

INTERMOLECULAR NUCLEAR RELAXATION AND MOLECULAR PAIR DISTRIBUTION IN LIQUID MIXTURES

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ABSTRACT

^7Li and ^{23}Na relaxation times in aqueous solution of Li^+ and Na^+ in the presence of an increasing amount of Mn^{2+} are reported. From these measurements the cation-cation pair distribution function has been calculated. A distance of approach between Li^+ (or Na^+) and Mn^{2+} of $\approx 4.5 \text{ \AA}$ has been found.

The intermolecular proton relaxation rates of the acids CH_3COOD , $\text{CH}_3\text{CD}_2\text{COOD}$, and $\text{CD}_3\text{CH}_2\text{COOD}$ dissolved in water (D_2O) are presented and from these data simple acid-acid pair distribution functions are constructed. Association has been detected from excess intermolecular proton-proton interactions. In the solution of propionic acid the association is stronger as seen from the methylene group than from the methyl group.

In the pure alcohols CD_3OH and $\text{C}_2\text{D}_5\text{OH}$ and their mixtures with inert solvents intermolecular proton relaxation is entirely of rotational character and permits conclusions concerning the depth of the potential characterizing the pair distribution function.

1. INTRODUCTION

Usually the total relaxation rate $1/T_1$ of a nucleus is separated into two contributions

$$\frac{1}{T_1} = \left(\frac{1}{T_1} \right)_{\text{intra}} + \left(\frac{1}{T_1} \right)_{\text{inter}} \quad (1)$$

The intramolecular relaxation rate, $(1/T_1)_{\text{intra}}$, is caused by the interaction of the relaxing nucleus with the nuclei and the electrons of the same molecule in which the nucleus resides. The intermolecular relaxation rate, $(1/T_1)_{\text{inter}}$, is due to the interaction of the nucleus considered with all other nuclei and electrons of the system. In this paper the 'system' will be a liquid in all cases. Equation 1 is not without problems: rigorously, equation 1 in itself implies a definition of the concept 'molecule' which may be different from the usual concept 'molecule' as used by the chemist. Indeed, the distinction between the first and second term of equation 1 is the existence and nonexistence of correlated motion of the various sources of relaxation producing interactions around the reference nucleus for relatively short times—down to 10^{-10} s . We shall however not adopt this refined point of view, rather we shall follow

the usual way and define the borderline between intra- and intermolecular contribution as given by the geometry of ordinary chemical molecules. Only magnetic dipole-dipole interaction will be considered in the present article as the relaxation producing mechanism. Quadrupole interaction and scalar interaction may also be of importance but details cannot be described here due to the limited space. Relaxation by spin-rotation interaction and anisotropic chemical shift are typical intramolecular processes.

The other quantity we are interested in is the molecular pair distribution function which we denote as $p(r_0)$. We understand this function in the sense, that dp is the probability of finding a specified molecule (or nucleus) in $d\mathbf{r}_0$ at $\mathbf{r}_0$ relative to the reference nucleus selected at random, i.e. $dp = p(r_0) d\mathbf{r}_0$. The normalization of $p(r_0)$ is chosen to be

$$1 = \int p(r_0) d\mathbf{r}_0$$

where the integral is extended over the entire system, i.e. the liquid. Then the intermolecular relaxation rate caused by magnetic dipole-dipole interaction and the pair distribution function are interrelated in the following way¹: the intermolecular relaxation rate is a linear combination of a number of spectral intensities $J(\omega_1)$, $J(\omega_2)$, $J(\omega_3)$

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \gamma_I^2 \hbar^2 \{aJ(\omega_1) + bJ(\omega_2) + cJ(\omega_3)\} \quad (2)$$

a , b , and c being constants given by the theory and

$$\omega_1 = \omega_I - \omega_s$$

$$\omega_2 = \omega_I$$

$$\omega_3 = \omega_I + \omega_s$$

where ω_I and ω_s are the nuclear magnetic resonance frequencies of the relaxing nucleus and that of the interaction partner, respectively (in the case of like spins $\omega_I = \omega_s$, $a = 0$). $J(\omega)$ is the Fourier transform of the time correlation function

$$g(t) = \mathcal{N} \frac{\overline{Y_2^m(O)} \cdot \overline{Y_2^{m*}(t)}}{r^3(O) \cdot r^3(t)} \quad (3)$$

$$J(\omega) = \int_{-\infty}^{+\infty} g(t) e^{-i\omega t} dt. \quad (4)$$

For $g(t)$ we write:

$$g(t) = \mathcal{N} \int \int \frac{Y_2^{m*}(\theta, \phi)}{r^3} \cdot \frac{Y_2^m(\theta_0, \phi_0)}{r_0^3} p(r_0) P(r_0, r, t) d\mathbf{r}_0 d\mathbf{r}. \quad (5)$$

$Y_2^{m*}(\theta, \phi)$ is the spherical harmonic of order 2. On the left hand side of equations 3 and 5 the superscript m is dropped which indicates that for the isotropic system to be treated here $g(t)$ does not depend on m . θ and ϕ are the polar and azimuthal angles of the vector $\mathbf{r}$ relative to the laboratory system, the z direction being given by the magnetic field. $\mathbf{r} = \{\theta, \phi, r\}$, $\mathbf{r}$ connects the

reference nucleus with another particle which is the interaction partner. Both particles undergo diffusion relative to one another, thus $\mathbf{r} = \{\theta(t), \phi(t), r(t)\}$. θ_0, ϕ_0 and r_0 stand for $\mathbf{r} = \{\theta(O), \phi(O), r(O)\}$. $P(\mathbf{r}_0, \mathbf{r}, t)$, the propagator, determines

$$dP = P(\mathbf{r}_0, \mathbf{r}, t) d\mathbf{r},$$

the probability that a particle is in $d\mathbf{r}$ at $\mathbf{r}$ relative to the reference nucleus at time t if we know that it was at $\mathbf{r}_0$ at time 0. The number $\mathcal{N}$ which appears in equations 3 and 5 is the number of magnetic dipoles present in the system, e.g. for 1 mole water $\mathcal{N} = 2.6 \times 10^{23}$. The fact that $g(t)$ is written as a sum of $\mathcal{N}$ 'self-correlation' terms implies that all cross-correlation terms between different particles are neglected.

The function $P(\mathbf{r}_0, \mathbf{r}, t)$ generally is not known precisely. Very often $P(\mathbf{r}_0, \mathbf{r}, t)$ is approximated by the solution of the translational diffusion equation. Use of jump-models for the derivation of $P(\mathbf{r}_0, \mathbf{r}, t)$ is another possibility².

Equation 5 contains the quantity we are interested in, namely the pair distribution function $p(\mathbf{r}_0)$. In principle one has to introduce any given functional form of $p(\mathbf{r}_0)$, to solve the integral equation 5 and then to see whether the calculated intermolecular relaxation rate is in agreement with the observed one. Usually for pure liquids the efficiency of such a method is not great for several reasons: (a) the intermolecular relaxation rate is not very sensitive to relatively weak maxima and minima in $p(\mathbf{r}_0)^{3,4}$; (b) the molecule which carries the relaxing spin in most cases is not of spherical symmetry with respect to the nucleus considered whereas equation 5 is derived only for spherical particles with the spin in their centre—Hubbard's recalculation of the intermolecular relaxation rate has taken account of this complication⁵; (c) $P(\mathbf{r}_0, \mathbf{r}, t)$ is not known precisely; (d) correlation effects among the motions of different particles are neglected, no theoretical treatment has as yet been given to investigate this question.

So the usefulness of a direct evaluation of equation 5 seems to be confined to mixtures where *a priori* very little is known about $p(\mathbf{r}_0)$ and where even a rough knowledge of $p(\mathbf{r}_0)$ is of value.

