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Proton Spin-Lattice Relaxation Studies of Intermolecular Interactions in the Mixtures of Chloroform and Proton-Acceptor Solvents

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Proton spin-lattice relaxation measurements were carried out on chloroform in carbon tetrachloride, benzene, pyridine, acetone, and dimethylsulfoxide (DMSO) in order to investigate the effect of the intermolecular interaction on the spin-lattice relaxation time, T_1, of chloroform. It was found that the order of the effects of solvents on T_1 is as follows: DMSO>acetone, pyridine>benzene, carbon tetrachloride; this order corresponds to that of the association constant of chloroform with these solvents. The T_1 values of benzene and acetone were also determined on chloroform-benzene and chloroform-acetone mixtures. On the basis of the results obtained on these solutions together with the results on the T_1 of chloroform in various solvents, we estimated the lifetimes of the chloroform-benzene complex and of the chloroform-acetone hydrogen-bonding complex. We tried to keep the proton-density constant throughout the solutions, in order to avoid an ambiguity arising from its change, by adopting the corresponding deuterated compounds.

Proton magnetic resonance (PMR) relaxation studies are an important and useful tool for the study of the microdynamic behavior of liquids.[1,2] Giulotto, Lanzi, and Tosca[3] studied the hydrogen-bonded molecular clusters of phenol in carbon tetrachloride, and showed that the proton spin-lattice relaxation is sensitive to the molecular clustering. Recently Anderson and Fryer[4] and Anderson[5,6] examined both theoretically and experimentally the effect of molecular association on the rotatory motions of molecules in the liquid state; they concluded that the molecular association moved as a unit whose lifetime is longer than the molecular rotational correlation time, τ_c, (for most molecular liquids, τ_c is of the order of 10^{-11}—10^{-12} sec) should affect the spin-lattice relaxation considerably.

Huntress[7,8] studied the quadrupolar relaxation experiments on chloroform and chloroform-*d* and on equimolar mixtures of chloroform-*d*—benzene and chloroform—benzene-d_6, and calculated the rotational diffusion constants from the relaxation times obtained. Huntress interpreted the change in the reorientation of chloroform molecules between neat and benzene solutions in terms of the formation of a complex between chloroform and benzene. However, Anderson showed that the proton spin-lattice relaxation time, T_1, of benzene in chloroform-*d* is equal to those in benzene-d_6 and in carbon tetrachloride. He concluded that the complex between chloroform and benzene is a weak one and does not move as a unit.

In this paper, we will present the experimental results of our proton spin-lattice relaxation studies of mixtures of chloroform and various proton-acceptor solvents (basic solvents), including a chloroform-benzene mixture, and will discuss the intermolecular association and microdynamic behavior of molecules.

It has been well established that the chloroform proton is active and possesses the ability of forming hydrogen bonding, and various chloroform solutions have been studied extensively by means of various experimental techniques.[9-12] So far, PMR chemical shift measurements[11-17] have often been made on mix-

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tures of chloroform and several basic solvents, such as dimethyl sulfoxide (DMSO), acetone, triethylamine, pyridine, acetonitrile, some ethers and ketones, and aromatic solvents. The results have been interpreted in terms of hydrogen-bonding formation or in terms of the formation of a complex between chloroform and solvents, and the association constant has been estimated by means of various procedures.

The greatest advantage of the PMR relaxation study may be its sensitivity to the molecular microdynamic motions and the change in molecular motions due to intra- or intermolecular interactions. We consider that information obtained through T_1 measurements, together with the results of the chemical shift and infrared absorption measurements, should lead us to understand in detail the nature of intermolecular interaction.

We therefore carried out PMR relaxation measurements on the following chloroform solutions: chloroform — chloroform-*d* — carbon tetrachloride, chloroform — chloroform-*d* — benzene-d_6, benzene — benzene-d_6 — chloroform-*d*, chloroform — chloroform-*d* — acetone-d_6, acetone — acetone-d_6 — chloroform-*d*, chloroform — chloroform-*d* — pyridine-d_5, and chloroform — chloroform-*d* — DMSO-d_6. In order to avoid the ambiguity arising from the variation in the proton density, we tried to keep the proton density of the solutions constant by adopting a deuterated analogue.

