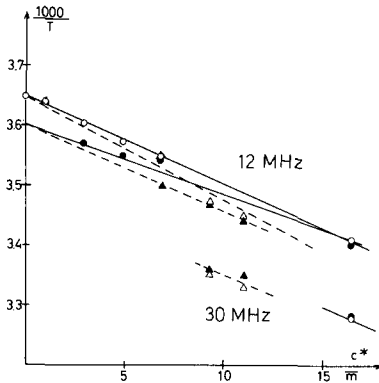


Fig. 5 Temperatures of the maximum relaxation rate as a function of salt concentration for LiBr and LiCl solutions in glycerol. Open symbols, Maxima of proton relaxation rate (O, LiBr; Δ , LiCl) filled symbols, ^7Li relaxation rate (quadrupolar mechanism, \bullet , LiBr; \blacktriangle , LiCl).

only be done approximately. At high temperatures the slope of $1/T_1$ versus $1/T$ should yield directly the activation energy

$$\frac{\tau_c}{\tau_c^0} = \exp(E_a/kT)$$

because, according to eqns. (11), (30)

$$J(\omega) \rightarrow 2\tau_c \overline{V(0)^2}$$

$$J_d(\omega) \rightarrow \frac{4}{15} b^6 \tau_d$$

when $\omega\tau_c$, $\omega\tau_d$ become much less than 1. However, in glycerol E_a is itself a function of the temperature. In a suitable temperature range we find $E_a/R = 4.8 \times 10^3$ for all systems. On the other hand, if we use the $(1/T_1)_{\max}$ values at the two frequencies 12 and 20 MHz, the resulting activation energy is much larger, i.e. $E_a/R = 6.5 - 8.5 \times 10^3$. This is partly due to the fact that the time correlation function is not strictly exponential. The functional form of the time correlation function may vary as the temperature decreases. However, it should also be kept in mind that the experimental error may contribute somewhat to the great difference in activation energies. In the present situation we chose a

mean value of $E_a/R = 6 \times 10^3$ for the transformation of the correlation times to a common temperature.

As the reference temperature we take the temperature at which $(1/T)_{1\max}$ for 12 MHz occurs for pure glycerol [4], that is

$$T = 274 \text{ } ^\circ\text{K}$$

(see also ref. 22). Then

$$\tau_c(c^*) = 7.7 \times 10^{-9} \exp \left[6 \left(3.65 - \frac{1000}{T_{\max}} \right) \right] \quad (31)$$

and

$$\tau_d(c^*) = 8.2 \times 10^{-9} \exp \left[6 \left(3.65 - \frac{1000}{T_{\max}} \right) \right] \quad (32)$$

The result is shown in Fig. 6. It may be clearly seen that the correlation time of the quadrupole interaction is the same as the correlation time of the magnetic dipole-dipole interaction. At low concentrations the quadrupolar correlation time is slightly longer than the dipolar one. This should be so, because the motion around Li^+ is slower than in the bulk and according to eqn. (18) the proton relaxation rate measures the mean correlation time over the entire solution. At higher concentrations then the two correlation times are virtually the same; here in eqn. (28) $X_1 \approx 1$. Actually in eqn. (28) instead of τ_{s1} there should also be a combined expression

$$\frac{\tau_{s1} \tau_r}{\tau_r + k' \tau_{1s}}$$

with $0 < k' < 2$. This would make $\tau_d < \tau_{s1}$, but obviously this effect is just compensated by the factor $1 + \epsilon$.

Summarizing we arrive at the following result: The correlation time of the quadrupole relaxation is about the same as the rotational correlation time of the solvent molecules. Consequently the collision model and the symmetric ion-solvent electronic state model with fast solvent molecule replacement can be excluded.