We shall give two examples for a 'direct' evaluation of $p(\mathbf{r}_0)$ from equation 5, firstly the ion-ion pair distribution function between two cations in an aqueous electrolyte solution, and secondly the pair distribution function between two carboxylic acid molecules at relatively low concentration in aqueous solution. In both these cases the concentration of the particles, the distribution of which is desired, is comparatively small, i.e. small as compared with the particle concentration in the liquid. Furthermore—at least in the first type of system—the distances between the interacting particles are large; both these facts justify the use of a propagator $P(\mathbf{r}_0, \mathbf{r}, t)$, which is derived from the diffusion equation, in first approximation.

It is clear that the propagator $P(\mathbf{r}_0, \mathbf{r}, t)$ and the distribution function occurring in equation 5 are in some way interrelated. So in a second approach to the determination of the cation-cation distribution function we shall correct the propagator in a simple and intuitive way.

The third example which we wish to discuss concerns methanol and ethanol as pure liquids and in their mixtures with inert solvents. Whereas in

the two former examples we shall consider $P(\mathbf{r}_0, \mathbf{r}, t)$ and $p(\mathbf{r}_0)$ to be essentially independent of one another, now with the alcohols, we shall have the other limiting case and shall use the fact that the propagator $P(\mathbf{r}_0, \mathbf{r}, t)$ corresponds to very tight binding of two alcohol molecules. Having established this tight binding—by study of the experimental results—and the corresponding form of the propagator, it will then be possible to draw certain conclusions regarding $p(\mathbf{r}_0)$, namely the depth of the potential well implied in $p(\mathbf{r}_0)$.

2. THE CATION-CATION RADIAL DISTRIBUTION FUNCTION FOR $\text{Li}^+ - \text{Mn}^{2+}$ AND $\text{Na}^+ - \text{Mn}^{2+}$

Here we make use of the magnetic dipole-dipole interaction between the nuclei ${}^7\text{Li}$ or ${}^{23}\text{Na}$ and the unpaired electrons of the ion Mn^{2+} . The ${}^7\text{Li}$ relaxation in Li^+ solutions have been studied in the presence of Mn^{2+} . In all these systems the nuclear magnetic resonance frequencies (of ${}^7\text{Li}$ and ${}^{23}\text{Na}$) are very much less than the reciprocal of the time constants characterizing molecular motions.

It may be shown that in this situation equation 2 reads¹

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \gamma_I^2 \gamma_s^2 \hbar^2 S(S+1) \frac{\pi}{15} \{12J(O) + 28J(\omega_s)\} \quad (6)$$

γ_I = gyromagnetic ratio for the nucleus the relaxation of which is studied, here ${}^7\text{Li}$ or ${}^{23}\text{Na}$.

γ_s = gyromagnetic ratio for the unpaired electrons of the paramagnetic ions. S = spin of the paramagnetic ion ($S = \frac{5}{2}$ for Mn^{2+}).

ω_s = electron spin resonance frequency.

It is also useful to write the analogous expression for $1/T_2$ ¹

$$\left(\frac{1}{T_2}\right)_{\text{inter}} = \gamma_I^2 \gamma_s^2 \hbar^2 S(S+1) \frac{\pi}{15} \{14J(O) + 26J(\omega_s)\}. \quad (7)$$

One sees:

$$\frac{1}{T_1} = \frac{1}{T_2} \quad \text{if} \quad J(O) = J(\omega_s), \quad \text{and}$$

$$\left(\frac{1}{T_2}\right) / \left(\frac{1}{T_1}\right) = 7/6 = 1.17 \quad \text{if} \quad J(O) \gg J(\omega_s).$$

As already mentioned we take the propagator $P(\mathbf{r}_0, \mathbf{r}, t)$ to be the solution of the diffusion equation

$$P(\mathbf{r}_0, \mathbf{r}, t) = \frac{1}{(8\pi Dt)^{3/2}} \exp \left\{ -\frac{(\mathbf{r} - \mathbf{r}_0)^2}{8Dt} \right\} \quad (8)$$

where D = mean translational self-diffusion coefficient of the two interacting ions e.g.

$$D = \frac{1}{2}(D_{\text{Li}^+} + D_{\text{Mn}^{2+}}).$$

Since both ions move relative to one another, the diffusion coefficient has

been multiplied by a factor of 2 in equation 8¹. Usually one takes a step function for $p(r_0)$ in equation 5

$$\begin{aligned} p(r_0) &= 0 & \text{for } r_0 < d \\ p(r_0) &= \text{const.} = 1/V & \text{for } r_0 \geq d. \end{aligned} \quad (9)$$

V is the volume of the system, d is the closest distance of approach between the ions.

For this distribution function $g(t)$, equation 5 can be calculated in a closed form:

$$\begin{aligned} g(t) &= N \int_0^\infty \rho e^{-2D\rho^2 t} \left\{ \int_d^\infty \frac{J_{\frac{5}{2}}(\rho r)}{r^{\frac{5}{2}}} dr \right\}^2 d\rho \\ N &= \mathcal{N}/V \end{aligned} \quad (10)$$

$J_{\frac{5}{2}}$ = Bessel function of order $\frac{5}{2}$; and the Fourier transform is

$$\begin{aligned} J(\omega) &= \frac{N}{dD} \int_0^\infty \frac{(J_{\frac{5}{2}}(u))^2}{u^3} \frac{du}{1 + (9\omega^4 \tau^2 / u^4)} \\ u &= \rho \cdot d, \quad \tau = \frac{d^2}{6D}. \end{aligned} \quad (11)$$

It may be shown that the combination of equations 6, 7 and 11 yields

$$\left(\frac{1}{T_1} \right)_{\text{inter}} = \gamma_I^2 \gamma_s^2 \hbar^2 S(S+1) \frac{16\pi\tau N}{25d^3} \{1 + \frac{7}{3} \hat{f}(\omega_s \tau)\} \quad (12)$$

$$\left(\frac{1}{T_2} \right)_{\text{inter}} = \gamma_I^2 \gamma_s^2 \hbar^2 S(S+1) \frac{56\pi\tau N}{75d^3} \{1 + \frac{13}{7} \hat{f}(\omega_s \tau)\} \quad (13)$$

which is valid if the electron spin relaxation time $\tau_s \gg \tau$. This is indeed true for our solutions, $\tau \approx 10^{-11}$ s (see below) and $\tau_s = 3 \cdot 10^{-9}$ s¹⁰, $\hat{f}(\omega_s \tau)$ is a bell shaped function with the properties^{8,9}

$$\begin{aligned} \hat{f}(\omega_s \tau) &= 1 & \text{for } \omega_s \tau \rightarrow 0 \\ \hat{f}(\omega_s \tau) &= 0 & \text{for } \omega_s \tau \rightarrow \pm \infty. \end{aligned}$$

So far the cation-cation distribution function is only characterized by the distance of the step in this function from the reference ion. This distance is d , the closest distance of approach. Since τ may be obtained from the frequency dependence of the experimental $(1/T_1)_{\text{inter}}$, d can be calculated from the absolute value of the relaxation rates according to equations 12 and 13.

Since the step function is certainly only a rough approximation to reality we improved the form of $p(r_0)$ by writing

$$\begin{aligned} p(r_0) &\equiv f_m(r_0) \frac{1}{V} = \frac{\{(r_0 - a)/(d - a)\}^m}{1 + \{(r_0 - a)/(d - a)\}^m} \cdot \frac{1}{V} \quad \text{for } a \leq r_0 \\ p(r_0) &\equiv 0 & \text{for } a > r_0 \end{aligned} \quad (14)$$

The parameter m determines the steepness of the function $p(r_0)$; for $m \rightarrow \infty$ we obtain the step function, see Figure 1. For all m we have $f_m(a) = 0$ and $f_m(d) = \frac{1}{2}$.