Experimental

Materials The chloroform and benzene were reagent-grade samples purchased from the Tokyo Kasei Co., Ltd., and were distilled by the usual procedures before use. The acetone and carbon tetrachloride were spectroscopic-grade samples from the Tokyo Kasei Co., Ltd., and were used without further purification. The chloroform-*d*, benzene-d_6, acetone-d_6, DMSO-d_6, and pyridine-d_5 were provided by E, Merck AG, Darmstadt, and were also used without further purification.

The atmospheric oxygen dissolved in the sample was carefully removed by several freeze-pump-thaw cycles in a NMR tube, then, under a vacuum, the sample tube was sealed. After sealing, the sample was used for the experiment immediately.

NMR measurements. The NMR spectrometer used in this study was JNM-C-60H spectrometer of Japan Electron Optics. Lab. operated at 60 MHz. The T_1 measurements were made at 25±1°C by the adiabatic rapid-passage and saturation-recovery methods with sampling. The experimental errors were within ±3%. The chemical shifts were measured by the usual side-band technique, with cyclohexane as the internal standard. The solution viscosities were measured at 25±0.1°C with a Cannon-Ubbelohde viscometer.

In the viscosity measurements, however, deuterated analogues were not used because the isotopic effects of deuterium on the viscosity are considered to be small.

Results and Discussion

The results of the chemical-shift and T_1 measurements of five chloroform solutions are shown in Figs. 1 and 2 respectively.

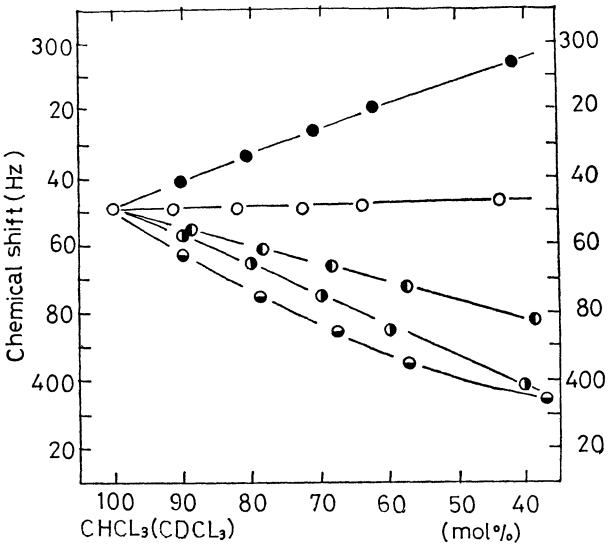

Fig. 1. Plots of chemical shifts of chloroform proton in various solvents *vs.* apparent mole fraction of chloroform.
solvent; benzene-d_6 (●), carbontetrachloride (○), acetone-d_6 (◐), pyridine-d_5 (◑), DMSO-d_6 (◒).
The number of chloroform proton per unit volume is constant; $N=29.8\times10^{20}$.
Apparent mole fraction of chloroform was varied by addition of chloroform-*d*.

