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Proton Spin-Lattice Relaxation Studies of Intermolecular Interactions in Acetic Acid Solution

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Proton spin-lattice relaxation measurements were carried out by the rapid-passage method on the hydroxyl and methyl protons of acetic acid in carbon tetrachloride, benzene-d_6, and chloroform-d in order to investigate the effect of the self-association of acetic acid on the spin-lattice relaxation. It was found that there exists a maximum of the relaxation rate in carbon tetrachloride, and two maxima in benzene-d_6 and chloroform-d, on dilution with a solvent. This relaxation behavior was attributed to the change in the self-association mechanism of acetic acid. We tried to keep the proton-density constant in all solution in order to avoid any ambiguity arising from the change in density by using the analogous deuterated compounds.

Previously we have studied the effect of the intermolecular interaction on the proton spin-lattice relaxation time, T_1, of chloroform, benzene, and acetone in solution.[1] We found that T_1's are sensitive to the intermolecular interaction or the molecular association, even if its lifetime is very short. In this paper, we will study the spin-lattice relaxation of the hydroxyl and methyl protons of acetic acid in carbon tetrachloride, chloroform-d, and benzene-d_6 respectively.

Hydrogen bonding in carboxylic acids has been investigated by a number of workers using nuclear magentic resonance and infrared spectroscopy.[2–4] Reeves and Schneider[5] have investigated the dilution curves of the chemical shift of the hydroxyl proton of acetic acid in a series of non-interacting solvents, such as carbon tetrachloride and cyclohexane, and found that, on dilution, the resonance moves first to a low field, but on further dilution moves to a higher field compared with its position in pure acetic acid. They have interpreted these results in terms of a polymer-dimer equilibrium in a concentrated acid solution and a dimer-monomer equilibrium in more dilute solutions. Reeves[6] has studied the changes in the chemical shift of the hydroxyl proton in some carboxylic acids on dilution in several solvents, and given evidence for the existence of chain-like hydrogen-bonded polymers in solutions and for the formation of weak acid-solvent complexes in dichloro-

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1) K. Sato and A. Nishioka, This Bulletin, **44**, 1506 (1971).

2) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Company, San Francisco, California (1960).

3) J. C. Davis, Jr., and K. K. Deb, *Adv. Magnetic Resonance*, **4**, chap. 4 (1970).

4) R. Foster and C. A. Fybe, *Progr. NMR Spectry*, **4**, chap. I (1969).

5) L. W. Reeves and W. G. Schneider, *Trans. Faraday Soc.*, **54**, 314 (1958).

6) L. W. Reeves, *Can. J. Chem.*, **39**, 1711 (1961).

methane and 1,2-dichloroethane. Many other chemical shift studies have been made of acetic acid and some carboxylic acids in solutions, and valuable information has been obtained.

Relaxation measurements of carboxylic acids have also been made by several authers. Tatsumoto[7] has studied ultrasonic absorption in propionic acid and discussed the disociation mechanism and the solvent effect on relaxation. Goldammer and Zeidler[8] have measured the proton and deuteron spin-lattice relaxation time of methyl and the self-diffusion coefficient in a binary mixture of water and acetic acid.

It is the purpose of the present study to investigate the effect of the self-association, the change in the association mechanism of acetic acid, and the intermolecular interaction with a solvent on the spin-lattice relaxation, and to discuss the microdynamic behavior of acetic acid in solution. We believe that the information on the microdynamic behavior together with that on the equilibrium properties will aid us in understanding in detail the nature of acetic acid in solution.

Experimental

Materials. The acetic acid was a super-special-grade sample purchased from the Wako Pure Chem. Co., Ltd., and the carbon tetrachloride was a spectroscopic-grade sample purchased from the Tokyo Kasei Co., Ltd. The acetic acid-d_4, benzene-d_6, and chloroform-*d* were provided by E, Merck AG, Darmstadt, and were used without further purification. All the materials were stored in a water-free atmosphere. The proton-density of all the solutions was kept constant by using analogous deuterated compounds in order to avoid any ambiguity in the spin-lattice relaxation arising from its change. In the NMR spectrum at a high gain, no signals due to impurities were observed. The atmospheric oxygen dissolved in the samples was removed carefully by several free-pump-thaw cycles in a NMR sample tube, and then under a vacuum the tube was sealed. After sealing, the NMR measurements were carried out immediately.