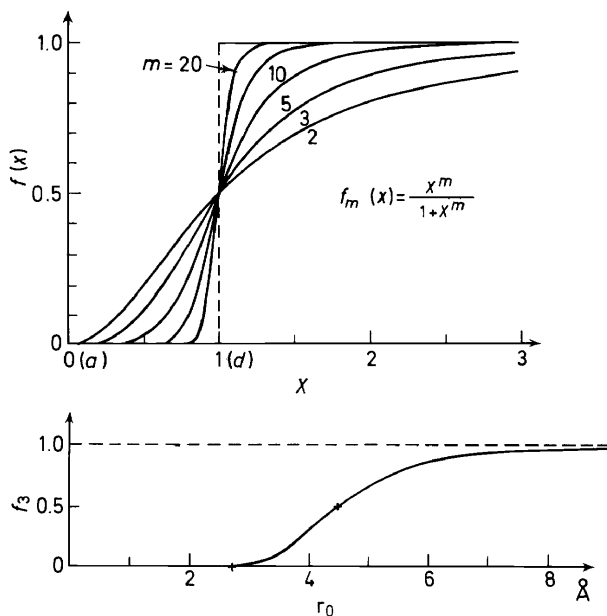


Figure 1. Upper part: Graphical representation of the function $f_m(x)$. Lower part: $f_3(r_0)$ for the pair distribution Li^+ (or Na^+) ion- Mn^{2+} ion at 25°C .

Furthermore, we corrected the propagator

$$P(r_0, r, t) = f_m(r) \cdot (8\pi Dt)^{-\frac{3}{2}} \exp \left\{ -\frac{(r - r_0)^2}{8Dt} \right\}$$

in an intuitive way in order to take account of the repulsive force which hinders the two cations to approach towards one another. With these two modifications equations 10 and 11 take on the form

$$g(t) = N \int_0^\infty \rho e^{-2D\rho^2} \left\{ \int_a^\infty f_m(r) \frac{J_{\frac{3}{2}}(\rho r)}{r^{\frac{3}{2}}} dr \right\}^2 d\rho \quad (15)$$

$$J(\omega) = \frac{N}{D} \int_0^\infty \left\{ \int_a^\infty f_m(r) \frac{J_{\frac{3}{2}}(\rho r)}{r^{\frac{3}{2}}} dr \right\}^2 \frac{\rho^3}{\rho^4 + (9\omega^2\tau^2/d^4)} d\rho, \quad (16)$$

and in particular, for the extreme narrowing case: $9\omega^2\tau^2/d^4 \ll \rho^4$

$$J(0) = \frac{N}{D} \int_0^\infty \left\{ \int_a^\infty f_m(r) \frac{J_{\frac{3}{2}}(\rho r)}{r^{\frac{3}{2}}} dr \right\}^2 \frac{d\rho}{\rho} \quad (17)$$

which can no longer be evaluated in a closed form.

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In Figure 2 the longitudinal and transversal relaxation rates of ^7Li at 25°C are shown. ^7Li is present as Li^+ in aqueous solution at a constant concentration 1 M (M = molarity, moles l^{-1}). The relaxation rates are given as a function

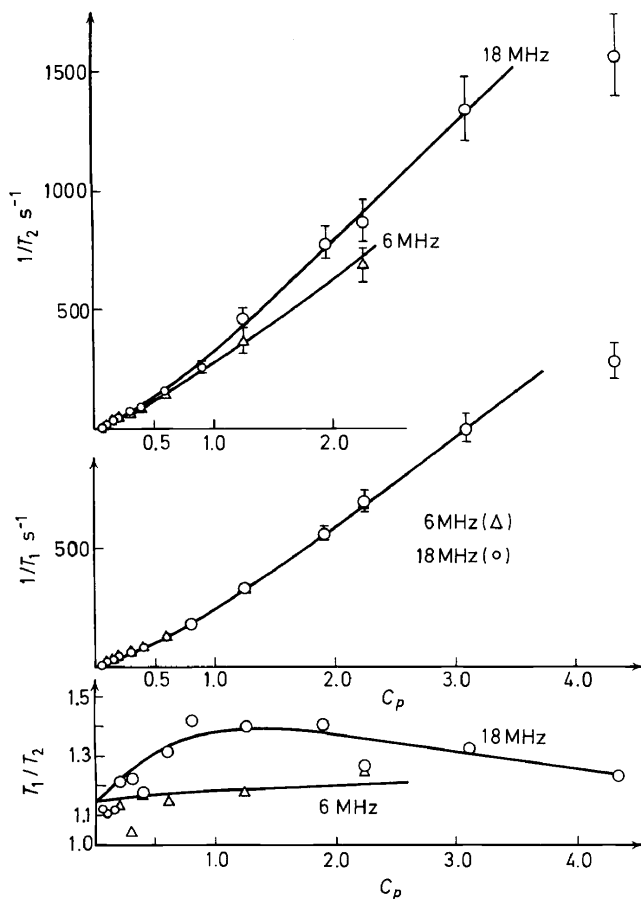


Figure 2. Transversal and longitudinal relaxation rates of ^7Li in solutions of 1 M LiCl with increasing concentration of MnCl_2 (C_p , in moles l^{-1} , M), at 25°C .

of C_p , the concentration of Mn^{2+} (C_p in moles l^{-1}). Both salts are chlorides. The data are presented for two frequencies: 18 MHz and 6 MHz. $1/T_1$ is seen to be independent of the frequency within the experimental error, whereas $1/T_2$ increases slightly as the frequency increases by a factor 3. The ratio T_1/T_2 is also given in Figure 2 and will be discussed below. From the independence of frequency of $1/T_1$ we conclude that either $\tau\omega_s \ll 1$ or $\tau\omega_s \gg 1$.

This question can easily be answered: in the former case frequency independence should be preserved when the temperature is raised, in the latter case frequency dependence should appear at higher temperature.

Figure 3 shows that $\tau\omega_s \gg 1$ is indeed correct at room temperature. At 86°C we find

$$\frac{1/T_1(6 \text{ MHz})}{1/T_1(18 \text{ MHz})} = 1.3.$$

(At low temperatures, $\vartheta < 25^\circ$, we find $1/T_1(6 \text{ MHz})$ slightly less than

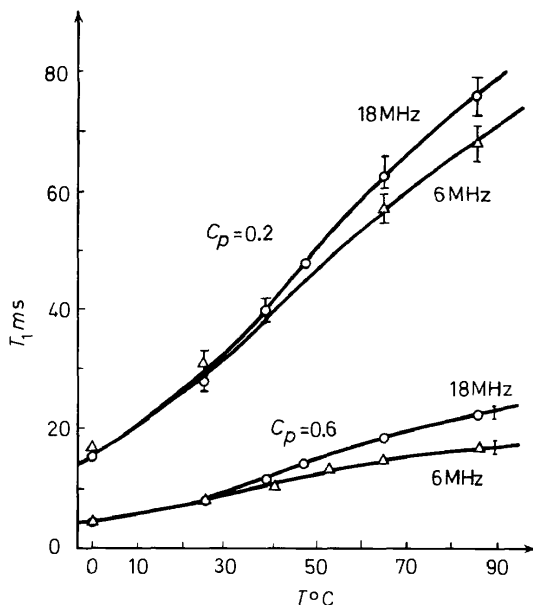


Figure 3. T_1 of ^7Li as a function of the temperature in two solutions: 1 M LiCl + 0.2 M MnCl₂ and 1 M LiCl + 0.6 M MnCl₂.

$1/T_1(18 \text{ MHz})$. This finding must be ascribed to a systematic experimental error). Thus from equation 6

$$\frac{1 + \frac{7}{3}\hat{f}(\omega_s\tau)}{1 + \frac{7}{3}\hat{f}(3\omega_s\tau)} = 1.3$$

($\omega_s = 6.38 \cdot 10^{10} \text{ s}^{-1}$ is the electron spin resonance frequency corresponding to a ^7Li nmr frequency 6 MHz). Graphical evaluation yields $\tau = 1.57 \cdot 10^{-11} \text{ s}$ at $\vartheta = 86^\circ\text{C}$.