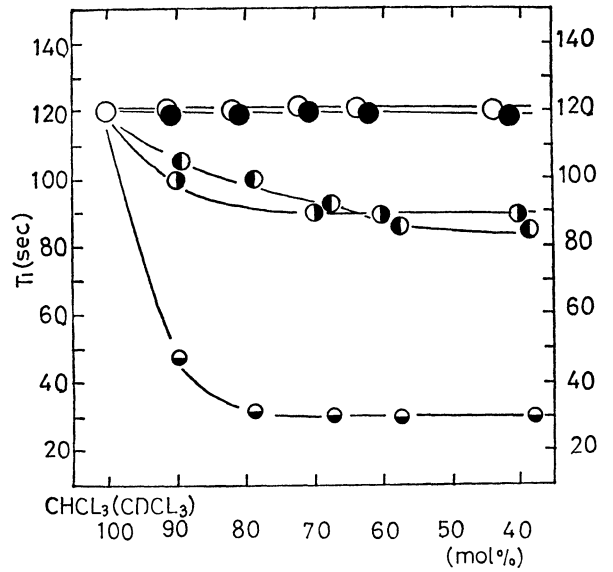

Fig. 2. Plots of T_1's of chloroform proton in various solvent *vs.* apparent mole fraction of chloroform.
solvent; benzene-d_6 (●), carbontetrachloride (○), acetone-d_6 (◐), pyridine-d_5 (◑), DMSO-d_6 (◒).
The number density of chloroform proton is constant; $N=29.8\times10^{20}$.
Apparent mole fraction of chloroform was varied by addition of chloroform-*d*.

Before proceeding to a discussion of each solution, we should like to make several remarks. Strictly speaking, the solutions studied are systems of three components which contain two deuterated analogues. We examined the PMR chemical shift of the chloroform of all solutions in order to test whether or not isotopic effects on the intermolecular interaction between chloroform and basic solvents are negligible.

It is clear from Fig. 1 that the concentration dependence of the chemical shift is almost identical with the literature data.[11-17] Therefore, it may be considered that the isotopic effects on the intermolecular interaction are negligible.

Secondly, we must consider the proton relaxation mechanism of chloroform. Winter[1,18] proposed that, in addition to the dipolar relaxation, the scalar coupling between a proton and chlorine nuclei modulated by the rapid quadrupolar relaxation of the latter may become another relaxation mechanism. On the other hand, Pritchard and Richards[19] proposed that the spin-rotation interaction is another important relaxation mechanism and that the scalar coupling may be unimportant.

In any case, it may be reasonable to assume that the dipolar relaxation mechanism is predominant for the chloroform proton; this assumption is supported by the experimental fact that the T_1 value of the chloroform proton changes from 80 sec for neat chloroform[20] to 120 sec for 40% chloroform in chloroform-*d*. Because the scalar coupling and the spin-rotation mechanisms should not be unchanged by deuterated dilution, this change in T_1 value may be due to the predominant intermolecular dipole-dipole interaction. Moreover, because of the small gyromagnetic ratio, deuteron and chlorine are considered to contribute negligibly to the relaxation of chloroform in this study.

Thirdly, let us consider the effect of the self-association of chloroform.[7,8,21,22] Jumper, Emerson, and Howard,[21] from the PMR chemical shift, estimated the self-association constant of chloroform to be $K=0.16\pm 0.006$ $(\mathrm{m\cdot f})^{-1}$. This value of K is roughly of an order of magnitude smaller than the association constant found for the association of chloroform to basic solvents studied in this paper. Jumper *et al.* found also that, in carbon tetrachloride, the fraction of chloroform participating in the self-association decreases. The T_1 values measured in carbon tetrachloride do not change over the experimental concentration range of chloroform, so we may conclude that the self-association of chloroform is not so strong as to affect the proton spin-lattice relaxation of chloroform in solution. Therefore, the change in T_1 accompanied by dilution with basic solvents may really be due to the effect of intermolecular chloroform-solvent interaction.

Finally, the effect of the macroscopic solution viscosity on T_1 must be considered. According to the Debye-B.P.P. theory,[1,23] the spin-lattice relaxation rate, $1/T_1$, is proportional to the solution viscosity, η. However, it has been well recognized that the B.P.P. theory gives τ_c values of an order of magnitude larger than those estimated from the experiment.[24,25] The proportionality between $1/T_1$ and η is considered to be doubtful. Bull and Jonas[26] studied the pressure dependence of T_1 on benzene and acetone, and showed that the proportionality between $1/T_1$ and η does not hold.