Since a symmetric common electron state model with slow, diffusive,

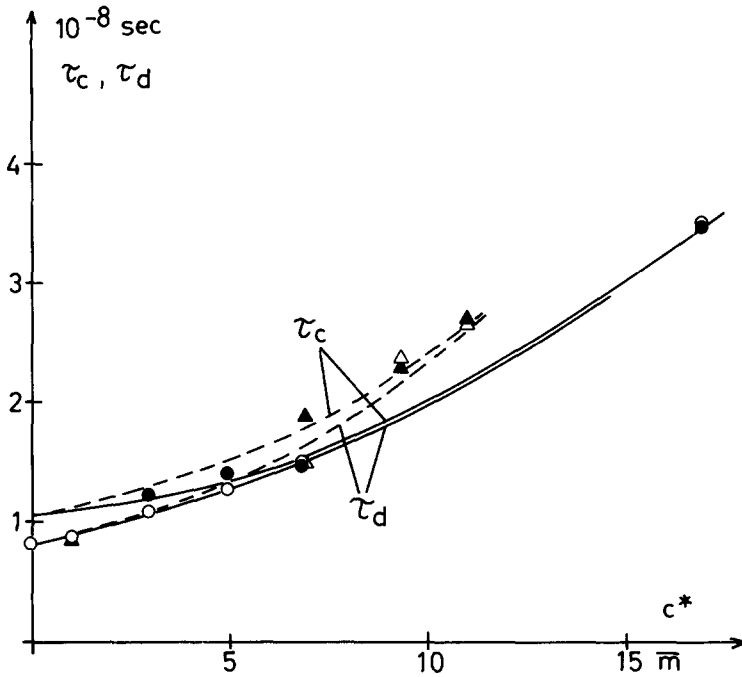


Fig. 6 Correlations time τ_d for magnetic dipole-dipole interaction (opens symbols) and correlation time τ_c for quadrupolar relaxation mechanism (filled symbols) as a function of the salt concentration in solutions of LiBr (O, ●) and LiCl (Δ , \blacktriangle) in glycerol. The temperature is $T = 274$ °K.

solvent replacement should have about the same correlation time as the one corresponding to molecular reorientations this latter possibility cannot strictly be ruled out.

THE ABSOLUTE VALUE OF THE RELAXATION RATE

We have now to investigate whether the absolute value of the quadrupolar part of the total relaxation rate can be accounted for in terms of the electrostatic theory. If this should be so, then this fact would very strongly support the validity of the electrostatic model.

The procedure of calculating the absolute value of the quadrupolar relaxation was as follows: In eqns. (2), (3), (4) we introduced the spectral densities which were obtained from the correlation functions (19), (20), (20a). Next the suitable numerical values were inserted, i.e. the nuclear and electronic quantities

$$Q_{7\text{Li}} = -0.042 \times 10^{-24} \text{ cm}^2$$

$$1 + \gamma_{\infty} = 0.74$$

$$m = 2.67 \text{ D}$$

From the density of glycerol and from a molecular model we estimated the radius of the glycerol molecule: $r_{g1} = 2.8 \text{ \AA}$; $r_{\text{Li}^+} = 0.7 \text{ \AA}$. Then for the distance of the point dipole in the first solvation sphere from the central ion we estimate that $r_o = 3 \text{ \AA}$; for simplicity we set $r_* = r_o$. Furthermore, we set $P = 1$ which implies the assumption that delocalized quenching effects of the field gradient are absent in glycerol solution [11a,15]. As already mentioned, the correlation time in the first solvation sphere of Li^+ differs from that in the bulk; we set

$$\tau_{s1} = b\tau_{s2} = b\tau_d$$

Use of all these quantities in eqns. (3) and (4) gives

$$a_1 = 26.7 \times 10^8 \left\{ \frac{\tau_{s2}}{1 + 4\omega^2\tau_{s2}^2} + 11.7 [1 - \exp(-6\lambda)] \frac{b\tau_{s2}}{1 + 4\omega^2\tau_{s2}^2 b^2} \right\} \text{ s}^{-2}$$

$$\alpha_2 = 26.7 \times 10^8 \left\{ \frac{\tau_{s2}}{1 + \omega^2 \tau_{s2}^2} + 11.7 [1 - \exp(-6\lambda)] \frac{b \tau_{s2}}{1 + \omega^2 \tau_{s2}^2 b^2} \right\} s^{-2} \quad (34)$$

With our value for the activation energy for the reorientational motion of glycerol we set for τ_{s2} in eqns. (33), (34)

$$\tau_{s2} = 1.46 \times 10^{-10} \exp\left[6\left(\frac{1000}{T} - 3.0\right)\right] s$$

