

Proton Magnetic Relaxation Study of Water Orientation Around I^- and Li^+

A. Geiger¹ and H. G. Hertz¹

Received December 1, 1975; revised January 12, 1976

Proton relaxation time measurements are performed for 6 m aqueous solutions of 7LiI and 6LiI in D_2O containing small amounts of H_2O . The measurements are done at low temperatures and yield maxima of the relaxation rate plotted against $1/T$. From the maxima of the relaxation rates, proton- I^- and proton- Li^+ distances in the first coordination sphere of the ions are determined, and from the knowledge of the ion-water oxygen distance it is shown that for iodide a somewhat broadened H-bonded configuration is valid and that for Li^+ the electric dipole orientation deviates from the radial direction. In order to test the reliability of the method a proton- ^{127}I interaction study is also performed in KI solution in glycerol. The I-H distance obtained is in satisfactory agreement with that found in the aqueous system.

KEY WORDS: Nuclear magnetic relaxation; hydration of ions; solvation of ions; molecular motions in liquids.

1. INTRODUCTION

In a previous communication in this journal one of the present authors⁽¹⁾ gave a preliminary and qualitative description of the possibility of studying the hydration structure—more generally, the solvation structure—of the iodide in solution. The iodide ion is one of the most important structure-breaking ions, not alone in aqueous solution⁽²⁻⁴⁾; therefore, knowledge of its solvation structure is of particular interest. If such an investigation were successful, it would be the first experimental determination of structural details in the strict sense around a structure-breaking ion.

The basic principle of these experiments is the evaluation of proton magnetic relaxation time measurements in iodide solutions with the particular

¹ Institut für Physikalische Chemie und Elektrochemie der Universität Karlsruhe, Karlsruhe, West Germany.

requirement that the vast majority of the solvent molecules contain only deuterons (and other nonmagnetic nuclei) and that there be only very few solvent molecules which carry ordinary hydrogen nuclei, i.e., protons. By this means the proton relaxation mechanism is partly due to the magnetic dipole-dipole interaction with the magnetic moment of the iodide nucleus, and this fact in turn should yield information about the direct neighborhood of the iodide ion. However, it has already been mentioned in that article⁽¹⁾ that difficulties appeared because in the corresponding experimental study a relaxation mechanism, which is as yet unknown, was found in addition to the magnetic dipole-dipole interaction which prevented the numerical evaluation of the measurements. It is the purpose of the present paper to give details of these experiments, with improvement of the measurements and of the procedure of evaluation.

2. FORMULATION OF THE PROBLEM

We say that we know the solvation structure of an ion if we know the ion-solvent pair distribution function. This function, if known, would give the probability density of finding a solvent molecule at a given distance and orientation relative to the center of the (spherical) ion. In the present study the orientational part of the pair distribution function is not the primary subject of the investigation.⁽⁵⁻⁷⁾ In water this limitation is inherent in the nuclear properties of ¹²⁷I and ¹⁷O. Both these nuclei have a rather large electric quadrupole moment. Therefore, our structural information in the system I⁻-H₂O has to be confined to the ion nucleus-water proton radial distribution function. The question of the orientation of the water molecule then can only be treated in a qualitative and indirect way.

Since our method is not an interference method, we cannot hope to get information regarding the total continuous distribution function. What we can only do is construct a model function which is characterized by a small number of parameters. Then, by a finite set of measurements, we can try to determine these parameters. A model function which we have often used is the following⁽⁶⁾:

$$\left. \begin{aligned} \hat{p}(r) &= 0 & \text{for } r < a \\ \hat{p}(r) &= p_0/(r - r_0)^n & \text{for } a \leq r \leq b \\ \hat{p}(r) &= c' \equiv N/V & \text{for } r > b \end{aligned} \right\} \quad (1)$$

Here $\hat{p}(r) dr$ is the probability of finding a solvent proton in dr at a distance r from the center of the ion, a is the closest distance of approach of the

proton toward the center of the ion, b is the radius of the second coordination sphere of the ion, N/V is the number of solvent protons per unit volume, r_0 and n are constants, and n characterizes the steepness of the pair distribution function. The constant p_0 is given by the relation

$$\hat{n}_c = 4\pi \int_0^b \hat{p}(r)r^2 dr \quad (2)$$

where \hat{n}_c is the first coordination number of the ion with respect to the protons. In normal water $\hat{n}_c/2$ is usually defined as the hydration number of the ion. If $n = 0$, then

$$p_0 = c' \quad (3)$$

when n is large, we say that we have a rigid hydration sphere (with respect to the ion-proton separation); in the limit $n \rightarrow 0$ a hydration sphere as a specific structural entity would be entirely absent. We see that our model pair distribution function is characterized by five parameters: a , \hat{n}_c , n , b , r_0 . The quantities b and r_0 are of minor importance and may easily be estimated; thus we are left with three unknowns. Our procedure will be to determine a , the closest distance of approach of the proton toward the iodide ion, from our measurement. We shall give a reasonable estimate for \hat{n}_c ; it turns out that knowledge of \hat{n}_c is not very critical for the determination of a . Indeed, the steepness parameter n must remain undetermined; the uncertainty of the final result due to this fact will be discussed below.

Of course, if we pick out a pair, ion-solvent molecule, then we can choose the solvent molecule as the reference particle instead of the ion. Then $p(r) dr$ is the probability of finding an ion (of the kind considered here) in dr at a distance r relative to the solvent proton considered. We have

$$p(r) = (N_i/N)\hat{p}(r) \quad (4)$$

and

$$n_c = (N_i/N)\hat{n}_c \quad (5)$$

where N_i and N are the total numbers of ions (cations or anions) and solvent protons considered, respectively, and n_c is the first coordination number of the solvent proton with respect to the ion.

The experimental quantity which we will study is the nuclear magnetic relaxation rate $1/T_1$.^(3,8,9) In electrolyte solutions of high fluidity, such as aqueous solutions at room temperature, $(1/T_1)^2$, the proton relaxation rate

caused by the magnetic interaction with the iodide ion, is given by the relations

$$\left(\frac{1}{T_1}\right)^I = \frac{4}{3} \gamma_I^2 \gamma_s^2 \hbar^2 S(S+1) g(n, k, l) \frac{n_c}{a^6} \tau_c + \Delta + \left(\frac{1}{T_1}\right)_{el} \quad (6)$$

$$\Delta = \frac{16}{45} \pi \gamma_I^2 \gamma_s^2 \hbar^2 S(S+1) \frac{c'_1}{bD} = \frac{32}{15} \pi \gamma_I^2 \gamma_s^2 \hbar^2 S(S+1) \frac{c'_1 \tau_t}{b^3}$$

$$\tau_t = \frac{b^2}{6D}$$

if $n > 1$, and

$$\left(\frac{1}{T_1}\right)^I = \frac{16}{45} \pi \gamma_I^2 \gamma_s^2 \hbar^2 S(S+1) \frac{c'_1}{aD} + \left(\frac{1}{T_1}\right)_{el} \quad (7)$$

$$= \frac{32}{15} \pi \gamma_I^2 \gamma_s^2 \hbar^2 S(S+1) \frac{c'_1 \tau_t}{a^3} + \left(\frac{1}{T_1}\right)_{el}$$

$$\tau_t = \frac{a^2}{6D}$$

if $n = 0$;

$$k = r_0/a, \quad l = b/a \quad (7a)$$

$g(n, k, l)$ is defined as

$$\frac{g(n, k, l)}{a^6} = \frac{\int_a^{a(1-k)} [du/u^n (u+ka)^4]}{\int_a^{la} [r^2 dr / (r-ka)^n]}$$

i.e., $g(n, k, l)/a^6$ is proportional to the mean-square magnetic field at the relaxing nucleus. The term $g(n, k, l)$ is a function of the model parameters n, k, l ; $0 < g(n, k, l) \leq 1$, and $g(n, k, l) = 1$ if n is large; further values of the function $g(n, k, l)$ have been given elsewhere.⁽⁵⁾ The rest of the notation is as follows: S is the spin of the ionic nucleus (here ^{127}I , $I = 5/2$), γ_I is the gyromagnetic ratio of the proton, γ_s is the gyromagnetic ratio of the ionic nucleus, τ_c is the rotational correlation time for the vector connecting the relaxing proton with the ion nucleus in the first coordination sphere, $\bar{D} = \frac{1}{2}(D + D_1)$, D is the self-diffusion coefficient of the solvent molecule, D_1 is the self-diffusion coefficient of the ion considered, and $(1/T_1)_{el}$ is the contribution to the proton relaxation rate caused by the electrons of the ion (in this case the iodide ion); thus, the remaining terms on the right side of Eqs. (6) and (7) are the contribution due to the magnetic interaction with the iodide nucleus.