In this study, for example, the η of a carbon tetrachloride solution of chloroform (the mole fraction of chloroform is 40%) is about 1.3 times that of neat chloroform. Nevertheless, T_1 does not change entirely. Therefore, we did not carry out the corrections of the solution viscosity on T_1 in this study.

Now, we should like to turn our attention to the results obtained. It is clear from Fig. 2 that we can classify the solutions studied into three groups. The first group, in which the T_1 values of chloroform are not affected by the presence of solvents, includes chloroform-carbon tetrachloride and chloroform-benzene solutions. Especially, it is interesting that the π-complex between chloroform and benzene does not affect the spin-lattice relaxation of chloroform greatly. Several interpretations of the molecular microdynamics of the π-complex will be shown in the successive discussion in connection with the results of Huntress and Anderson.

The second group, in which T_1 values of chloroform are affected to some extent through the intermolecular interaction with basic solvents, includes chloroform-acetone and chloroform-pyridine solutions. In these solutions, the intermolecular interactions are due to the hydrogen bonds, which is considered to be stronger than the π-complex. Indeed, Abraham[27] pointed out that the complex between chloroform and benzene is essentially similar to other hydrogen bonds; that is, it is essentially electrostatic in character, but because of the weak ionic character of the C–H bond, it is considerably less stable than the more common hydrogen bonds.

The chloroform-DMSO solution is classified in the third group, in which T_1 values of chloroform are affected considerably by the strong intermolecular interaction. In this solution, the spin-lattice relaxation rate of chloroform increases by a factor of about 4 as a result of the presence of a small amount of DMSO. Anderson has also shown that the T_1 value of DMSO protons is affected by the presence of chloroform. Therefore, it may be concluded that the intermolecular interaction between chloroform and DMSO is the strongest, and that the associated species should move as a unit with a lifetime longer than the rotational or translational correlation times of DMSO and chloroform.

The order of the affinity of solvents in associating with chloroform is found to be as follows: DMSO> acetone, pyridine>benzene, carbon tetrachloride. This order corresponds well to that of the association constants between chloroform and solvents described above, obtained through the chemical shift measure-

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ment.[11-17] Thus, in addition to the information about the microdynamic molecular motion, the strength of the association can be estimated through PMR relaxation measurements. Moreover, if the rotational or translational correlation times of each component molecule are known, the order of the lifetimes of the association can also be presumed.

Hubbard[28] has derived an equation for the intermolecular relaxation time which takes account of both the rotational and translational molecular motions:

$$(1/T_1)\text{inter} = (\pi\hbar^2\gamma^4 N/10r^3)\tau_t[1 + 0.233\ (b/r)^2 + 0.15(b/r)^4 + \cdots] \quad (1)$$

where N is the number of spins per unit of volume, r is the molecular radius, b is the distance of the nucleus from the center of the molecule, and τ_t is the translational correlation time, and where all other notations represent their ordinary meanings. We assume, as has been described above, that for the chloroform proton the intermolecular dipole-dipole relaxation is predominant over the other relaxation mechanisms within the experimental conditions in this study. Therefore, Eq. (1) is applicable in calculating τ_t of chloroform in solutions. The following values of r and b were used in the calculation: r=2.81 Å, b=1.10 Å. The radius was obtained by assuming hexagonal closed packing, and b was taken to be equal to the C–H bond length.[29]

In Figs. 3 and 4 respectively, the T_1 values of benzene — benzene-d_6 — chloroform-d, and acetone — acetone-d_6 — chloroform-d solutions are shown. The result of T_1 measured in carbon tetrachloride is also shown in Fig. 3. The T_1 values of both benzene and acetone are affected by the presence of chloroform, but not the T_1 of benzene in carbon tetrachloride. These results imply that the molecular motions of