However, since the apparent activation energy of the quadrupole relaxation in the range $1000/T < 3.2 \text{ K}^{-1}$ is somewhat smaller, ($E_a/R \approx 5 \times 10^3$) we interpreted this deficiency in activation energy as being due to an increasing symmetry quenching effect as the temperature decreases, which means in terms of eqns. (33), (34) that at lower temperature the parameter λ becomes smaller. By some preliminary fitting attempts we were led to the relation

$$\lambda = \lambda_0 \exp\left(-0.8 \frac{10^3}{T}\right) \quad (35)$$

With these data the motion of the magnetization according to eqn. (2) was computed with a first trial set of the two quantities b and λ_0 . Then by a least mean square fit over a suitable range of time t the motion was approximated by a single exponential. This gives the effective T_1 corresponding to the fact that in all cases only an ordinary exponential decay of $M_z^o - M_z^o$ was observed. This computed $(T_1)_{\text{eff}}$ was compared with the experimental one at all the temperatures investigated. In the next step a new set of the two parameters b and λ_0 was tried, a new $(T_1)_{\text{eff}}$ was found by least mean square fit to the computed motion of the magnetization, the result was again compared with the experimental T_1 and so forth until optimal agreement with the experimental results was achieved using the optimization procedure Bromin [28]. The results of this computation coincides virtually with the solid line drawn through the experimental points of Figs. 1 and 2; only at the lowest temperatures do the computed results differ markedly from the experimental behaviour; here the dashed lines give the computed relaxation rate. The parameters of the best fit are

$$\text{LiBr: } b = 2.1; \lambda_0 = 1.0$$

$$\text{LiCl: } b = 2.7; \lambda_0 = 0.8$$

Are these values acceptable? Clearly the results for b are the values which we know already; to a good approximation they can be taken from Fig. 6. The temperature dependence of the interaction factor via the quenching parameter λ introduces a slight shift of the resulting τ_c . With eqn. (35) our result for λ_0 yields $\lambda = 0.055$ at $T = 273$ °K which means that the field gradient is reduced to 30 % of the value we had in the absence of local symmetry. Of course, it may be considered as a very small deficiency that λ_0 is slightly smaller for the LiCl solution as the high ion concentration should in any case destroy local symmetry around an ion. In much of our recent work, and also in non-aqueous solutions, we used the model of non-localized quenching of the field gradient, that is we put the polarization factor $P \neq 1$. From electrostatic arguments [9,11a,12a], the figure $P = 1/2$ is suggested and usually used. This would give a reduction to 25 % of the field gradient without any correlation effect. One sees that our results for λ is very reasonable and we can safely conclude that the electrostatic model is completely satisfactory.

THE DIRECT ION-ION CONTRIBUTION

From the point of view of a naive electrostatic model one would expect that the ions themselves, being represented by point charges should give a distinct contribution to the quadrupolar relaxation rate. In contrast to this, inspection of Figs. 1 - 4 clearly shows that the absolute value of the relaxation rate at the temperature of the relaxation maximum is virtually a constant quantity and does not increase with the ion concentration. As we see from eqn. (12), if the ions contribute to the mean squared field gradient $\overline{V(0)^2}_1$, such an increase of the relaxation rate must be observable. Indeed, the observation that the ion contribution to the quadrupolar relaxation rate is unmeasurably small is not unique. In aqueous solutions the halide nuclear magnetic relaxation rates in Li^+ solutions show very weak ion-ion effects up to appreciable concentrations [13], whereas the $^7\text{Li}^+$ relaxation in the same solution suffers a strong increase over and above that which is to be expected from correlation time effects [14]. Obviously in glycerol the anions do not approach closely towards the Li^+ ions. Formulas for the calculation of the ion-ion-contribution have been given elsewhere [12b]. A suitable evaluation yields a fairly short correlation time for the ion-ion contribution

($\tau_c' = 1.2 \times 10^{-9}$ s at $T = 286$ °K [29]) and at 300 °K the relaxation contribution is only 1/30 of that due to the glycerol molecules [29]. In Figs. 1 and 2 at the lowest temperature the experimental relaxation rate lies well above the computed one corresponding to the glycerol effect; possibly this additional relaxation effect is due to the ion-ion contribution with its short correlation time (and other fast processes).