It may be seen from Eqs. (5), (6), and (7) that $(1/T_1)^I$ vanishes as the ion concentration $c'_i = N/V \rightarrow 0$. For the iodine nucleus, $\gamma_s^2 S(S+1)$ is a relatively small quantity; thus, in order to make the relaxation rate $(1/T_1)^I$ observable, c'_i must be great, i.e., of the order of some moles per liter. This has the consequence that studies regarding the solvation properties of the isolated ion are precluded. We can only get information when the concentration is high, and this in turn implies that on the average one of the nearest neighbors of the iodide ion will be a cation. On the other hand, the measurement of $(1/T_1)^I$ at high concentration has the advantage that the rotational correlation time τ_c in Eq. (6) can be estimated⁽¹⁰⁾:

$$\tau'_c \lesssim \tau_c \lesssim 4\tau'_c$$

if n is large, and

$$\tau_c \approx a^2/3D$$

if $n \rightarrow 0$.⁽¹¹⁾

Here τ'_c is the mean rotational correlation time of a solvent molecule in the electrolyte solution at a concentration $\approx 5 \bar{m}$ (\bar{m} is the aquamolality, moles salt per 55.5 moles solvent). As an example, we quote $\tau'_c = 1.8 \cdot 10^{-12}$ sec in aqueous KI solution at 25°C.^(3,12)

The quantity $(1/T_1)_{el}$ in Eqs. (6) and (7) is as yet unknown. Probably the relaxation mechanism is similar to that caused by spin-rotation interaction.⁽⁹⁾ As a consequence, it is to be expected that $(1/T_1)_{el} \rightarrow 0$ as the temperature is lowered sufficiently. Measurements of the temperature dependence of $(1/T_1)^I$ can be done. Extrapolation to low temperatures, if needed, will yield the proton-iodine nucleus magnetic dipole-dipole interaction alone. Such measurements are in progress at this laboratory.

In the present study, however, we followed up another procedure. We performed measurements at low temperature in order to determine the correlation time τ_c directly. The principle of this procedure is as follows: At low temperatures one has to replace the correlation times τ_c in Eq. (6), and τ_t in (6) and (7) by the functions $\phi_r(\omega\tau_c)$ and $\phi_t(\omega\tau_t)$, respectively.^(8,3,13) The quantity ω is the nuclear magnetic resonance frequency. The explicit forms of these functions are given in the Appendix. The term $\phi_r(\omega\tau_c)$ is to be used if the pair distribution function is a very sharp function, i.e., $n \rightarrow 6$ and $g(n, k, l) = 1$. The other function $\phi_t(\omega\tau_c)$ is to be applied in the situation where the pair distribution represents a uniform particle distribution, i.e., $n \rightarrow 0$. In the Appendix we shall present a third function $\phi'_r(\omega\tau_c)$ where the form of the potential is unspecified.

Now all these functions have the property that they go through a maximum when τ_c (or τ_t) is varied and the resonance frequency is kept

constant. At the maximum, τ_o (or τ_v) may be calculated from simple relations of the form

$$\tau_o\omega = k_r, \quad \tau_v\omega = k_t \quad (8)$$

where the constants k_r and k_t ($k_r, k_t \approx 1$) depend on the type of motion considered and the kind of interacting nuclei. Some numerical values of the constants k_r and k_t are given in the Appendix. Then, in the next step, knowing τ_o (τ_v) and the function $\phi_r(\omega\tau_o)$ [$\phi_t(\omega\tau_v)$] at the maximum, the "structural" quantity a occurring in Eqs. (6) and (7) may be determined. This is the final result we wish to obtain. A variation of τ_o (or τ_v) is accomplished by a variation of the temperature.

A lowering of the temperature such that $\omega\tau_o \approx 1$, $\omega\tau_v \approx 1$ for aqueous solutions of iodide is feasible only in few cases. A concentrated solution of LiI in H₂O forms a system for which this can be done. Hence we shall report experimental results for aqueous LiI solutions. This has the disadvantage that Li⁺ is a structure-forming ion and thus, at high concentrations, part of the structure-breaking effect of I⁻ is compensated by the structure-forming effect of Li⁺. On the other hand, this system offers the advantage that magnetic interaction of the proton with the ⁷Li nucleus can also be studied. The proton-Li⁺ nucleus separation in the hydration sphere of Li⁺ is fairly well known, and thus the simultaneous study of the proton-⁷Li interaction may serve as a verification of the results regarding the proton-¹²⁷I interaction.

Another system where iodide also acts as a structure-breaking ion⁽²⁾ is the solution of I⁻ in glycerol. This system has two advantages: (1) The molecular motion in the viscous glycerol is so slow that $\omega\tau_o \approx 1$ already at room temperature. Thus, cryogenic equipment which makes the measurements more difficult is not needed. (2) KI is sufficiently soluble in glycerol so that it is possible to study a system in which the anions and cations are structure breakers (or are at least indifferent). Of course, there is less general interest in the solvation sphere of I⁻ in glycerol than that in the hydration sphere of I⁻; also, due to the many conformations of glycerol the question of orientation of the solvent molecule is more difficult to answer. In spite of this, it seemed to be of interest to perform the corresponding measurements with the solution of KI in glycerol in order to examine the reliability of our method with an entirely different system.

3. EXPERIMENTAL

All measurements were carried out on a pulse spectrometer consisting of a homemade rf transmitter and receiver. This set of instruments (and two

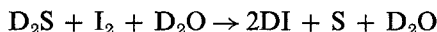
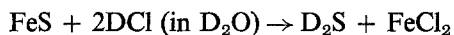
other pulse spectrometers) were connected to a process control computer (Mincal 523, Dietz, Mülheim, F.R.G.). The computer system is set up as follows⁽¹⁴⁾: A reentrant steering routine communicates with three teletypes, one for each spectrometer, and assembles the input in a multitasking mode in several control strings which describe the pulse-sampling sequences necessary for the desired measurements and which are executed by a real-time operating system. The pulse separations in the pulse sequences are generated by the executive by means of a homemade program-controlled clock with a precision of $\pm 1 \mu\text{sec}$. 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 conversion frequency of 100 KHz. Improvement of the signal-to-noise ratio is not only accomplished by signal accumulation but also by integration over certain ranges of the signals recorded. In this way we were able to perform measurements using very weak signals with a signal difference/noise ratio as low as 1/20. All proton relaxation measurements were standardized so as to give $T_1 = 3.60 \text{ sec}$ for pure water at $t = 25^\circ\text{C}$.

All measurements reported are given as a function of the temperature. The temperature control was done in the following way: A gas stream flowed 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 means of a thermocouple directly before the sample. The 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 up to 3°C between the two measuring points, which corresponds to a temperature gradient of $1^\circ/\text{cm}$ along the sample. As the "temperature of the sample" we took the mean value of these temperatures assuming that the temperature varies linearly along the sample. Of course, all samples were carefully freed from oxygen in the usual way.

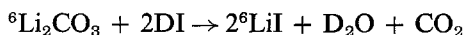
${}^7\text{LiI} \cdot 2\text{H}_2\text{O}$ was of highest purity commercially available (Merck AG Darmstadt). ${}^7\text{LiI} \cdot 2\text{H}_2\text{O}$ was dissolved in D_2O (99.9% D_2O content, Merck), and most of the protons were removed by a repeated solvent evaporation and dissolution procedure. The salt concentration was determined by titration.

Then a calibration sample consisting of 1.5% H_2O and 98.5% D_2O (99.9%) plus a trace of CuCl_2 was prepared. The free induction signal of the calibrated sample was compared with that of the ${}^7\text{LiI}$ solution in D_2O , giving the proton content of the latter solution. The following precautions had to be observed: readjustment of 90° pulses and corrections for variations in the filling height, water concentration, and thickness of sample walls.