The activation energy for translational diffusion in H_2O is about 4 kcal mole $^{-1}$, thus $\tau = 5 \cdot 10^{-11} \text{ s}$ at $\vartheta = 25^\circ\text{C}$. This gives $\hat{f}(\omega_s\tau) < 0.1$ which explains our finding that the frequency dependence is beyond detectability at room temperature. As a consequence we shall neglect the second term in the brackets of equation 12. Then we are left with the 'extreme narrowing' formula which only contains $J(0)$ according to equations 17. The self diffusion coefficient D depends on the concentration. We put

$$\frac{1}{D} = \frac{1}{D_0}(1 + \delta c_p + \dots), \quad \delta = \text{const.}$$

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This is one reason for the deviation from linearity of $(1/T_1)_{\text{inter}}$ as shown in Figure 2. We may write equation 17 as

$$J(O) = g \cdot J(O)_{\text{step function}} = g \cdot \frac{2}{15} \frac{N}{dD}$$

where the factor g takes account of the effect of the real smooth distribution function. Further: $N = N_0 c_p$, $N_0 = 6.02 \cdot 10^{-20} \text{ cm}^{-3}$. Taking all these results together we obtain for equation 12

$$\left(\frac{1}{T_1} \right)_{\text{inter}} = \gamma_I^2 \gamma_s^2 \hbar^2 S(S+1) \frac{8\pi \cdot g N_0 c_p}{75d} \left(\frac{1}{D_0} + \dots \right)$$

and

$$\left(\frac{d(1/T_1)_{\text{inter}}}{dc_p} \right)_{c_p=0} = \gamma_I^2 \gamma_s^2 \hbar^2 S(S+1) \frac{8\pi g N_0}{75d D_0}$$

where we have set $d = \text{const.}$, i.e. we have neglected a possible concentration dependence of d , the parameter of approach. D_0 we take from conductivity data. Since the ionic conductivity of Mn^{2+} is not available, we use the value for Mg^{2+} . Mg^{2+} and Mn^{2+} have the same ionic radius. At infinite dilution $D_0 = \frac{1}{2} (D_{\text{Mg}^{2+}} + D_{\text{Li}^+}) = 0.87 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. This has to be divided by 1.17, since we have a constant concentration of 1 M LiCl^{11} ; i.e. $D_0 = 0.75 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Our experimental slope of $(1/T_1)_{\text{inter}}$ at $c_p \rightarrow 0$ is, see Table I,

$$\{d(1/T_1)_{\text{inter}}/dc_p\}_{c_p=0} = 180 \text{ s}^{-1} \text{ M}^{-1}$$

for both frequencies. Then with the step function ($g = 1$) our result is: $d = 4.9 \cdot 10^{-8} \text{ cm}$.

Table 1. ^7Li relaxation times in the system $\text{LiCl} + \text{MnCl}_2$ at lower concentrations, $\vartheta = 25 \pm 0.5^\circ \text{C}$.

c_p mol l^{-1}	T_1 ms	$1/T_1$ s^{-1}	T_2 ms	$1/T_2$ s^{-1}
(a) at 6 MHz				
0.05	121	8.27		
0.1	61	16.4	55	18.2
0.2	31	32.2	27.5	36.4
0.3	17.3	57.8	16.7	60
0.4	13.7	73	11.8	85
0.6	8.0	125	7.0	143
1.25	3.25	317	2.75	364
(b) at 18 MHz				
0.05	120	8.33	107	9.35
0.1	57.8	17.3	52.5	19.0
0.15	36.3	27.5	32.5	30.7
0.2	28.0	35.7	22.9	43.7
0.3	17.2	58.1	14.0	71.4
0.4	13.0	77	11.0	91
0.6	7.99	125	6.08	165
0.8	5.55	180	3.90	256
1.25	2.97	336	2.13	470

Next we performed the numerical calculation of the more general form of the integral in equation 17, $f_m(r)$ not being a step function. According to equation 14 we have to choose a distance a where $p(r_0) = f_m(r_0) = 0$. We assumed $a = 2.6 \text{ \AA}$, the distance from the Li^+ ion to the midpoint between two water molecules which are members of the tetrahedral first hydration sphere of Li^+ . We performed the calculation of the integral equation 17 at $d = 4.5 \text{ \AA}$. First we checked the reliability of the numerical calculation through comparison of its result with the exact mathematical solution using the step function for $f_m(r_0)$, namely $2/15 d$. The number of computational operations needed for the evaluation of the double integral is of the order 10^5 , so one necessarily obtains an appreciable amount of computational and rounding errors. The computation was carried out until the result was within 4.3 per cent of the theoretical value of $2/15 d$. Then we chose a number of parameters m and calculated the results listed in Table 2.

Table 2. Double integral in equation 17 in per cent of $2/15d$.

m	$a \text{ \AA}$	$d \text{ \AA}$	
stp. fct.	—	4.5	95.69
33	2.6	4.5	94.09
3	2.6	4.5	88.21
4	2.6	4.5	90.27
5	2.6	4.5	92.10
3	2.0	3.0	90.10
3	2.5	3.0	93.39

We see from this table that the influence of the smoothed distribution is small. The double integral with $m = 3$ is by a factor 0.93 smaller than the one with $m \rightarrow \infty$ (step function) for the same parameter d . Conversely, accepting $m = 3$ to be a reasonable approximation of the truth we have to reduce our parameter d previously found for the step function by 0.93. So our final result is (see Figure 1)

$$p(r_0) = \frac{\{(r_0 - 2.6)/(4.5 - 2.6)\}^3}{1 + \{(r_0 - 2.6)/(4.5 - 2.6)\}^3} \cdot \frac{1}{V}$$

Had we used only the corrected pair distribution function and the uncorrected propagator, then the result would be $d = 4.7 \text{ \AA}$. With our d as obtained with the step function, $d = 4.9 \text{ \AA}$, we can calculate $\tau = d^2/6D = 5.3 \cdot 10^{-11} \text{ s}$ which confirms our previous finding.

We add a brief comment regarding the transversal relaxation rate. For a correlation time $\tau = 5 \cdot 10^{-11} \text{ s}$ we expect $T_1/T_2 = 1.17$ (see equations 12 and 13). Our experimental error for T_1 and T_2 is several per cent. We see that at 6 MHz, T_1/T_2 is close to the expected value, but at 18 MHz, T_1/T_2 seems to be larger than 1.17, the effect being outside the experimental error. The easiest way to explain this effect is to assume that there is some contribution from scalar interaction to $1/T_2$. In this event the correlation time for this mechanism should be rather long: it should be equal to the electron spin relaxation time $\tau_s = 3 \cdot 10^{-9} \text{ s}$. Then $(1/T_1)_{\text{scalar}} \sim \tau_s$ and τ_s increases as the frequency increases. Assume that at 6 MHz the scalar contribution to $1/T_2$

is 10 percent, then at 6 MHz, $T_1/T_2 = 1.28$ and one estimates from the frequency dependence of τ_s^{12} that $T_1/T_2 = 1.35$ at 18 MHz. The physical model underlying this estimate is the following. A very small fraction of Li^+ ions is close to the Mn^{2+} —probably to a MnCl^+ or MnCl_2 -complex—for a rather long time. Thus τ_s acts as the correlation time for scalar coupling.

In Figure 4 results for LiNO_3 in solutions with $\text{Mn}(\text{NO}_3)_2$ are presented. The initial slope is again $\approx 180 \text{ s}^{-1}/\text{M}$, and the approach parameter one