THE MAGNETIC DIPOLE-DIPOLE CONTRIBUTION TO THE ${}^7\text{Li}$ RELAXATION RATE

We shall now discuss the difference between the two upper curves in Figs. 1 and 2 which represents the magnetic dipole-dipole contribution to the ${}^7\text{Li}$ relaxation rate. This contribution is caused by the magnetic moments of the solvent protons. As we are concerned with an interaction between different nuclei we should use the formula for "unlike nuclei" [1]

$$\left(\frac{1}{T_1}\right)^{\text{LiH}} = K_{\text{Li}} \left[\frac{1}{3} \frac{\tau_c^*}{1 + (\omega_I - \omega_S)^2 \tau_c^{*2}} + \frac{\tau_c^*}{1 + \omega_I^2 \tau_c^{*2}} + 2 \frac{\tau_c^*}{1 + (\omega_I + \omega_S)^2 \tau_c^{*2}} \right] \quad (36)$$

$$K_{\text{Li}} = \frac{2}{5} \gamma_I^2 \gamma_S^2 \hbar^2 \frac{S(S+1)n_H}{r^6} \quad (36a)$$

where ω_I is the magnetic resonance frequency of ${}^7\text{Li}$ (angular frequency); ω_S magnetic resonance frequency of ${}^1\text{H}$ (angular frequency); S the spin of proton ($S = 1/2$); γ_I, γ_S the gyromagnetic ratios of ${}^7\text{Li}$ and ${}^1\text{H}$, respectively; r the distance between Li^+ and the centre of solvent molecules in the first coordination sphere; and n_H the number of protons in the first coordination sphere ($n_H = 8n_S$ in glycerol). In eqn. (36) the contribution from all the solvent protons outside the first coordination sphere is neglected.

Since $\omega_S = 2.57\omega_I$ we have

$$\left(\frac{1}{T_1}\right)^{\text{LiH}} = K_{\text{Li}} \left[\frac{1}{3} \frac{\tau_c^*}{1 + 2.48\omega_I^2 \tau_c^{*2}} + \frac{\tau_c^*}{1 + \omega_I^2 \tau_c^{*2}} + \frac{2\tau_c^*}{1 + 12.72\omega_I^2 \tau_c^{*2}} \right] \quad (37)$$

and numerical evaluation shows that at the maximum of $(1/T_1)^{\text{LiH}}$ at given frequency

$$\omega_T \tau_c^* = 0.69 \quad (38)$$

and

$$\left(\frac{1}{T_1}\right)_{\text{max}}^{\text{LiH}} = K_{\text{Li}} \frac{0.77}{\omega_T} \quad (39)$$

It can be seen that the curve representing $(1/T_1)^{\text{LiH}}$ for the LiCl solution (Fig. 2) is markedly shifted towards higher temperatures which corresponds to slower motion. This effect is not so strong for the LiBr solution which is of lower concentration (Fig.1.). From Figs. 1 and 2 we find

$$\left(\frac{1}{T_{\text{max}}}\right)_{\text{LiBr}} = 3.52 \times 10^{-3} \text{ } ^\circ\text{K}^{-1}$$

$$\left(\frac{1}{T_{\text{max}}}\right)_{\text{LiCl}} = 3.34 \times 10^{-3} \text{ } ^\circ\text{K}^{-1}$$

According to eqn. (38) at these temperatures $\tau_c^* = 9.2 \times 10^{-9}$ s ($\omega/2\pi = 12$ MHz). When we transform this correlation time to our standard temperature $T = 274$ °K (with $E_a/R = 6 \times 10^3$) we obtain

$$\tau_c^* = 2 \times 10^{-8} \text{ s for } 4.9 \text{ m LiBr solution}$$

$$\tau_c^* = 6 \times 10^{-8} \text{ s for } 9.3 \text{ m LiCl solution}$$

Let us discuss these results. For the situation of independent translational motion of the two pair partners we estimated 12b,30

$$\tau_c^* \approx \frac{r^2}{3D_{g1}}$$

which gives $\tau_c^* = 3 \times 10^{-7}$ s. D_{g1} is the self-diffusion coefficient of glycerol. In the pure liquid $D_{g1} = D_{g1}^0 \approx 2.0 \times 10^{-9}$ cm²/s at 274 °K [31] at high salt concentration $D_{g1} \approx (1/2) D_{g1}^0$, $D_{\text{Li}^+} \approx D_{g1}$. We see that this time is one order of magnitude longer than τ_c^* for the LiBr solution. Thus the model of independent translational motion is not correct; rather

we seem to have short time fluctuating attachment of the small Li^+ ion to the surrounding glycerol molecules. In the more concentrated LiCl solution τ_c^* comes closer to the estimate corresponding to independent translational motion. However, it should be kept in mind that $(1/T_1)^{\text{LiH}}$ is a rather small difference of two larger quantities and as such it has a relatively large experimental error.