The ${}^6\text{LiI}$ solution in D_2O was prepared according to the following reactions⁽¹⁵⁾:



The DI solution was treated with D_3PO_2 in order to remove I_3^- , and D_3PO_3 was prepared by exchange reaction in D_2O :



A small amount of H_2O was added. The salt concentration was determined by titration, and the amount of ${}^1\text{H}$ was determined by signal comparison as above. ${}^6\text{Li}_2\text{CO}_3$ was purchased from Union Carbide Co., U.S.A. KI (suprapur, Merck) was dried at 120°C . The solution in glycerol was prepared by weighing in the presence of P_2O_5 ,⁽¹⁶⁾ 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 better than 97%).

4. RESULTS AND EVALUATION

4.1. LiI in Water

We performed three sets of measurements:

1. The proton relaxation rate of a $c^* = 6\text{ m}$ solution of ${}^7\text{LiI}$ in H_2O as a function of the temperature (m , molality scale). This quantity is denoted as $1/T_1 = 1/T_1(T)$ (T is the temperature in degrees Kelvin). The results are shown in Fig. 1.
2. The proton relaxation rate of a $c^* = 6\text{ m}$ solution of ${}^7\text{LiI}$ in a solvent of composition $(1 - x_1)\text{D}_2\text{O} + \text{H}_2\text{O}x_1$ as a function of the temperature. The quantity x_1 is the mole fraction of H_2O when the solution was prepared. This relaxation rate is denoted $(1/T_1)^{(1)} = (1/T_1)^{(1)}(T)$. We measured $x_1 = 0.011 \pm 0.002$. The results are given in Fig. 2.
3. The proton relaxation rate in a $c^* = 6\text{ m}$ solution of ${}^6\text{LiI}$ in a solvent of composition $(1 - x_2)\text{D}_2\text{O} + x_2\text{H}_2\text{O}$ as a function of the temperature. In this solution the mole fraction of H_2O was $x_2 = 0.022 \pm 0.002$. This relaxation rate is denoted $(1/T_1)^{(2)} = (1/T_1)^{(2)}(T)$. The results are given in Fig. 3.

When we varied the temperature we varied the correlation time τ_c or τ_t . The functional interconnection between τ_c and T is not known precisely. However, we did not need to know this relationship because we only measured

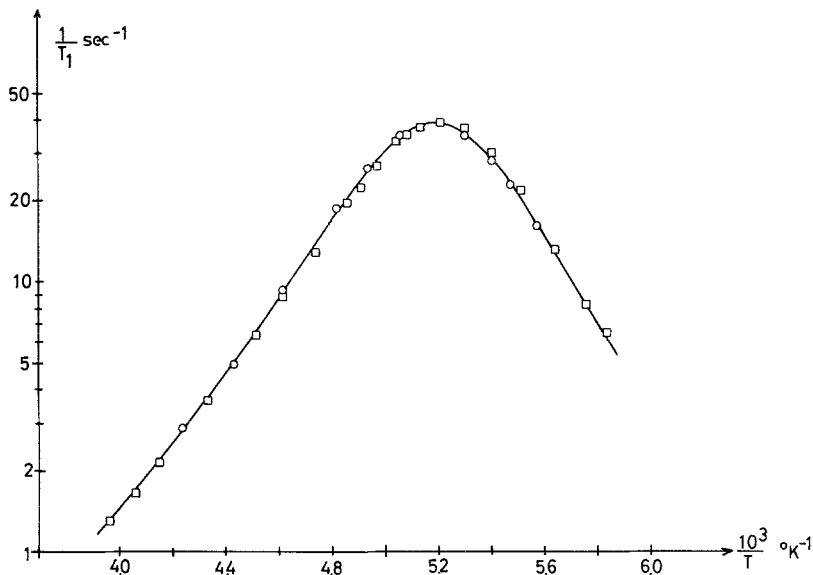


Fig. 1. Proton relaxation rate of a $c^* = 6 \bar{m}$ LiI solution in H_2O as a function of the reciprocal absolute temperature $1/T$ (\bar{m} is the aquamolality scale, moles salt per 55.5 moles solvent). $\nu = 60$ MHz.

the temperature at which the relaxation rates are maximum. Of course, the approximate relation between τ_c and T is

$$\tau_c = \tau_0 e^{E_A/RT} \quad (9)$$

but this relation is not of much value because with our measurements we cannot ascertain that τ_c is a quantity whose significance is the same over the entire temperature range investigated. The quantity we wish to know is the $(1/T_1)^I$ given in Eqs. (6) and (7), but with the correlation times τ_c or τ_t replaced by the functions $\phi_r(\omega\tau_c)$, $\phi_t(\omega\tau_c)$; $(1/T_1)_{\text{el}} = 0$ at low temperatures. The interrelation between the experimental quantities $(1/T_1)$, $(1/T_1)^{(1)}$, and $(1/T_1)^{(2)}$ and the desired one is the following:

$$(1/T_1)^{(1)} = (1/T_1)^{\text{1HD}} + (1/T_1)^I + (1/T_1)^{\text{Li}} \quad (10)$$

$$(1/T_1)^{(2)} = (1/T_1)^{\text{2HD}} + (1/T_1)^I + \varepsilon_2(1/T_1)^{\text{Li}} \quad (11)$$

whence

$$(1/T_1)^I = \{(1/T_1)^{(2)} - (1/T_1)^{\text{2HD}} - \varepsilon_2[(1/T_1)^{(1)} - (1/T_1)^{\text{1HD}}]\}/(1 - \varepsilon_2) \quad (12)$$

$(1/T_1)^{\text{Li}}$ is the relaxation contribution due to the magnetic dipole-dipole interaction between ${}^7\text{Li}$ and the proton, and ε_2 is the ratio of the squares of the magnetic moments of ${}^6\text{Li}$ and ${}^7\text{Li}$:

$$\varepsilon_2 = \gamma_{{}^6\text{Li}}^2 I_6(I_6 + 1) / \gamma_{{}^7\text{Li}}^2 I_7(I_7 + 1) = 0.076$$

$(1/T_1)^{\text{iHD}}$, $i = 1, 2$, is the contribution to $(1/T_1)^{\text{H}}$, $i = 1, 2$, due to the solvent protons and deuterons in the solution. We have

$$(1/T_1)^{\text{iHD}} = (1/T_1)[\epsilon_1 + (1 - \epsilon_1)x_i] \quad i = 1, 2 \quad (13)$$

with

$$\epsilon_1 = \frac{2}{3} \frac{\gamma_D^2}{\gamma_H^2} \frac{I_D(I_D + 1)}{I(I + 1)} = 0.041 \quad (14)$$

$\frac{2}{3}\epsilon_1$ is the ratio of the squares of the magnetic moments of the deuteron and proton, γ_D is the gyromagnetic ratio of the deuteron, and I_D is the spin of the deuteron ($I_D = 1$). The factor $\frac{2}{3}$ is due to the fact that interaction between like spins and unlike spins are compared.⁽⁸⁾

It should be mentioned that Eq. (14) is not quite exact. This is so because for like spins (proton-proton) another linear combination of the spectral densities⁽⁸⁾ is valid as for unlike spins (see also Appendix). This effect would shift the maximum of $(1/T_1)^{\text{iHD}}$, $i = 1, 2$, toward lower temperatures. On the other hand, there is a dynamic isotope effect in D_2O solution which shifts the maximum toward higher temperature. Within the limits of our experimental error these two tendencies compensate each other.

The quantity $(1/T_1)^{\text{iHD}}$ determined from Eq. (13) with the experimental $1/T_1$ and $x_1 = 0.011$ is shown in Fig. 2 as the smooth curve below the

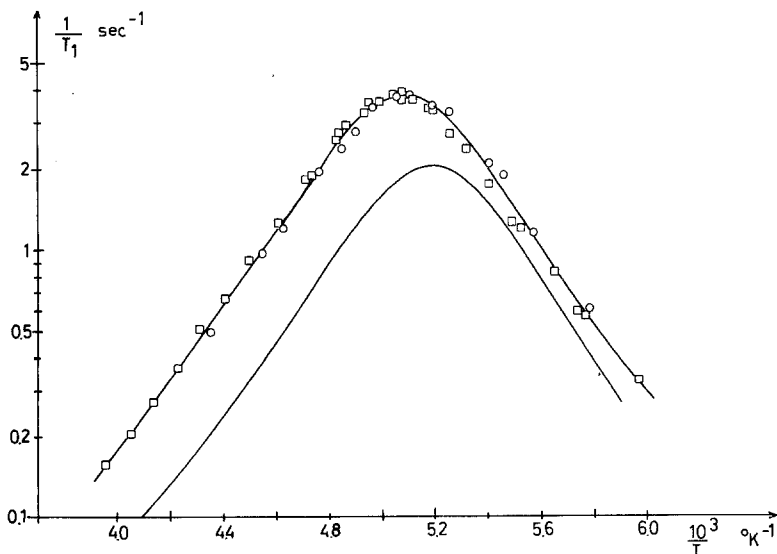


Fig. 2. Experimental curve: proton relaxation rate of a $c^* = 6 \bar{m}^7 \text{LiI}$ solution containing the solvent 1.1% H_2O + 98.9% D_2O . Lower curve: relaxation rate of Fig. 1 multiplied by a factor 0.0525 (see text). $\nu = 60 \text{ MHz}$.