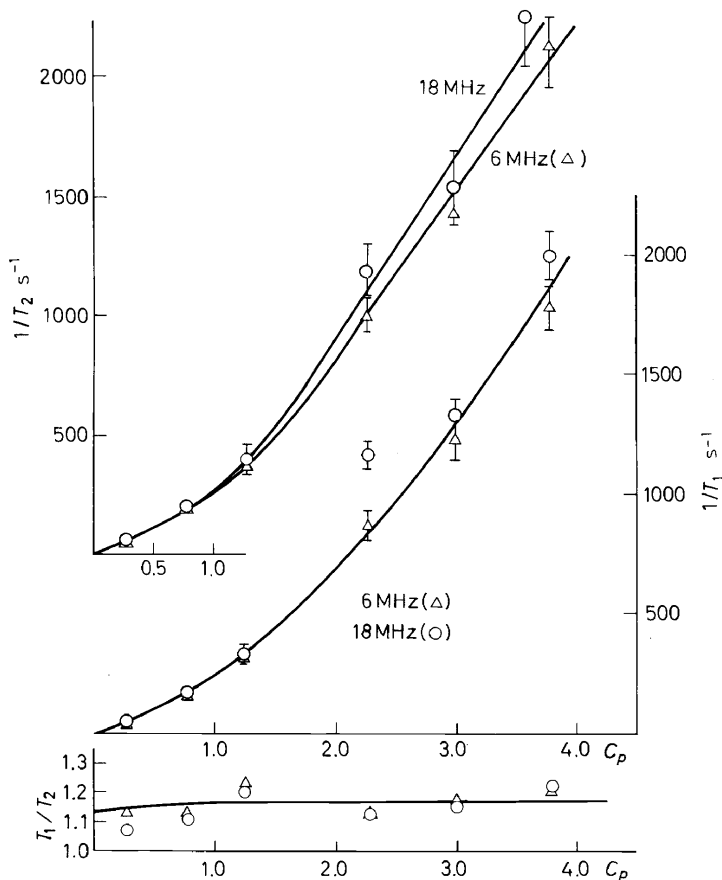


Figure 4. Transversal and longitudinal relaxation rates of ^7Li in solutions of 1 M LiNO_3 with increasing concentration (C_p) of $\text{Mn}(\text{NO}_3)_2$ at 25°C .

calculates is the same as that for $\text{LiCl} + \text{MnCl}_2$. Thus the cation-cation distribution does not depend markedly on the nature of the anion. The ratio T_1/T_2 however does not show an anomalous increase which we have ascribed to scalar interaction in the case of the chloride. Thus, in nitrate solutions scalar interactions are less as will again be seen shortly.

Figures 5 and 6 show the ^{23}Na relaxation rate in $\text{Na}^+ + \text{Mn}^{2+}$ solutions. Again $c_{\text{Na}^+} = 1 \text{ M}$, being kept constant in all experiments. It is seen that the general relaxation behaviour of Na^+ is very similar to that of Li^+ . Within

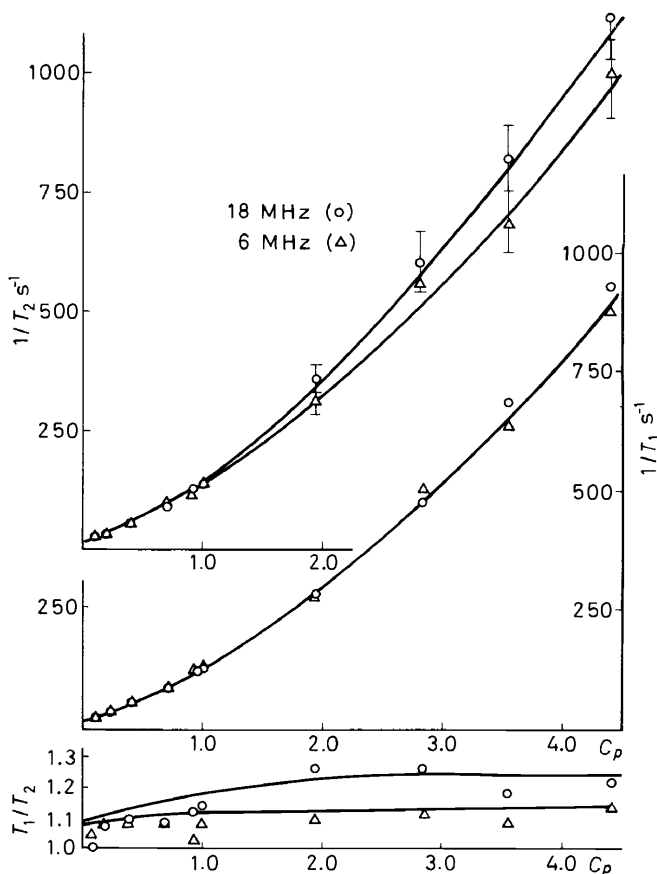


Figure 5. Transversal and longitudinal relaxation rates of ^{23}Na in solutions of 1 M NaCl with increasing concentration (c_p) of MnCl_2 at 25°C .

the experimental error there is no frequency dependence of $1/T_1$. However at high concentration we find $1/T_1$ (18 MHz) $>$ $1/T_1$ (6 MHz) which cannot be physically correct and must be due to a systematic error in our experiments. We get a consistent description if we assume that $1/T_1$ (6 MHz) = $1/T_1$ (18 MHz) at $c_p \approx 4$ M, then $1/T_1$ (6 MHz) is 10 per cent larger than $1/T_1$ (18 MHz) at low concentrations and

$$\frac{1 + \frac{7}{3}\hat{f}(\omega_s\tau)}{1 + \frac{7}{3}\hat{f}(3\omega_s\tau)} = 1.10$$

yields $\tau \approx 4.5 \cdot 10^{-11}$ s. The quadrupole relaxation rate of Na^+ is greater than that of Li^+ . At $c_p \rightarrow 0$, $1/T_{1\text{Na}^+} = 17 \text{ s}^{-1}$ ^{13,14}, at $c_p = 1$ M we estimate a quadrupole contribution $1/T_{1\text{Na}^+} \approx 25 \text{ s}^{-1}$ (viscosity and water reorientation time in MgCl_2 solutions increase by ≈ 40 per cent at $c = 1$ M). From these numbers and our experimental data given in Figure 5 and 6 we find the magnetic dipole-dipole contribution to the increase of $1/T_1$:

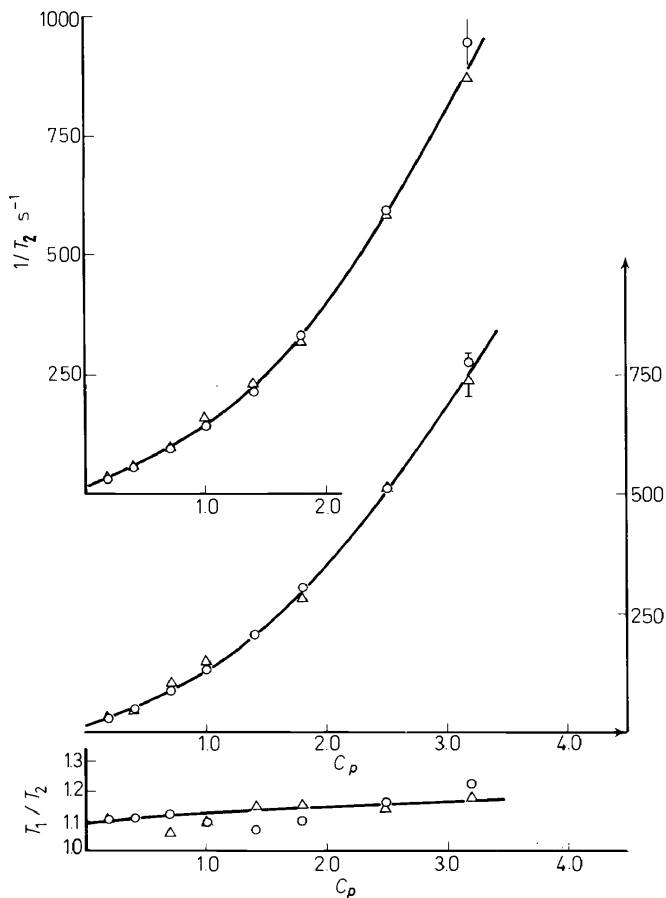


Figure 6. Transversal and longitudinal relaxation rates of ^{23}Na in solutions of 1 M NaNO_3 with increasing concentration (c_p) of $\text{Mn}(\text{NO}_3)_2$ at 25°C .

$\{d(1/T_1)_{\text{inter}}/dc_p\}_{c_p=0} = 80 \text{ s}^{-1}$. The mean self diffusion coefficient in 1 M NaCl is $\approx 0.93 \cdot 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, then with $1 + \frac{2}{3} \cdot f(\omega_s \tau) = 1.185$ we calculate from equation 12, $d = 4.7 \text{ \AA}$. With this d , $\tau = d^2/6D = 4.0 \cdot 10^{-11} \text{ s}$ which we consider to be in satisfactory agreement with our τ as previously estimated. Thus we obtain the result that the approach between Na^+ and Mn^{2+} is described by substantially the same $p(r_0)$ as that obtained for Li^+ and Mn^{2+} .