Lastly we compute r , the distance between the Li^+ ion and the proton in the first solvation sphere. Introduction of the nuclear quantities in eqn. (36a) yields

$$K_{\text{Li}} = 2.58 \times 10^{-38} \frac{n_{\text{H}}}{r^6} \quad (r \text{ in cm})$$

and with $(1/T_1)_{\text{max}}^{\text{LiH}} = 6.5 \text{ s}^{-1}$ we obtain from eqn. (39) with $n_{\text{H}} = 32$ ($\omega/2\pi = 12 \text{ MHz}$)

$$r = 3.3 \text{ \AA}$$

With $r_g = 2.8 \text{ \AA}$ and $r_{\text{Li}^+} = 0.7 \text{ \AA}$ this result is fully satisfactory.

ION RELAXATION OF ^{133}Cs DISSOLVED IN GLYCEROL

A relaxation mechanism based on distortions of the electron cloud may indeed not be expected to be very efficient for Li^+ because here the number of electrons is exceptionally small. This situation is quite different for Cs^+ with its many electrons and thus, in order to give support for the electrostatic model on a broader basis, we report some experimental results concerning Cs^+ dissolved in glycerol. Fortunately, the quadrupole moment of ^{133}Cs is rather small, so that its magnetic relaxation time can be measured over wide ranges of temperature and in practically all organic solvents - if there are salts of sufficient solubility. This is not so easy or even impossible for other ions with noble gas structure and a high number of electrons. Here under certain conditions the relaxation times become extremely short [15,16,18,19]. ^{133}Cs has another advantage for the present study. Its magnetic moment is small. As a consequence the nuclear magnetic relaxation is exclusively caused by quadrupole interaction. This was already known from aqueous Cs^+ solutions [32]. We checked the correctness of the statement again by performing part of our measurements in fully deuterated glycerol (glycerol- d_8). The results in this solvent were almost the same as in normal glycerol. The corresponding experimental data are

presented in Figs. 7 and 8. This behaviour shows that the dynamical isotope effect which occurs when the ^1H nuclei are replaced by ^2H nuclei is small and may be neglected. With our Li salt studies in glycerol we did not apply any dynamic corrections regarding isotope effects, and we find the justifications for this omission in our ^{133}Cs relaxation results.

However, ^{133}Cs has one appreciable disadvantage for our study. As already mentioned in the introduction, the spin of ^{133}Cs is $I = 7/2$. Hubbard [21] showed that in this case the variation of the magnetization with time should be described by a combination of four exponentials. However, explicit formulas are not available. The only region which can be studied quantitatively is the one for which the frequency dependence of $1/T_1$ disappears; this is the region of "extreme narrowing" [1]; here $\omega\tau_c \ll 1$ which for the present system occurs at temperatures above room temperature. Thus, in the so-called dispersion range, i.e. in the range where $1/T_1$ is frequency dependent, we have to be content with a qualitative evaluation of our experimental results.

The most important information we are seeking is the correlation time for the quadrupolar relaxations. As before, if we find a maximum of the relaxation rate as a function of the correlation time (or as a function of the temperature), then, at the maximum the correlation time is determined by the resonance frequency

$$\omega\tau_c = K''$$

But for ^{133}Cs the constant K'' is not known. All we can do is to estimate $K'' = 0.55$ so that we have the same interconnection between τ_c and ω as for ^7Li , the other quadrupolar nucleus we studied in this work.