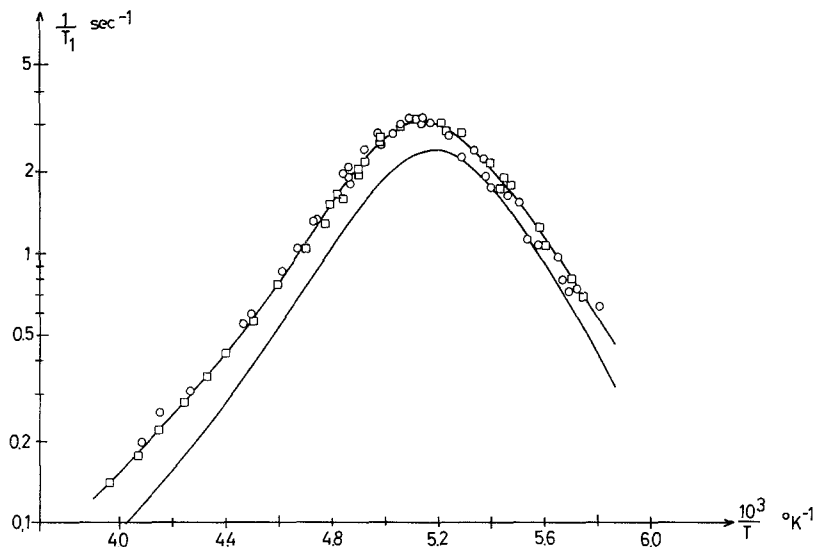


Fig. 3. Experimental curve: proton relaxation rate of a $c^* = 6 \bar{m}$ ${}^6\text{LiI}$ solution containing the solvent 2.2% $\text{H}_2\text{O} + 98.8\%$ D_2O . Lower curve: relaxation rate of Fig. 1 multiplied by a factor 0.062 (see text). $\nu = 60$ MHz.

experimental one for $(1/T_1)^{(1)}$. In the same way, $(1/T_1)^{2\text{HD}}$ is calculated with $x_2 = 0.022$ and is shown in Fig. 3. From Fig. 3, $(1/T_1)^2 - (1/T_1)^{2\text{HD}}$ is determined, and likewise from Fig. 2, $(1/T_1)^1 - (1/T_1)^{1\text{HD}}$ is determined; this quantity is shown as the dashed curve in Fig. 4. Then $(1/T_1)^1$ is calculated from Eq. (12), and the result is presented as curve I in Fig. 4. Finally, knowing $(1/T_1)^1$, we obtain $(1/T_1)^{\text{Li}}$ from Eq. (10) and present it as curve II in Fig. 4.

4.1.1. Hydration Data for I^-

As can be seen from Fig. 4, the maximum value of the proton-iodine contribution $(1/T_1)^{\text{I}}$ is

$$(1/T_1)^{\text{I}} = 0.72 \pm 0.25 \text{ sec}^{-1}$$

The experimental error of the low-proton-concentration data in Fig. 3 is estimated to be $\pm 5\%$, the experimental error of the data in Fig. 1 is $\pm 3\%$, and the uncertainty due to proton content is also $\pm 3\%$. The maximum occurs at 197.5°K. We worked with a resonance frequency $\omega/2\pi = 60$ MHz; thus, with the relation given in the Appendix [Eq. (A5)], we find

$$\tau_0 = 2.5 \cdot 10^{-9} \text{ sec at } 197^\circ\text{K}$$

According to Fig. 1, the maximum of $1/T_1$ occurs at 193°K. The quantity $1/T_1$ corresponds to a relaxation mechanism involving interactions between

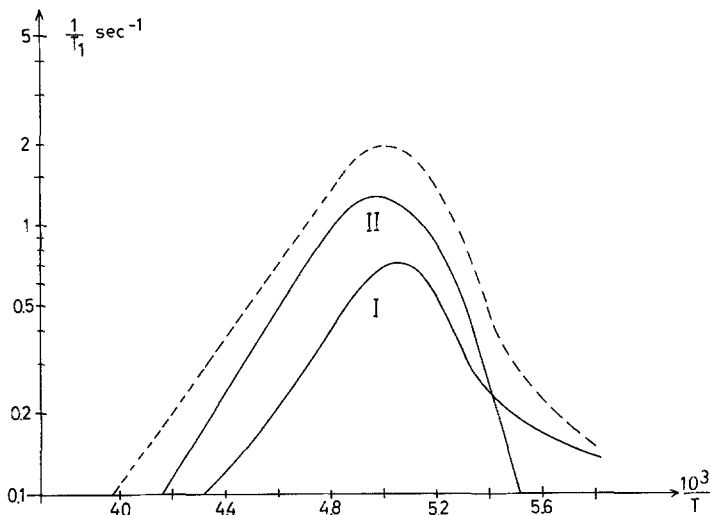


Fig. 4. Dashed curve: Difference between experimental curve and calculated curve as shown in Fig. 2. Curve I: $^{127}\text{I}-^1\text{H}$ contribution to the proton relaxation rate in a $c^* = 6 \bar{m}$ aqueous LiI solution. Curve II: $^7\text{Li}-^1\text{H}$ contribution to the proton relaxation rate in the same solution.

equal spins (proton-proton). Thus, according to Eq. (A26) we have $\tau_c^{\text{H}_2\text{O}} = 1.6 \cdot 10^{-9}$ sec at 193°K . This correlation time partly corresponds to the intramolecular vector and partly to the intermolecular vector. Using the approximation in Eq. (9) with $E_A = 6$ kcal/mole, we obtain $\tau_c = 3.5 \cdot 10^{-9}$ sec for the vector proton-iodide at $T = 193^\circ\text{K}$, i.e., this vector reorients more slowly than the mean proton-proton vector.

Next, in order to evaluate $(1/T_1)^{\text{I}}$ according to Eq. (6), we calculate the translational part of the relaxation rate, Δ . We need b , the radius of the second coordination sphere of I^- with respect to the water protons. The I^- -O distance in the second hydration sphere is $\approx 5.2 \text{ \AA}$.⁽¹⁷⁾ From this we estimate $b = 4 \text{ \AA}$. Then, by means of Eqs. (A11)-(A14) we find $\Delta = 0.05 \text{ sec}^{-1}$, which gives as the first-coordination-sphere contribution: $(1/T_1)^{\text{I}} - \Delta = 0.67 \pm 0.25 \text{ sec}^{-1}$. For the evaluation of this quantity, we consider two models: Model I assumes a symmetric arrangement of the water molecules in the first hydration sphere. The electric dipole moment of H_2O has the radial direction. In this situation we have

$$\hat{n}_c = 2n_h$$

where n_h is the (first) hydration number of I^- , and according to Eq. (5)

$$n_c = \hat{n}_c(N_i/111) = 2n_h(N_i/111) = n_h c^*$$

where $c^* = N_i/55.5$ is the ion concentration in the molality scale. Model II

assumes an asymmetric or hydrogen-bonded configuration. One of the protons is located on the vector connecting I^- with O. In this situation we have

$$\begin{aligned}\hat{n} &= n_c \\ n_c &= \hat{n}(N_l/111) = (n_h/2)c^*\end{aligned}$$

and the second proton of the water molecule must be counted as belonging to the second coordination sphere. We set $n_h = 8$, which is in agreement with x-ray-diffraction data.⁽¹⁷⁾ Then, using Eqs. (A2) and (A6), we obtain

$$\text{Model I: } a = 2.60^{+0.21}_{-0.14} \text{ \AA}$$

$$\text{Model II: } a = 2.47^{+0.18}_{-0.13} \text{ \AA}$$

In calculating the parameter a for model II we have applied a small correction (0.04 sec^{-1}) taking account of the second water proton which points away from the iodide ion.