Again the effects caused by scalar interaction between the spins of Na^+ and Mn^{2+} , which should be observable through the T_1/T_2 ratio, are stronger for the chloride than for nitrate (see Figures 6 and 5). The correlation time seems to be shorter here than for Li^+ . However the experimental results which are relevant for this question are just at the limit of experimental error. In Figure 7 the chemical shift of the ^{23}Na resonance in solutions of Mn^{2+} salts is depicted¹⁵. The shift is caused by scalar interaction¹⁶ and it will be seen that the scalar interaction is most effective for chlorides. The Li^+

chemical shift is much smaller¹⁵, the coupling constant is smaller but other factors are also important^{17, 18}.

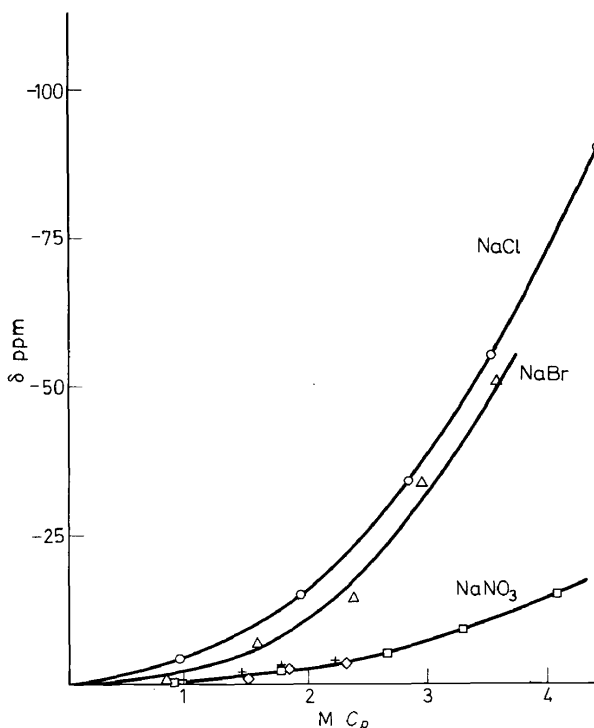


Figure 7. Chemical shift of the ^{23}Na resonance in solutions containing 1 M NaX and an increasing concentration (c_p) of MnX_2 . X = Cl, Br, NO_3 , as indicated in the Figure; X = $\frac{1}{2}\text{SO}_4$: +; X = ClO_4 : $\diamond$ ($\theta = 25^\circ\text{C}$).

3. MOLECULAR DISTRIBUTION FOR CARBOXYLIC ACIDS IN AQUEOUS SOLUTION

Next we consider aqueous solutions of carboxylic acids. The two examples, with which we shall deal at present, are acetic acid and propionic acid. The pair distribution functions of these acids in aqueous solution are of great interest because they might reveal what is called hydrophobic association, i.e. association which is due to the presence of the hydrophobic alkyl groups.

In these diamagnetic liquids we always have the situation of 'extreme narrowing', i.e. $\omega_I\tau \ll 1$, which has the consequence that spectral intensities at $\omega = 0$ are the only ones which occur in equation 2, equation 17 being again the correct expression for $J(0)$. For $f_m(r)$ we use the step function and, as may be shown¹, the result to be used is:

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \gamma_I^4 \hbar^2 I(I+1) \frac{8\pi N_I}{15 dD}. \quad (18)$$

Since we apply this formula to carboxylic acids dissolved in D_2O the meaning

of the symbols is as follows: $(1/T_1)_{\text{inter}}$ = intermolecular relaxation rate of a given proton in the acid (see below), γ_I = gyromagnetic ratio of the proton, $I = \frac{1}{2}$ = spin of the proton, N_I is the number of protons per cm^3 in the solution (water is always D_2O !), d = closest intermolecular distance of approach between the acid protons considered, D = self diffusion coefficient of the acid. From equation 18 we see that

$$\left(\frac{1}{T_1}\right)_{\text{inter}} \cdot \frac{D}{N_I} \equiv A = \text{const.} \quad (19)$$

should hold. If however we find

$$\left\{\left(\frac{1}{T_1}\right)_{\text{inter}} \cdot \frac{D}{N_I}\right\}_{N_I \text{ small}} > \left\{\left(\frac{1}{T_1}\right)_{\text{inter}} \cdot \frac{D}{N_I}\right\}_{N_I \text{ large}}$$

then, since d is considered to be constant and given by the geometry of the molecules, equation 18 must have the form

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \gamma_I^4 \hbar^2 I(I+1) \frac{8\pi (KN_I)}{15} \frac{1}{dD} \quad (18a)$$

where $K > 1$ at small concentrations and $K = 1$ at high concentrations, i.e. the local concentration of spins around the reference molecule is greater than the average concentration in the whole solution. In other words, we have a nonuniform molecular distribution which may also be called association.

In *Figure 8a* the intermolecular relaxation rate of CH_3COOD in D_2O is shown as a function of the concentration: number of acid molecules/ cm^3 . These data are obtained from the total proton relaxation rate of CH_3COOD in D_2O and from the deuteron relaxation rate of CD_3COOH in H_2O . Details will be published elsewhere¹⁹. The experimental uncertainty of the intermolecular relaxation rate is ± 15 per cent. The self-diffusion coefficient of CH_3COOD in D_2O has also been measured²⁰ and the product $(1/T_1)_{\text{inter}} \cdot D/N$ may be calculated. The result is shown in *Figure 8c*. It is clearly seen that this product is larger at small acid content than for the pure acid. Thus we have a crowding of acid molecules around one acid molecule selected at random. In principle one could assume an appropriate $p(r_0)$, which is not a step function but which has a distinct maximum at small interparticle distances, and calculate the integral equation 17 numerically as we did for the electrolyte solutions. But as we have not yet performed these calculations, here we shall present another, simpler procedure.

From equation 18 we calculate the distance d for the neat acetic acid ($D = 0.97 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 25°C). The result is $d = 3.17 \text{ \AA}$. This d is an effective distance of approach taking account of the nonspherical shape of the molecule and of internal rotation of the CH_3 group. Then we calculate $(1/T_1)_{\text{inter}}$ according to equation 18 for the mixture, D being given. The result is the dashed line in *Figure 8a*. $\Delta(1/T_1)_{\text{inter}}$, the difference between the observed and calculated intermolecular relaxation rate, is due to the interaction with acid protons which are closer to the reference molecule than they should be, were the uniform random distribution valid. We consider the

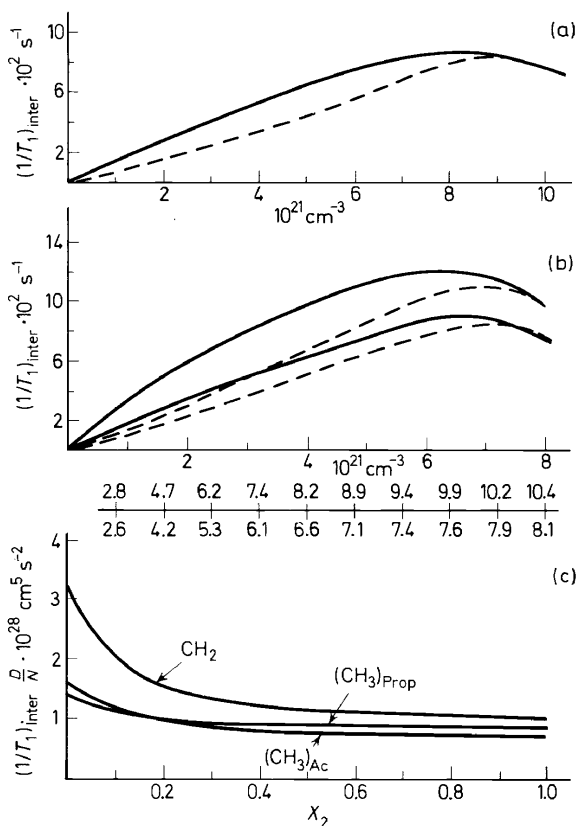


Figure 8. Intermolecular relaxation rates of protons in (a) $\text{CH}_3\text{COOD} + \text{D}_2\text{O}$, (b) $\text{CD}_3\text{CH}_2\text{COOD} + \text{D}_2\text{O}$, $\text{CH}_3\text{CD}_2\text{COOD} + \text{D}_2\text{O}$ as a function of the acid concentration N , given as acid molecules per cm^3 . Dashed curves: calculated intermolecular relaxation rates. (c) $(1/T_1)_{\text{inter}} \cdot D/N$ as a function of the mole fraction of acid, x_2 . In the top of (c) the two concentrations in units of 10^{21} molecules per cm^3 corresponding to the mole fraction are given.