All our relaxation results in Cs halide-glycerol solutions are shown in Figs. 7 and 8. It may be seen from these figures that the maxima of the quadrupolar relaxation of ^{133}Cs occur in the same temperature range where they were observed for the ^7Li relaxation; furthermore, at the resonance frequency 12 MHz, the maxima have practically the same position on the temperature scale as the maxima of the proton relaxation rates in the same solution. Again, at these maxima for the 12 MHz curves we have

$$\begin{aligned}\tau_c &\approx 7.3 \times 10^{-9} \text{ s for } \text{Cs}^+ \\ \tau_d &\approx 8.2 \times 10^{-9} \text{ s for } ^1\text{H}\end{aligned}$$

As with the Li^+ solutions the change of the resonance frequency from 12 to 30 MHz shifts the maxima towards lower $1000/T$ values (higher temperature):

$$\tau_c \approx 2.9 \times 10^{-9} \text{ s for } \text{Cs}^+$$

$$\tau_d \approx 3.3 \times 10^{-9} \text{ s for } {}^1\text{H}$$

and the ratios of the maximum relaxation rates at low and high frequency are very close to 2.5 as they should be. The maximum of the ${}^{133}\text{Cs}$ relaxation rate in the 11 m CsCl solution is markedly lower than those of these two other CsCl solutions. This must be due to a systematic error caused by some misadjustment of the apparatus. Here the position of the maximum on the $1000/T$ scale should be taken as the only valid experimental result.

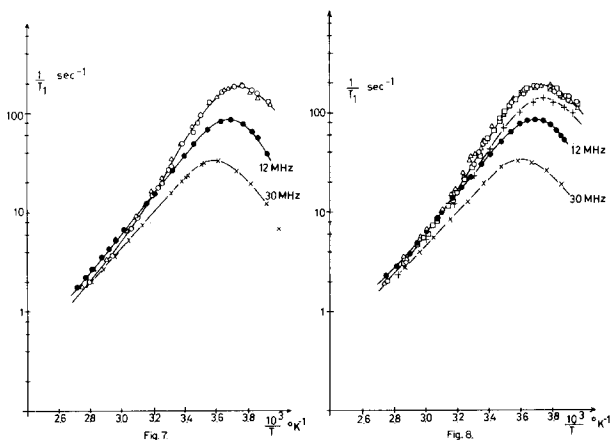


Fig. 7 ${}^{133}\text{Cs}$ relaxation rate of a $c^* = 4.9 \bar{m}$ CsBr solution in glycerol (O) and glycerol- d_8 (Δ) as a function of the temperature (12 MHz). Proton relaxation rate of the same solution at 12 MHz (\bullet) and 30 MHz (x).

Fig. 8 ${}^{133}\text{Cs}$ relaxation rate of various CsCl solutions (O, 4.9 \bar{m} ; \square , 9.0 \bar{m} ; +, 11 \bar{m}) in glycerol and a $c = 4.9 \bar{m}$ CsCl solution in glycerol- d_8 (Δ) as a function of the temperature (12 MHz). Proton relaxation rate of a $c = 9 \bar{m}$ CsCl solution in glycerol at 12 MHz (\bullet) and 30 MHz (x).

Apart from the coincidence of the temperature of the proton and Cs relaxation maxima the most striking feature of Figs. 7 and 8 is the fact that now all these relaxation maxima occur at temperatures lower than 274 $^\circ\text{K}$ ($100/T = 3.65$) which corresponds to the pure solvent glycerol. In contrast to this, for Li-halide solutions the maximum of relaxation occurred at higher temperatures. This means that Cs^+ causes an acceleration of

the molecular motion as compared with pure glycerol. This effect is well known; glycerol is one of the solvents in which the so-called structure breaking effect is produced by large inorganic ions with low charge. One of the most obvious manifestations of the structure breaking effect is the observation that the molecular motion becomes faster than in the neat liquid.

From the temperature of maximum relaxation rate taken from Figs. 7 and 8 we computed the correlation times of the proton and Cs relaxation at a fixed temperature 274°K as a function of the salt concentration using eqns. (31) and (32). The result is given in Fig. 9 and it shows that the correlation time of the quadrupolar interaction is virtually the same as the correlation time of the magnetic dipole-dipole interaction.

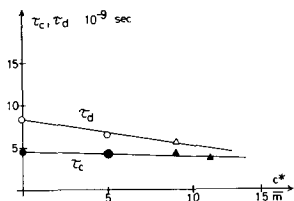


Fig. 9 Correlation time τ_d for magnetic dipole-dipole interaction (open symbols) and correlation time τ_c for quadrupolar relaxation mechanism (filled symbols) as a function of salt concentration in solution of CsBr (O,●) and CsCl (Δ , \blacktriangle) in glycerol. The temperature is $T = 274^\circ\text{K}$.