Finally, we examine what we can denote as model III: a uniform distribution of the water protons around the iodide ion, i.e., no hydration sphere of I^- in the usual sense. Application of Eq. (A17) yields $a = 1.7^{+0.3}_{-0.2} \text{ \AA}$, which clearly is not realistic. We may multiply the purely translational relaxation formula equation (7) by a factor 2 [($1/T_1$)_{el} = 0] in order to take into account a certain crowding of water molecules around I^- . This gives $a = 2.1^{+0.4}_{-0.2} \text{ \AA}$, a distance which is still too small. Thus, model III may be ruled out, and we have to decide between models I and II. To do this, we calculate the I^- -O separation R_{I^-O} from our I^- - 1H distances. Model I gives $R_{I^-O} = 3.25 \text{ \AA}$, and Model II gives $R_{I^-O} = 3.43 \text{ \AA}$ ($r_{OH} = 0.96 \text{ \AA}$). From the sum of the ion and water radii one expects $R_{I^-O} = 3.60 \text{ \AA}$.⁽¹⁷⁾ This leads us to the result that the asymmetrical hydration water configuration is the real one. Very likely, the translational or uniform contribution Δ has been underestimated by Eq. (6), and increasing Δ somewhat would lead to a slightly greater I^- -O distance. Our findings are in agreement with Narten's interpretation of his x-ray-diffraction data on concentrated NH_4I solution that some water hydrogen lie between I^- and O, having a distance around 2.6 \AA from I^- .⁽²⁰⁾ We may note here that the asymmetrical anion-water configuration has also been found for⁽⁵⁾ F^- and Cl^- .^(20a)

So far the I^- - 1H pair distribution function was assumed to be a δ function. In the next section an argument will be given which shows that a δ function is not a realistic model. Moreover, from our knowledge that I^- is a structure-breaking ion, it follows that the distribution function must be spread over a wider range. This leads us to the conclusion that the Gaussian form of the correlation function [Eq. (A18)], is a better description of the real situation. Then, according to Eq. (A21'), our experimental $(1/T_1)_{\max}K$ is smaller by a factor 0.65 when compared with Eq. (A6). Furthermore, if we

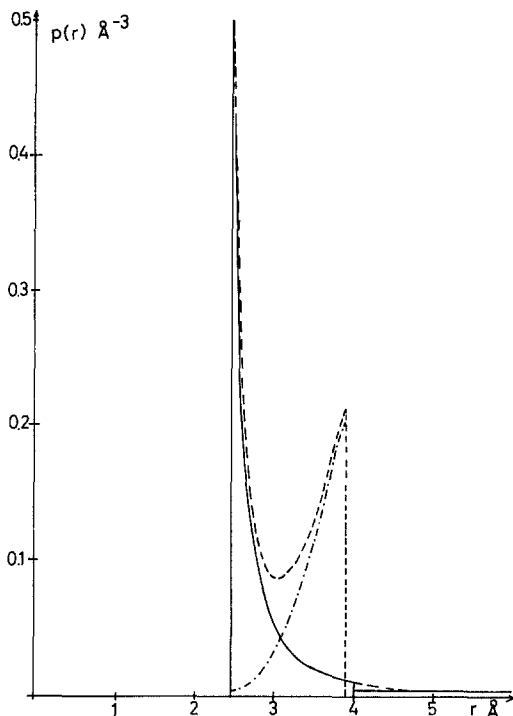


Fig. 5. Model radial-pair-distribution function between I^- and the water protons in a $6 \text{ } m$ LiI solution at 197°K . The dashed part of the curve is not quantitatively connected with the experimental result and is only given in an approximate form.

leave our result for a unchanged, we have to apply Eq. (A21), which yields $g(n, k, l) = 0.65$. With $b = 4 \text{ \AA}$ and $a = 2.6 \text{ \AA}$, we have $l = 1.6$ [see Eq. (7a)]. From the numerical knowledge of $g(n, k, l)^{(5)}$ and putting $k = 0.9$, we find $n \approx 2$. The corresponding model pair distribution function is shown in Fig. 5. As already mentioned, the second coordination sphere of iodide with respect to the solvent protons is due to the "second water proton" which points away from the ion. The small relaxation contribution of this second proton was only taken into account qualitatively. One sees that the probability density of finding a water proton in the exact hydrogen bond position is only about $\frac{1}{2}$. Now, according to Eq. (A20), the correlation time is redefined, and we have $\tau_c = 1.74 \cdot 10^{-9}$ sec at 197°K .

The line width of the ^{127}I magnetic resonance in $6 \text{ } m$ LiI solution was measured down to a temperature of 247°K . Here the relaxation time was $(T_1)_{127^\circ\text{I}} = 1.33 \cdot 10^{-5}$ sec. Linear extrapolation on a semilogarithmic plot to $1000/T = 5.0$ ($T = 200^\circ\text{K}$) yielded $(T_1)_{127^\circ\text{I}} = 4.2 \cdot 10^{-7}$ sec. This is much

longer than the correlation time τ_c ; thus, the ^{127}I relaxation time cannot serve as the correlation time for the $^{127}\text{I}-^1\text{H}$ interaction.²

4.1.2. The Hydration of Li^+

The maximum of the $^1\text{H}-^7\text{Li}$ relaxation contribution occurs at a temperature of 201°K. As can be seen from Fig. 4, at this maximum

$$(1/T_1)_{\text{max}} = 1.26 \pm 0.30 \text{ sec}^{-1}$$

The estimate of the experimental error is the same as given above.

We are in a position to compare this result with that part of the relaxation rate of ^7Li (as Li^+) in aqueous solution which is caused by the magnetic dipole-dipole interaction with the water protons. Corresponding measurements have been performed, although those investigations were done with another objective.^(18,19) The mean value of the maximum relaxation rate obtained in several aqueous Li halide solutions was $(1/T_1)_{\text{max}} = 3.0 \pm 0.3 \text{ sec}^{-1}$ at 30 MHz (after a suitable correction due to the dynamical isotope effect). Hence, according to Eq. (A2), we have

$$\frac{K_{\text{HLi}}}{K_{\text{LiH}}} = \frac{S_{^7\text{Li}}(S_{^7\text{Li}} + 1)n_c}{S_{^1\text{H}}(S_{^1\text{H}} + 1)\tilde{n}_c} = 5 \cdot \frac{c^*}{2 \cdot 55.5} = 0.27$$

($c^* = 6 m$). With $\omega_{^1\text{H}} = 2\omega_{^7\text{Li}}$ we expect [see Eqs. (A8), (A10) and (A23), (A25)]:

$$\frac{(1/T_1)_{\text{max}}^{\text{H} \leftrightarrow \text{Li}}}{(1/T_1)_{\text{max}}^{\text{Li} \leftrightarrow \text{H}}} = 0.27 \cdot \frac{0.43}{0.23} \cdot \frac{1}{2} = 0.25$$

or

$$\frac{(1/T_1)_{\text{max}}^{\text{H} \leftrightarrow \text{Li}}}{(1/T_1)_{\text{max}}^{\text{Li} \leftrightarrow \text{H}}} = 0.27 \cdot \frac{0.66}{0.28} \cdot \frac{1}{2} = 0.32$$

when we assume an exponential or Gaussian function as the correlation function, respectively. This gives the expected maximum proton relaxation rates 0.75 ± 0.075 and $0.96 \pm 0.09 \text{ sec}^{-1}$ in the first and second cases, respectively. The latter value is closer to our present result, and therefore we shall use the Gaussian time correlation function Eq. (A18) for the evaluation of the experimental result.

The correlation time at the relaxation maximum of the vector connecting Li^+ with the proton in the first coordination sphere is [see Eq. (A22)]: $\tau_c = 1.70 \cdot 10^{-9} \text{ sec}$ (201°K). Let us compare this figure with the corresponding one for the vector I^{-1}H . We transform this number to the temperature of the maximum of the $\text{H}-^{127}\text{I}$ relaxation rate, i.e., $T = 201^\circ\text{K} \rightarrow T = 197^\circ\text{K}$.