'half-space' defined by the solid angle 2π around the C—C bond direction of the acid molecule and containing only the methyl group. Thus the carboxylic oxygens and the OD hydrogen are not contained in this half of the space surrounding a molecule. We estimate the mean distance between the reference proton in the methyl group and the methyl protons of the associated acid molecule—which of course are in the 'half-space' indicated above—to be $b \approx 2 \text{ \AA}$. The vector connecting one of these associated protons with the reference proton is considered to be of almost constant length for a time $\tau \approx 10^{-11} \text{ s}$. After this time the associated partner molecule has lost its local correlation with the reference molecule. This time is also the reorientational correlation time of the vector. Then the rotational intermolecular relaxation rate is

$$\left(\frac{1}{T_1}\right)_{\text{rot}} = \frac{3}{2} \gamma^4 \hbar^2 \frac{3\tau_c}{b^6} \quad (19)$$

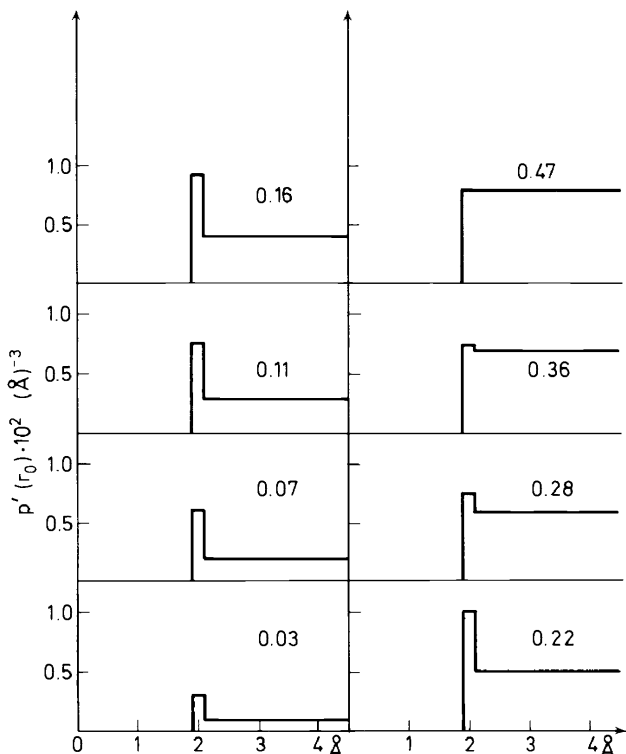


Figure 9. Schematic representation of acid-acid pair distribution function for acetic acid dissolved in D_2O . The association probability p_{ass} is obtained by multiplying the peak height by $2\pi r_0^2 \Delta r_0 = 5 \text{ \AA}^3$. Numbers indicate mole fraction of acetic acid.

$$\Delta 1/T_1 = p_{\text{ass}} \left(\frac{1}{T_1} \right)_{\text{rot}}, \quad (20)$$

where p_{ass} is the probability for an acid molecule to be somewhere in the 'half-space' described above with an intermolecular proton-proton distance $\approx b$. With $b = 2 \text{ \AA}$ and $\tau_c = 10^{-11} \text{ s}$ one calculates $(1/T_1)_{\text{rot}} = 0.4 \text{ s}^{-1}$. This is about the relaxation rate one finds for the intramolecular contribution in fluid organic liquids where a proton interacts with 2–3 other protons²¹. We calculate p_{ass} according to equation 20 from our $\Delta 1/T_1$ results, transform to the probability density $p'(r_0) = p_{\text{ass}}/2\pi r_0^2 \Delta r_0$ and obtain the estimate of one possible type of pair distribution function as depicted in Figure 9. Δr_0 was assumed to be $\Delta r_0 = 0.2 \text{ \AA}$, the probability density $p'(r_0)$ is given in $\text{\AA}^{-3}$ and is understood in the sense to give the probability density to find any acid molecule in dr_0 at r_0 (in the 'half space'). Thus the 'primed' probability density p' is connected with the one previously used by $p'(r_0) = \mathcal{N}p(r_0)$ where $\mathcal{N}$ is the number of (acid) molecules in the system.

Of course the schematic molecular distribution function shown in Figure 9

is only one simple type which is possible; a broader distribution may as well lead to the intermolecular relaxation rate observed.

In Figure 8b we present the proton intermolecular relaxation rates for the two propionic acids $\text{CD}_3\text{CH}_2\text{COOD}$ and $\text{CH}_3\text{CD}_2\text{COOD}$, both in D_2O . The self-diffusion coefficient for the neat acid at 25°C is $D = 0.91 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. For the effective d we find $d = 1.15 \text{ \AA}$. Then the same procedure as described for acetic acid yields radial distribution functions (probability densities) as given in Figure 10. $(1/T_1)_{\text{rot}}$ for the methylene group is $\approx 0.27 \text{ s}^{-1}$.

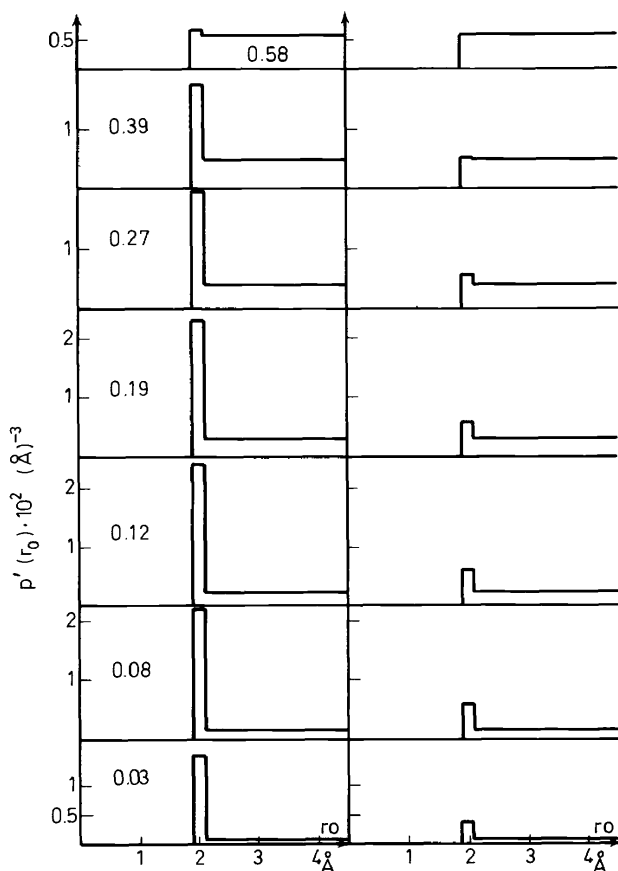


Figure 10. Schematic representation of acid-acid pair distribution function for propionic acid dissolved in D_2O . Left-hand part of the figure: methylene-methylene group distribution; right-hand part: methyl-methyl group distribution. For other details see legend of Figure 9.

Again these distribution functions are only defined in the half-space containing the alkyl group as described above. It is seen that the probability to find a methylene group close to a methylene group is greater than the corresponding probability for a pair of methyl groups.