Next we have to examine whether the absolute value of $1/T_1$ can be calculated satisfactorily in terms of the electrostatic model. At sufficiently high temperature we may apply eq. (12) with $x_1 = x_2 = 1$. Let us consider $1/T_1$ at $T = 333^\circ\text{K}$, i.e. $1000/T = 3.0$. First we use eqn. (19) alone i.e. we set $G_2 = 0$. This corresponds to the FOS (Fully Oriented Solvation) model defined by us previously [16]. The Cs relaxation rate at this temperature is 5 s^{-1} ; the correlation time is $\tau_c = 1.5 \times 10^{-10}\text{ s}$. Then, with the numerical quantities as above and $\gamma_\infty = 110$, $P = 1/2$, $n_s = 6$, $\lambda \rightarrow \infty$ we calculated $r_o = 3.9\text{ \AA}$. This is 15% less than the sum of the ion radius ($= 1.65\text{ \AA}$) and the radius of glycerol assumed to be 2.8 \AA . With the model of a non-orientated solvation sphere [16] (NOS model) we find $r_o = 3.6\text{ \AA}$, still a reasonable value. In the NOS model the strict radial orientation of the solvent electric dipoles in the first coordination sphere is replaced by random orientation. Finally, the fully random distribution (FRD model [16]) which is described by the expression G_2 according to eqn. (20) ($r_* = r_o$) yields $r_o = 2.54\text{ \AA}$ which indeed seems to be too small and which shows that the third model probably is not realistic.

Summarizing, we have shown that for the nuclear magnetic relaxation of $^{133}\text{Cs}^+$ dissolved in glycerol the electrostatic model is also fully satisfactory.

THE MAGNETIC RELAXATION OF ^7Li AND ^{133}Cs DISSOLVED IN WATER

The electrostatic model yielded an acceptable explanation of the quadrupolar relaxation rates in aqueous solution at room temperature. As already indicated, for aqueous solutions at room temperature we are in the domain of "extreme narrowing" conditions, i.e. $\omega\tau_c \ll 1$. We wished to confirm the correctness of the electrostatic model for these solutions also by a measurement of the correlation time governing the relaxation mechanism. Li halides (apart from fluoride) are very soluble in water and the concentrated solutions can be cooled down to temperatures of about -100°C . The temperature control is more difficult at such temperatures. Therefore, our results in the aqueous systems probably are less precise and evaluation of the data has been performed in a more qualitative way.

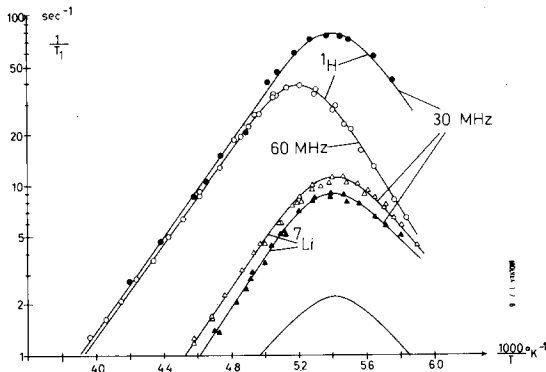


Fig. 10 Proton relaxation rate (\bullet 30 MHz, \circ 60 MHz) and ^7Li relaxation rate (Δ) in a $c^* = 6.2 \text{ m}$ LiI solution in H_2O , ^7Li relaxation rate (\blacktriangle) in a $c^* = 6 \text{ m}$ LiI solution in D_2O ; both quantities are plotted as a function of the temperature. Lower smooth curve: difference of ^7Li relaxation rates in H_2O and in D_2O .

Figure 10 shows the proton relaxation rates in 6.2 m LiI solution at two different resonance frequencies as a function of $1/T$. Furthermore, the ^7Li relaxation rate of the same solution and of a 6.2 m LiI solution in D_2O is given in the figure. The ^7Li relaxation rate in the latter system is

caused by quadrupole interaction. It may be seen that the maximum in the relaxation rate is observable for all systems and that, for a given frequency (here $\nu = 30$ MHz), the maximum due to the quadrupolar relaxation occurs at very much the same temperature at that of the proton relaxation rate*.