² We wish to thank Mr. H. Weingärtner for performing these measurements.

By means of Eq. (9) with $E/R = 3 \cdot 10^3$ we find $\tau_c = 2.2 \cdot 10^9$ sec. This time is longer than that found for the motion of the vector $I^- - {}^1H$, and it is longer in spite of the fact that the first hydration sphere of I^- is much larger than that of Li^+ . We see that even at the high concentration of 6 *m* the effects of structure forming and structure breaking in their dynamical manifestations are still detectable. But if there is fast motion in the neighborhood of the iodide ion, there must also be a flatter effective potential well. This fact has already been taken into account in the preceding section when we replaced the δ function by a pair-distribution function of greater width.

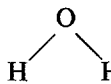
Further evaluation of the 1H - 7Li relaxation data also has to be done by applying Eq. (6) with the modifications as explained for the 1H - ${}^{127}I$ interaction. We set $b = 4 \text{ \AA}$; then we set $\Delta = 0.1 \text{ sec}^{-1}$, whereby we have multiplied the theoretical expression for Δ by a factor 2. This gives $(1/T_1)^{(1)} - \Delta = 1.16 \pm 0.3 \text{ sec}^{-1}$, and with $\gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) = 3.26 \cdot 10^{-37} \text{ cm}^6 \text{ sec}^{-2}$, we find from Eqs. (A2) and (A20)

$$a = 2.56 \pm 0.14 \text{ \AA}$$

This Li^+ -proton distance is smaller than expected if the electric dipole moment of H_2O has a radial direction (in this case we should have $a = 2.76 \text{ \AA}$). If we denote the angle between the dipole moment and the negative radial direction as ϑ , we obtain the result

$$\vartheta = 122.5 \pm 1.5$$

($\vartheta = 180^\circ$ corresponds to a radial orientation of dipoles). We have considered only that configuration in which Li^+ lies in a plane perpendicular to the



H plane and containing the bisector. Here the Li^+ -O distance was taken to be 2.08 \AA . Our result is in satisfactory agreement with x-ray and neutron-diffraction data reported by Narten, Vaslow, and Levy.^(20a) These authors found a LiD separation of 2.43 \AA in a 7 *m* LiCl solution. Quantum-chemical calculations show that the radial orientation of the dipole moment has the lowest energy.⁽²¹⁻²³⁾ We feel that the present investigation should not be regarded as a means of examining the correctness of these theoretical predictions. In our system, due to the high ion concentration, certainly each potential is strongly distorted.

4.2. Solvation of I^- in Glycerol

In Fig. 6 the experimental points shown as triangles give the proton relaxation rate in glycerol- d_8 with a small but unknown admixture of proton-containing glycerol. Furthermore, the proton relaxation rate in a $c^* = 3 \bar{m}$ KI

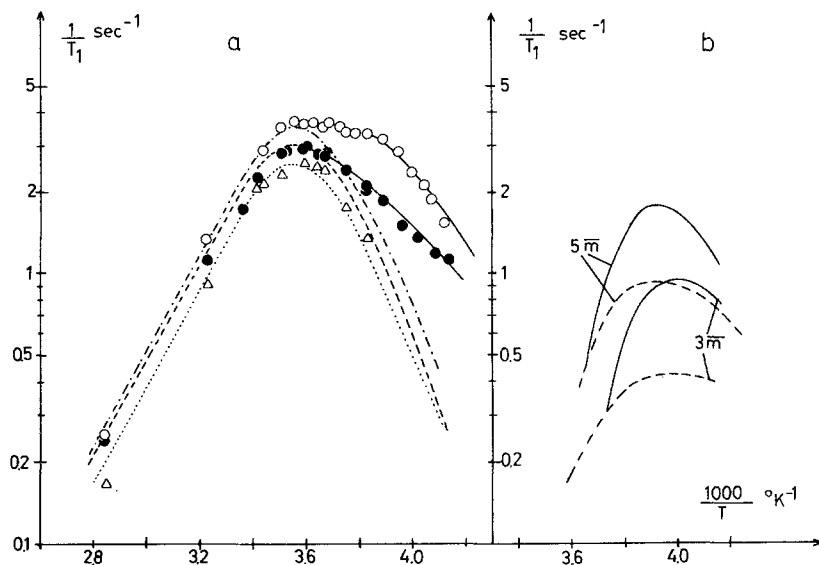


Fig. 6. (a) Δ , proton relaxation rate of glycerol- d_8 with a proton content of 3.2%; \bullet , proton relaxation rate of a $c^* = 3\bar{m}$ solution of KI in glycerol- d_8 with a proton content of 4.8%; \circ , proton relaxation rate of a $c^* = 5\bar{m}$ solution of KI in glycerol- d_8 with a proton content of 6.4%. The dotted curve is for the proton relaxation rate of a $3\bar{m}$ KI solution in normal glycerol, multiplied by a factor 0.077. The dashed curve is for the same relaxation rate, multiplied, however, by a factor 0.087. The dot-dashed curve is for the proton relaxation rate of a $c^* = 5\bar{m}$ KI solution in normal glycerol multiplied by a factor 0.1022. $\nu = 30$ MHz. (b) ^{127}I - ^1H contribution to proton relaxation in $c^* = 3\bar{m}$ and $c^* = 5\bar{m}$ solutions of KI in glycerol. Full curves, $\nu = 30$ MHz; dashed curves, $\nu = 60$ MHz.

solution in normal glycerol was measured as a function of the temperature (\bar{m} is the aquamolality, moles salt per 55.5 moles of glycerol). Let us denote this relaxation rate as $(1/T_1)_0$. Then in the equation ,

$$(1/T_1) = (1/T_1)_0 [e + (1 - e)x]$$

x was determined such that the maximum value of $1/T_1$ is equal to the maximum of the rate as given by the triangles. We obtained $x = 0.032$; thus, the proton content of glycerol- d_8 was 3.2%. Next the following two solutions were prepared: $c^* = 3\bar{m}$ KI in glycerol- d_8 and $c^* = 5\bar{m}$ KI in glycerol- d_8 . Comparison of the signal strength of the free induction signal of these two solutions with the glycerol- d_8 sample containing 3.2% protons showed that the relative proton content was 4.0:3.0:2.0. Consequently, the $c^* = 5\bar{m}$ and $3\bar{m}$ solutions had a proton content of 6.4 and 4.8%, respectively.

The proton relaxation rates of the two glycerol- d_8 -KI solutions were measured. The results are given as the filled circles ($3\bar{m}$) and open circles

($5\bar{m}$) in Fig. 6. The proton relaxation rate $(1/T_1)'_0$ of a $5\bar{m}$ KI in normal glycerol was measured. Then the relaxation rates

$$(1/T_1)_{3\bar{m}} = (1/T_1)'_0[\varepsilon + (1 - \varepsilon)4.8]$$

and

$$(1/T_1)_{5\bar{m}} = (1/T_1)'_0[\varepsilon + (1 - \varepsilon)6.4]$$

were calculated and plotted as the dashed and dot-dashed curves in Fig. 6. These quantities represent the proton-proton and proton-deuteron contribution to the relaxation rate. The differences between the experimental curves given as circles and these calculated curves is the ^{127}I -proton contribution to the relaxation rate; the corresponding curves are shown in Fig. 6b. It can be directly seen from Fig. 6a and b that the maximum of the ^{127}I - ^1H contribution occurs at lower temperatures than the contribution due to hydrogen-hydrogen interaction, i.e., the motion of the ^{127}I - ^1H vector is faster than the mean proton-proton vector in glycerol. This is distinctly different from the behavior we found in the aqueous solution of LiI , where the proton-iodine vector moved more slowly. Most probably, this is also true in the absence of the structure-forming ions Li^+ , i.e., in aqueous KI solution. In pure glycerol at 30 MHz the maximum of relaxation occurs at $1000/T = 3.52^\circ\text{K}^{-1(16)}$ ($t = 11.1^\circ\text{C}$) [our glycerol- d_3 measurements, Δ in Fig. 6a, yield a maximum at slightly lower temperatures (experimental error?)]. Thus, from Eq. (A26) $\tau_c^- = 3.3 \cdot 10^{-9}$ sec.