4. HYDROXYLIC INTERMOLECULAR RELAXATION RATE IN METHANOL AND ETHANOL

The proton relaxation rate of CD_3OH at 25°C is $1/T_1 = 9.3 \cdot 10^{-2} \text{ s}^{-1}$ ²² and the proton relaxation rate of $\text{C}_2\text{D}_5\text{OH}$ at 25°C is $1/T_1 = 16.9 \cdot 10^{-2} \text{ s}^{-1}$ ^{22, 23}. On the other hand, the total proton relaxation rate of CH_3OD at 25°C is $1/T_1 = 9.8 \cdot 10^{-2} \text{ s}^{-1}$ and that of $\text{C}_2\text{H}_5\text{OD}$ is $1/T_1 = 17.5 \cdot 10^{-2} \text{ s}^{-1}$ ^{22, 23}. The two former relaxation processes must be intermolecular because the intramolecular contribution is negligible. Thus we see that these intermolecular relaxation rates are almost as large as the total relaxation rates of the methyl and ethyl protons, which contain intramolecular and intermolecular contributions. We conclude that OH relaxation in the alcohols CD_3OH and $\text{C}_2\text{D}_5\text{OH}$ must be predominantly of rotational character which implies that the propagator $P(\mathbf{r}_0, \mathbf{r}, t)$ in equation 5 for the hydroxylic proton is of such a kind that the proton-proton distance does not vary over times of the order of the reorientational correlation time. Each OH proton has two nearest neighbour protons due to the two H-bonds coupled to a given molecule. The O—O distance in the liquid alcohols is $\approx 2.7 \text{ \AA}$ ²⁴ with the C—OH angle $\beta = 110^\circ$ and the C—O . . . HO angle $\alpha = 135^\circ$. This gives a proton-proton distance $b = 2.3 \text{ \AA}$.

Then the expected rotational relaxation rate is

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \left(\frac{1}{T_1}\right)_{\text{rot}} = \frac{3}{2} \gamma^4 \hbar^2 \frac{2\tau_c}{b^6} \quad (21)$$

Insertion of the numerical values yields $\tau_c = 7.8 \cdot 10^{-12} \text{ s}$ for methanol and $\tau_c = 1.43 \cdot 10^{-11} \text{ s}$ for ethanol. From the OD deuteron relaxation rate in these alcohols the correlation times $\tau_c = 3.7 \cdot 10^{-12} \text{ s}$ and $\tau_c = 8 \cdot 10^{-12} \text{ s}$ for methanol and ethanol, respectively, have been reported²⁵. The agreement is satisfactory and, by taking account of the influence of next nearest neighbours, could be improved. If the hydrogen bond had a life-time $> 10^{-10} \text{ s}$, then the correlation time should be longer than obtained, due to chain association. Very long and extended polymers should have very long rotational correlation times. Since we do not find such long times, we conclude that τ_h , the life time of attachment, is about equal to τ_c , then

$$\tau_h \approx \tau_c \approx \tau_0 \exp(E/RT)$$

gives us, with $\tau_h \approx 10^{-11} \text{ s}$, $\tau_0 \approx 10^{-14} \text{ s}$, $E \approx 4 \text{ kcal mole}^{-1}$ for the depth of the potential describing the pair distribution function between two alcoholic hydroxyl groups. Thus,

$$p'(r_0) = \text{const.} \exp\left(\frac{4000}{RT}\right)$$

with const. given by the requirement

$$1 = \int_{\Delta V} p'(r_0) d\mathbf{r}_0$$

where the integration is extended over the volume occupied by one hydrogen-bonded OH group.

It should be noted that equation 18 depends linearly on N , the concentra-

tion of interacting molecules in the liquid, whereas equation 21 does not depend on N . Experiments have shown²² that $(1/T_1)_{\text{inter}}$ for the OH protons of methanol and ethanol does not depend on the degree of dilution of the alcohols with inert solvents down to a mole fraction ≈ 0.3 of alcohol. Moreover $(1/T_1)_{\text{inter}}$ even increases strongly as a solvent of higher viscosity is added. Thus one sees that the OH—OH system behaves like a firmly coupled aggregate where the relative proton—proton motion in the time range $\approx 10^{-11}$ s is only of rotational character.

We conclude this section by the comment that the method just outlined, namely the demonstration that the propagator is of total or partial rotational form, has a wide field of application. One typical example is again the study of paramagnetic electrolyte solutions^{6, 12, 18} where the propagator of the vector connecting the water in the first hydration sphere with the central ion may be entirely of rotational character from which stable hydration can be inferred and this in turn may be reformulated in terms of pair distribution functions.

5. INTERMOLECULAR RELAXATION RATES CAUSED BY QUADRUPOLE INTERACTION

Nuclei with $I > \frac{1}{2}$ which reside in spherical ions usually relax by quadrupole interaction with electrical field gradients which are produced by other particles in the electrolyte solution. These particles are water (or solvent) molecules and other ions. Thus the relaxation process is of an intermolecular nature and should allow the determination of at least certain properties of the pair distribution functions. An attempt in this direction has previously been undertaken in this laboratory^{26, 27}. The result, however, must be considered as not being satisfactory as yet. The reason for this failure is now obvious and may be sketched as follows. If one considers the quadrupolar relaxation by point charges which represent the ions present in the solution, then the 'self-correlation' terms occurring in the time correlation function are formally the same as those for the magnetic dipole—dipole interaction (equation 5). In the dipole—dipole case the total correlation function is $\mathcal{N}$ times the 'self-correlation' function. But for the quadrupole relaxation the cross-correlation terms between different particles become very important and must be included in the treatment. They cause the screening of a given ionic charge sufficiently far apart from the reference ion, which is the well known charge cloud effect in electrolyte solutions. Thus the contribution to the relaxation from the majority of the ions is quenched. The ion—ion part of the quadrupolar relaxation rate may be expressed in an approximate form in terms of the closest distance of approach between the ions and of the radius of the ionic cloud. So the relaxation rate depends on two parameters characterizing the ion distribution and it has been shown that the experimental results for the relaxation of the ions Cl^- , Br^- , and I^- in aqueous solution of alkali metal halides may be interpreted satisfactorily in terms of these two parameters. The reader is referred to three forthcoming papers for further details^{28–30}. The quadrupole interaction vanishes if the surroundings of the nucleus in question is of cubic symmetry. A pair of particles cannot be of

cubic symmetry, but an arrangement of four or six particles around the reference particle can be so. As a consequence, any experimental demonstration that the quadrupole interaction vanishes at a given ionic nucleus implies symmetry in higher (not pair) molecular distribution functions. Corresponding effects have been found for the ion-water dipole distribution and for the ion-ion distribution in aqueous electrolyte solutions^{28,30}, see also¹¹. We quote here two other references which describe quadrupolar effects in ionic solutions from another point of view^{31,32}.

6. EXPERIMENTAL

The Li^+ and Na^+ relaxation times have been measured with a Bruker B-KR 304 s pulse spectrometer. For longer T_1 times the 90° - 90° pulse sequence method was applied; for shorter relaxation times it was necessary to employ the 180° - 90° technique. For weak signals, in particular at 6 MHz, measurements were performed by the aid of signal accumulation. T_2 measurements were done with the Carr-Purcell method and Gill-Meiboom modification. Care was necessary to prevent heating of the electrolyte solution during the Carr-Purcell procedure. Due to diode detection, base line shift had to be corrected. Equality of short proton T_1 and T_2 was checked with a CuCl_2 solution where both relaxation times are known to be equal³³.

Proton and deuteron relaxation time measurements of the carboxylic acids have been performed with spin-echo apparatus of conventional construction at 20 MHz and 12 MHz, respectively, the 90° - 90° pulse sequence being applied in all cases. The composition of the solutions was determined by weighing, the samples were freed from oxygen by the usual freezing-thawing technique. D_2O for the higher acid concentration was of deuteron content 99.7 per cent, the measurements at low acid concentration were made with D_2O of D content better than 99.8 per cent. We were unable to detect any proton signal in this D_2O . The acids were purchased from Roth, AG., Karlsruhe, and used without further purification.

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