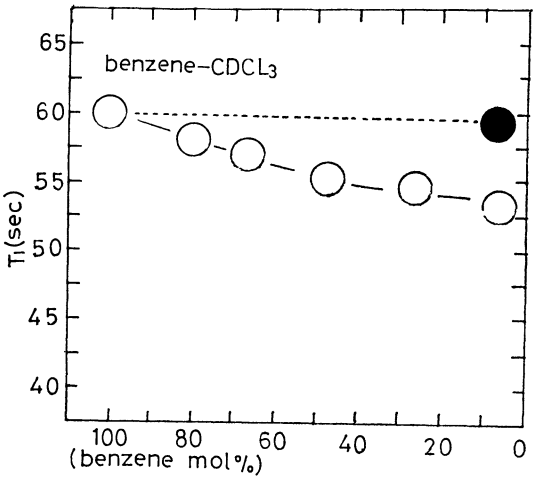

Fig. 3. Plot of T_1's of benzene in chloroform-d (○) and carbontetrachloride (●) *vs.* apparent mole fraction of benzene.
The number density of benzene proton is constant; N= 40.5×10^{20}.
Apparent mole fraction of benzene was varied by addition of benzene-d_6.

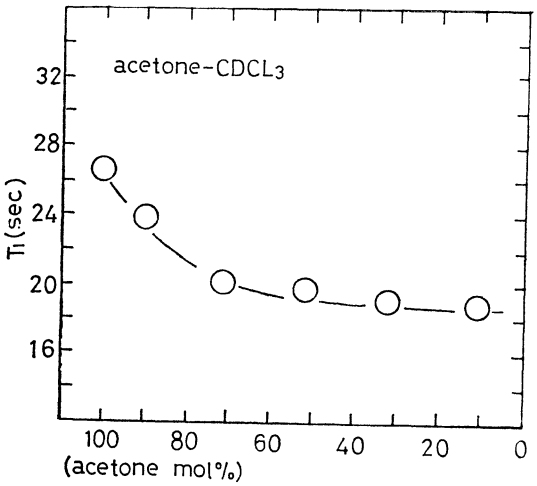

Fig. 4. Plot of T_1's of acetone in chloroform-d *vs.* apparent mole fraction of acetone.
The number density of acetone proton is constant; N= 48.8×10^{20}.
Apparent mole fraction of acetone was varied by addition of acetone-d_6.

benzene and acetone are influenced to some extent by the intermolecular interaction with chloroform, the former due to the π-complex, and the latter, to the hydrogen bond. These results do not, however, coincide with the those of Anderson. We speculate that this discrepancy may arise from the difference in the experimental temperature (Anderson made his experiment at 35°C).

It is reasonable to assume that the intramolecular dipole-dipole relaxation is predominant for both benzene and acetone protons because of their small fractions in the present study. As will be shown later, this assumption is supported by the fact that the τ_c values of benzene and acetone calculated by this assumption correspond to those of Bonera and Rigamonti.[30,2] We calculate τ_c using the following expression:[1,23]

$$(1/T_1)\text{intra} = 3/2\hbar^2\gamma^4 \sum \langle r_{ij}^{-6}\rangle \cdot \tau_c \quad (2)$$

where r_{ij} is the hydrogen-hydrogen interatomic distance. For benzene and acetone, the values of r_{ij} were taken from Zeidler's work.[31]

Chloroform-Benzene Solution. In Table 1, the (T_1) inter, τ_t of chloroform and the (T_1)intra, τ_c of benzene are shown at various solution compositions. The order of the magnitude of τ_t roughly agrees with Hertz's result[2]: 1.1×10^{-10} sec. The values of (T_1) intra and τ_c in neat benzene also agree with those of Bonera and Rigamonti. It may easily be seen that the translational motion of chloroform is not influenced by the π-complex with benzene, but that the rotational motion of benzene is influenced slightly. On the basis of this experimental fact, we conclude that the π-complex does move as a unit, but that its lifetime is short, probably of the order of 10^{-12} sec. According to the theory of Anderson, it is reasonable to consider