A previous study of the structure-breaking effect of I^- in glycerol⁽²⁴⁾ showed that τ_c^- , the mean correlation time of glycerol in the first solvation sphere of I^- , should be $\tau_c^- = 0.8 \tau_c^0$. However, using an activation energy $E_A/R = 3 \cdot 10^3$, when we convert the correlation time of the ^{127}I - ^1H vector found at the temperature of relaxation maximum (-17.4°C) to 11.1°C we find $\tau_c(\text{I-H}) = 0.46\tau_c^0$. Thus, the ^1H - ^{127}I interaction suffers an additional fast modulation over and above the one caused by the motion of the mean ^1H - ^1H vector. This shows that here enhanced fluidity caused by a structure-breaking ion is really found at the surface of the ion. This is in contrast to the model postulating A, B, and C regions around the structure-breaking ion in water.⁽²⁵⁾ These results have already been briefly reported in Sec. 5 of ref. 1. (The slight difference in the numerical result given there is due to an activation energy which was assumed to be a little higher.)

We turn to the determination of the closest distance of approach between I^- and the proton. At $5\bar{m}$ the relaxation contribution due to the ^{127}I - ^1H interaction is $1.8 \pm 0.3 \text{ sec}^{-1}$. The experimental error has been estimated as given before. The translational contribution Δ [see Eq. (6)] should not differ much from the value given for the aqueous system, and thus it may be neglected. The first coordination number of I^- with respect

to the glycerol molecules most likely is $n_s = 6$. The first coordination number of I^- with respect to the protons is $\hat{n}_c = 8 \cdot n_s = 48$. High-resolution NMR analysis yielded the result that in the $3 \bar{m}$ and $5 \bar{m}$ glycerol- d_8 solutions, among the total amount of protons there are 62 and 55% OH protons, respectively, the remainder being alkyl protons.³ Thus, the probability that a given hydrogen nucleus in a glycerol molecule is a proton is twice as great for hydroxyl as for alkyl hydrogen. Certainly the OH groups are closer to the I^- than the alkyl part. Therefore, we use a distribution parameter $n = 1$ in Eq. (1). The longest intramolecular proton-proton distance in the glycerol molecules is $\approx 4 \text{ \AA}$. Expecting $a \approx 2.5 \text{ \AA}$, we set $l = 6.5/2.5 = 2.6$, and with this number we get $g(1, 0.9, 2.6) = 0.175$.⁽⁵⁾ Applying Eq. (A6) and the reduction factor $g = 0.175$, we find

$$a = 2.55 \pm_{0.09}^{0.10} \text{ \AA}$$

This figure is in good agreement with the corresponding distance in aqueous solution.

Again, if we use the Gaussian time correlation function [Eq. (A18)], our observed relaxation rate would be compatible with a wider distribution of protons around I^- , which may be more realistic.

4.2.1. Measurements at 60 MHz

Finally, we have to establish that the correlation time is really determined by the molecular motions and not by the relaxation time of the iodine nucleus. Due to the large quadrupole moment, this relaxation time is very short.⁽²⁷⁾ We were able to measure the line width of ^{127}I as I^- in glycerol at temperatures $\geq 100^\circ\text{C}$. For lower temperatures the line becomes too broad and the signal is no longer detectable. We estimated the activation energy for the ^{127}I relaxation to be $E_A/R \approx 4 \cdot 10^3$. This gives $(T_1)_{^{127}\text{I}} \geq 5 \cdot 10^{-8} \text{ sec}$ at $t = -17.4^\circ\text{C}$. At this temperature the correlation time for the $^1\text{H}-^{127}\text{I}$ interaction was found to be $\tau_c = 4.9 \cdot 10^{-9} \text{ sec}$, i.e., $(T_1)_{^{127}\text{I}} > \tau_c$, and consequently $(T_1)_{^{127}\text{I}}$ should not act as the correlation time.

Furthermore, if the ^{127}I relaxation time were the correlation time, then this time must become longer when the temperature is increased. In order to examine the temperature dependence, we measured the $c^* = 3 \bar{m}$ and $c^* = 5 \bar{m}$ solutions in glycerol- d_8 at 60 MHz.⁽²⁸⁾ A simplified evaluation of the results yielded the $^1\text{H}-^{127}\text{I}$ contributions, which are shown as the dashed curves in Fig. 6b. At the maximum of these curves, according to Eq. (A5),

³ Unfortunately, during the preparation of the samples a small admixture of $\text{C}_2\text{H}_5\text{OH}$ was introduced in the solutions. Using the work of Vermold,⁽²⁸⁾ we can show that the presence of the ethanol molecules does not disturb the observed $^{127}\text{I}-^1\text{H}$ interaction effect.

$\tau_c = 2.5 \cdot 10^{-9}$ sec. One sees from Fig. 6b that the maxima corresponding to this correlation time occurs at slightly higher temperatures than those obtained previously (at 30 MHz $\tau_c = 3.3 \cdot 10^{-9}$ sec). Therefore, τ_c decreases as T increases, and the dynamic process is dominant in determining the correlation time since $(1/T_1)_{\max} \sim 1/\omega$. Lastly, it can be seen from Fig. 6b that the relaxation data obtained at 60 MHz lead to the same distance of approach a as given above.

APPENDIX

The proton relaxation rate caused by magnetic dipole-dipole interaction with another (unlike) nuclear spin S in a fixed distance a is given by the formula^(8,9,13)

$$\left(\frac{1}{T_1}\right)^I = \frac{4}{3}\gamma_I^2\gamma_S^2\hbar^2 S(S+1) \frac{n_c}{a^6} \cdot \phi_r(\omega_I\tau_c) = K \cdot \phi_r(\omega_I\tau_c) \quad (\text{A1})$$

with

$$K = \frac{4}{3}\gamma_I^2\gamma_S^2\hbar^2 S(S+1) \frac{n_c}{a^6} \quad (\text{A2})$$

and

$$\phi_r(\omega_I\tau_c) = \tau_c \left\{ \frac{1}{10} \frac{1}{1 + (1 - \varepsilon)^2 \omega_I^2 \tau_c^2} + \frac{3}{10} \frac{1}{1 + \omega_I^2 \tau_c^2} + \frac{6}{10} \frac{1}{1 + (1 + \varepsilon)^2 \omega_I^2 \tau_c^2} \right\} \quad (\text{A3})$$

where ω_I is the resonance frequency of the relaxing spin I , and $\omega_S = \varepsilon' \omega_I$ is the resonance frequency of the spin S . This formula holds if $n \geq 6$ and $g(n, k, l) = 1$. In this situation the correlation function for the magnetic dipole-dipole interaction is assumed to be

$$g_r(t) = \frac{2}{15a^6} e^{-t/\tau_c} \quad (\text{A4})$$

If the spin S is ^{127}I , then $\varepsilon' = \frac{1}{5}$, and $\phi_r(\omega_I\tau_c)$ for a given frequency has its maximum when

$$\omega_I\tau_c = 0.93 \quad (\text{A5})$$

If τ_c is given by Eq. (A5), then the relaxation rate at the maximum is

$$\left(\frac{1}{T_1}\right)_{\max} = K_{\text{HI}} \cdot \frac{0.45}{\omega_I} \quad (\text{A6})$$

where K_{HI} is the quantity K according to Eq. (A2) applied to the interaction partner ^{127}I .