All pertinent data we obtained from these measurements are collected in Table 1.

Table 1 SOME RELAXATION AND DYNAMICAL DATA IN AQUEOUS SOLUTION

Nucleus	$\frac{1000}{T}$ ($^{\circ}\text{K}^{-1}$)	τ_c, τ_d (ns)	E_A/R	$\tau_c^* r_{\text{LiH}}$ (ns) (\AA)	$(1/T_1)_{\text{obs}}^{\text{max}}$ in D_2O (s^{-1})	$(1/T_1)_{\text{calc}}^{\text{max}}$ in D_2O FOS model (s^{-1})	$(1/T_1)_{\text{calc}}^{\text{max}}$ in D_2O FRD model (s^{-1})
^1H	5.4 ^{a)}	3.3 ^{b)}	$\approx 3 \times 10^3$	3.7 ^{b)} 2.7 ^{b)}			
^7Li	5.4 ^{a)}	2.9 ^{d)}	$\approx 3 \times 10^3$		9	112	11.2
^1H	4.6 ^{c)}	8.2 ^{d)}	$\approx 4 \times 10^3$				
^7Li	4.6 ^{c)}	7.3 ^{d)}	$\approx 4 \times 10^3$		$\approx 30^{\text{e)}$	280 ^{e)}	28 ^{e)}
^{133}Cs	4.7 ^{c)}	5.0 ^{d)}	$\approx 4 \times 10^3$		86		78 ^{e)}

a) at 30 MHz.

b) at 185 $^{\circ}\text{K}$.

c) at 12 MHz.

d) at 217 $^{\circ}\text{K}$.

e) without relaxation contribution of ions.

We did not apply any correction taking into account dynamic isotope effects.

For instance the curve for the ${}^7\text{Li}$ relaxation rate in D_2O should be shifted somewhat towards lower temperatures because molecular motions would be faster if the solvent molecule were H_2O . This dynamic effect is estimated to cause a shift of 10 - 30 % of the correlation time. A number of similar results regarding Li halide solutions in water may be found elsewhere [34].

Finally, in Fig. 11 we present some data which show that ${}^{133}\text{Cs}$ in aqueous solution has qualitatively the same behaviour as in glycerol and has the same behaviour as the ${}^7\text{Li}$ relaxation (the experimental results are taken from ref. 34). The solution was a concentrated LiCl solution to which CsCl was added; the Cs^+ concentration was 1.1 m . The dynamical data obtained for this solution are also presented in table 1. Again one sees that all relevant correlation times are rather close to each other; the absolute value of the relaxation times can be computed satisfactorily. Concluding, we find that in aqueous solutions as in glycerol the electrostatic model yields a good description of the observed nuclear magnetic relaxation rates.

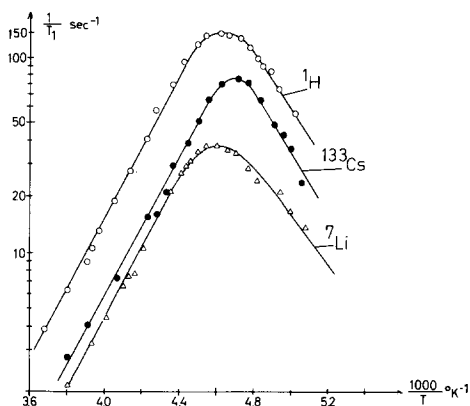


Fig. 11 Proton relaxation rate (O), ${}^{133}\text{Cs}$ relaxation rate (●) and ${}^7\text{Li}$ relaxation rate (Δ) in a solution containing 17.9 m LiCl and 1.1 m CsCl in H_2O as a function of the temperature.

*) When we prepared this paper we learned about a paper by Sutter and Harmon [33] in which the ${}^7\text{Li}$ relaxation in 10 m LiCl solution was studied as a function of the temperature. These authors found a maximum of the relaxatin rate at about the same temperature as we did. However, they reported that the ${}^7\text{Li}$ relaxatin rate in D_2O is greater than in H_2O . This is in contrast to our finding and also in contrast to all other results so far reported in the literature.

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