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Table 1. The values of (T_1)inter, τ_t (chloroform) and (T_1)intra, τ_c (benzene) of chloroform-benzene solution

Chloroform -benzene mole ratio	Chloroform		Benzene	
	(T_1)inter (sec)	$\tau_t \times 10^{10}$ (sec)	(T_1)intra (sec)	$\tau_c \times 10^{12}$ (sec)
100 : 0	120	2.9		
90 : 10	120	2.9	54	2.1_8
50 : 50	120	2.9	56	2.1_0
0 : 100			60	1.9_6

τ_t and τ_c were calculated by using Eqs. (1) and (2), respectively.

that the association whose lifetime is of the order of 10^{-12} sec does not modulate the molecular motion, the correlation time of which is about 10^{-10} sec. The slight influence on the rotational motion of benzene may be due to the fact that the C_6 rotation (the C_6 axis of benzene coincides with the C_3 axis of chloroform) in the π-complex is almost free. Indeed, Andrew and Eades[32] have found that benzene molecules reorient quite freely about the C_6 axis even in a solid.

The conclusion we proposed above does not conflict with that of Huntress that the tumbling motion of of chloroform is slowed by a factor of 4 by complexing with benzene. That is, the correlation time of the tumbling motion of chloroform is of the order of 10^{-12} sec, sufficiently short to be affected by π-complexing. Anderson has shown experimentally that the intramolecular spin-lattice relaxation of benzene is not affectedgreatly through π-complexing with chloroform at 35°C, and he has suggested that the molecular rotation of benzene about the C_2 axis takes place by large-angle jumps rather than by small diffusive steps. However, in the present study, no such insensibility of the spin-lattice relaxation of benzene to π-complexing was found. It seems necessary to reexamine this problem over a wide range of experimental conditions.

Chloroform-Acetone Solution. In Table 2, the (T_1)inter, τ_t and (T_1)intra, τ_c of chloroform and acetone respectively are shown. The values of (T_1)-intra and τ_c of acetone in neat acetone agree with those of Bonera and Rigamonti. It is clear from the table that both the translational motion of chloroform and the rotational motion of acetone in solution are affected to a certain degree by the intermolecular hydrogen-bonding interaction. Therefore, we may conclude that the hydrogen bond is moderately strong, and that its lifetime is of the order of 10^{-11} sec. One may consider that the association whose lifetime is of the order of 10^{-11} sec should reduce the molecular motion of acetone to a greater extent. According to Debye-B.P.P., τ_c is proportional to the third power of the radius of the molecule. Thus, if the association between chloroform and acetone is rigid and if its lifetime is much longer than the correlation time, the τ_c of acetone in the associated complex may be several times larger than that of acetone in the neat liquid. However, the chloroform-acetone association seems not so rigid as in a single molecule, and the C_3 rotation of the methyl group of acetone in the association is considered to be relatively free. From their line-width measurements Gutowsky and Pake[33] have found that the methyl groups rotate even in solid acetone. Because of these two situations, the τ_c of acetone might not become so large as expected.

Table 2. The values of (T_1)inter, τ_t (chloroform) and (T_1)intra, τ_c (acetone) of chloroform-acetone solutions

Chloroform -acetone mole ratio	Chloroform		acetone	
	(T_1)inter (sec)	$\tau_t \times 10^{10}$ (sec)	(T_1)intra (sec)	$\tau_c \times 10^{12}$ (sec)
100 : 0	120	2.9		
90 : 10	105	3.5	$18._7$	0.9_3
50 : 50	85	4.4	$19._6$	0.9_1
0 : 100			$26._5$	0.6_7

τ_t and τ_c were calculated by using Eqs. (1) and (2), respectively.

We expect that the lifetime of the chloroform-pyridine complex may be of the same order as that of the chloroform-acetone complex, and that the chloroform-DMSO complex may have the longest lifetime of all the solutions studied in this paper. A more detailed consideration of these solutions is possible, the spin-lattice relaxation measurements being made of pyridine and DMSO protons.

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