If the interaction partner is ^7Li , then one has

$$\omega_I \tau_c = 0.91 \tag{A7}$$

$$\left(\frac{1}{T_1}\right)_{\max} = K_{HLi} \cdot \frac{0.43}{\omega_I} \tag{A8}$$

and

$$\varepsilon' = 0.389$$

On the other hand, if ^7Li is the relaxing nucleus and the proton is the interaction partner, then

$$\omega_I \tau_c = 0.69 \tag{A9}$$

$$\left(\frac{1}{T_1}\right)_{\max} = K_{LH} \cdot \frac{0.23}{\omega_I} \tag{A10}$$

and

$$\varepsilon' = 2.57$$

In the case of a uniform pair-distribution function, i.e., $n \rightarrow 0$, we have the model of free relative translational motion for all particle separations greater than the closest distance of approach a . The correlation function is derived from the solution of the translational diffusion equation. The relaxation rate is given as⁽¹³⁾

$$\left(\frac{1}{T_1}\right)^I = \frac{3}{15} \pi \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \frac{c'}{a^3} \phi_t(\omega_I \tau_t) = K_{tr} \phi_{tr}(\omega_I \tau_t) \tag{A11}$$

with

$$K_{tr} = \frac{3}{15} \pi \gamma_I^2 \gamma_S^2 S(S+1) \frac{c'}{a^3} \tag{A12}$$

$$\tau_t = \frac{a^2}{6D} \tag{A13}$$

and

$$\phi_t(\omega_I \tau_t) = \tau_t \left\{ \frac{1}{10} f_0(\omega_{I1} \tau_t) + \frac{3}{10} f_1(\omega_I \tau_t) + \frac{6}{10} f_2(\omega_{I2} \tau_t) \right\} \tag{A14}$$

$$\omega_{I1} = \omega_I(1 - \varepsilon')$$

$$\omega_{I2} = \omega_I(1 + \varepsilon')$$

$$f_t(\omega \tau_c) = \frac{15}{x^4} \left\{ \frac{x}{2} - \frac{1}{x} + e^{-x} \left[\left(\frac{x}{2} - \frac{1}{x} \right) \sin x + \left(\frac{x}{2} + 2 + \frac{1}{x} \right) \cos x \right] \right\}$$

$$x = \sqrt{6\omega \tau_c} \tag{A15}$$

When the relaxing nucleus is the proton and the interaction partner is ^{127}I , then, for a given ω_{I} , $\phi_{\text{t}}(\omega_{\text{I}}\tau_{\text{t}})$ has its maximum for

$$\omega_{\text{I}}\tau_{\text{t}} = 1.55 \quad (\text{A16})$$

and the relaxation rate at the maximum is

$$(1/T_{\text{I}})_{\text{max}} = K_{\text{tr}}(0.255/\omega_{\text{I}}) \quad (\text{A17})$$

The correlation function is a Gaussian function

$$g(t) = \frac{2}{15a^6} e^{-t^2/4\tau_c^2} \quad (\text{A18})$$

The form of this correlation function is not derived from any dynamical model. Now the relaxation rate is given as

$$\left(\frac{1}{T_{\text{I}}}\right)^{\text{I}} K \sqrt{\pi} \left\{ \frac{1}{10} e^{-(1-\epsilon)^2 \tau_c^2 \omega_{\text{I}}^2} + \frac{3}{10} e^{-\tau_c^2 \omega_{\text{I}}^2} + \frac{6}{10} e^{-(1+\epsilon)^2 \tau_c^2 \omega_{\text{I}}^2} \right\} \quad (\text{A19})$$

and K is the same as given in Eq. (A2). If ^1H is the relaxing proton and ^{127}I is the interaction partner, we have the maximum relaxation rate for

$$\omega_{\text{I}}\tau_{\text{c}} = 0.65 \quad (\text{A20})$$

and

$$(1/T_{\text{I}})_{\text{max}} = K_{\text{HI}}(0.69/\omega_{\text{I}}) \quad (\text{A21})$$

or

$$(1/T_{\text{I}})_{\text{max}} = g(n, k, l) K_{\text{HI}}(0.69/\omega_{\text{I}}) \quad (\text{A21}')$$

if the distribution function is not a δ function. Likewise, if ^7Li is the interaction partner,

$$\omega_{\text{I}}\tau_{\text{c}} = 0.64 \quad (\text{A22})$$

and

$$(1/T_{\text{I}})_{\text{max}} = K_{\text{HLi}}(0.66/\omega_{\text{I}}) \quad (\text{A23})$$

However, if ^7Li is the relaxing nucleus and ^1H is the interaction partner, one finds

$$\omega_{\text{I}}\tau_{\text{c}} = 0.59 \quad (\text{A24})$$

and

$$(1/T_{\text{I}})_{\text{max}} = K_{\text{LiH}}(0.28/\omega_{\text{I}}) \quad (\text{A25})$$

For completeness we add the "equal spin" formulas corresponding to Eqs. (A5) and (A6):

$$\omega_{\text{I}}\tau_{\text{c}} = 0.62 \quad (\text{A26})$$

$$(1/T_{\text{I}})_{\text{max}} = K_{\text{HH}}(0.43/\omega_{\text{I}}) \quad (\text{A27})$$

and those corresponding to Eqs. (A16) and (A17):

$$\omega_1 \tau_t = 1.05 \quad (\text{A28})$$

$$(1/T_1)_{\max} = K_{\text{trHH}}(0.242/\omega_r) \quad (\text{A29})$$

With equal spins the Gaussian time correlation function yields

$$\omega_1 \tau_c = 0.40 \quad (\text{A30})$$

$$(1/T_1)_{\max} = K_{\text{HH}}(0.61/\omega_r) \quad (\text{A31})$$

For equal spins the linear combination of spectral densities is^(8,9,13)

$$1/T_1 = K \cdot \frac{3}{2} \tau_c \left\{ \frac{1}{5} f(\omega_1 \tau_c) + \frac{4}{5} f(2\omega_1 \tau_c) \right\}$$

REFERENCES

1. H. G. Hertz, *J. Solution Chem.* **2**, 239 (1973).
2. G. Engel and H. G. Hertz, *Ber. Bunsenges. Phys. Chem.* **72**, 808 (1968).
3. H. G. Hertz, in *Water, a Comprehensive Treatise*, F. Franks, ed. (Plenum Press, 1973), p. 301.
4. H. G. Hertz, *Ber. Bunsenges. Phys. Chem.* **75**, 572 (1971).
5. H. G. Hertz and C. Rädle, *Ber. Bunsenges. Phys. Chem.* **77**, 521 (1973).
6. H. G. Hertz and W. Y. Wen, *Z. Phys. Chem. (Frankfurt)* **93**, 313 (1974).
7. H. G. Hertz, H. Weingärtner, and B. M. Rode, *Ber. Bunsenges. Phys. Chem.* **79**, 1190 (1975).
8. A. Abragam, *Principles of Nuclear Magnetism* (Oxford, 1961).
9. T. C. Farrar and E. D. Becker, *Pulse and Fourier Transform NMR* (Academic Press, New York and London, 1971).
10. H. G. Hertz, R. Tutsch, and H. Versmold, *Ber. Bunsenges. Phys. Chem.* **75**, 1177 (1971).
11. H. G. Hertz, in *Molecular Motions in Liquids*, J. Lascombe, ed. (Reidel Publishing Co., 1974), p. 337.
12. L. Endom, H. G. Hertz, B. Thül, and M. D. Zeidler, *Ber. Bunsenges. Phys. Chem.* **71**, 1008 (1967).
13. H. E. Heinze and H. Pfeifer, *Z. Phys.* **192**, 329 (1966).
14. R. Dreher, A. Geiger, and H. J. Kuss, to be published.
15. G. Brauer, *Handbuch der präparativen anorganischen Chemie*, Vol. 1 (Stuttgart, 1960), pp. 262, 313.
16. J. P. Kintzinger and M. D. Zeidler, *Ber. Bunsenges. Phys. Chem.* **77**, 98 (1973).
17. R. M. Lawrence and R. F. Kruh, *J. Chem. Phys.* **47**, 4758 (1967).
18. K. Hermann, Thesis, Karlsruhe, 1973.
19. A. Geiger and H. G. Hertz, *Advances in Molecular Relaxation Processes*, in press.
20. A. H. Narten, *J. Phys. Chem.* **74**, 765 (1970).
- 20a. A. H. Narten, F. Vaslow, and H. A. Levy, *J. Chem. Phys.* **58**, 5017 (1973).
21. G. H. F. Diercksen and W. P. Kraemer, *Theor. Chim. Acta (Berlin)* **23**, 387, 393 (1972).
22. G. H. F. Diercksen and W. P. Kraemer, *Chem. Phys. Lett.* **5**, 570 (1970).

23. H. Lischka, Th. Plessner, and P. Schuster, *Chem. Phys. Lett.* **6**, 263 (1970).
24. G. Engel and H. G. Hertz, *Ber. Bunsenges. Phys. Chem.* **72**, 808 (1968).
25. H. S. Frank and W. Y. Wen, *Disc. Faraday Soc.* **24**, 133 (1957).
26. H. Versmold, *Ber. Bunsenges. Phys. Chem.* **78**, 1319 (1974).
27. H. G. Hertz, *Ber. Bunsenges. Phys. Chem.* **77**, 531 (1973).
28. A. Geiger, Thesis, Karlsruhe, 1973.