NMR Measurements. The NMR spectrometer used in this study was a JNM-C-60H spectrometer of Japan Electron Optics. Lab. operated at 60 MHz. The measurements of T_1 were carried out at 25±1°C by the adiabatic rapid-passage method with sampling. The experimental errors were found to be within ±3%. The corrections for the macroscopic solution viscosity were not carried out.[1]

Results and Discussion

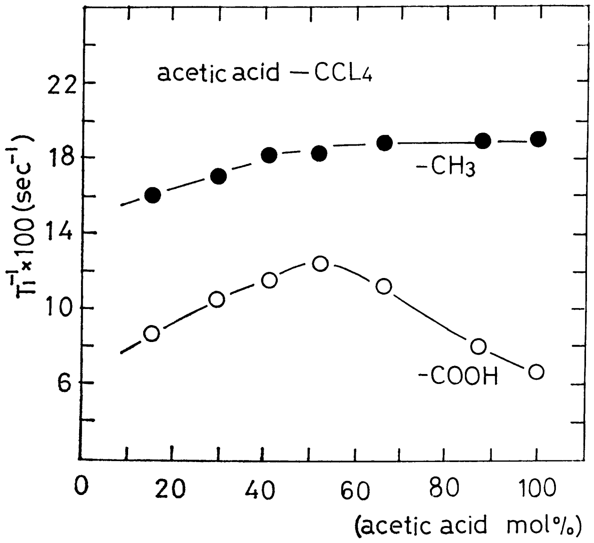

Fig. 1. Plots of $1/T_1$'s of the hydroxyl (○) and methyl (●) protons of acetic acid in carbon tetrachloride *vs.* apparent mole fraction of acetic acid.
The number of protons per unit volume is constant; $N=41.65\times10^{20}$.
Apparent mole fraction of acetic acid was varied by addition of acetic acid-d_4.

Carbon Tetrachloride Solution. In Fig. 1, the spin-lattice relaxation rate T_1^{-1}, of the methyl and hydroxyl proton of acetic acid *versus* the mole fraction of acid is shown. The proton density is constant at all compositions and equals to 41.65×10^{20} per unit of volume. It is clear that, on dilution with carbon tetrachloride, the T_1^{-1} of the hydroxyl proton gradually increases up to a value larger than that in pure acid by a factor of 2 and that a broad maximum exists at 50 mol% of acid. No distinct maximum is observed in the plot of the T_1^{-1} of the methyl *versus* mole fraction of acid, but on dilution beyond 50 mol% the T_1^{-1} decreases distinctly.

Goldammer and Zeidler have shown that the maximum of the relaxation rate of the methyl protons and deuterons exists at 50 mol% of acid in a water-acetic acid system, and that at this concentration the self-diffusion coefficient exhibits the minimum. The disagreement regarding the relaxation behavior of the methyl between their results and those in the present study is considered to reflect the difference in the association mechanism and in the acid-solvent interaction in aqueous and non-polar environments. If the self-diffusion coefficient is determined for a carbon tetrachloride solution, a detailed discussion will be possible.

Over the experimental range of the acid concentration studied, the polymers of acids may be predominant over the cyclic dimer.[9] The minimum of the hydroxyl proton chemical shift has been observed at a lower concentration than 5 mol% of acid in carbon tetrachloride,[5] at which point the dimer should be predominant. Therefore, we will discuss the results of the spin-lattice relaxation studied in this experiment in terms of changes in the length of the polymer chains. On dilution, the length of the chains is considered to increase gradually, probably because of the decrease in the dielectric constant of the solution; the polymer must become more stable and rigid to compensate for the entropy decrease of the solution. As the microdynamic molecular motions of the stable and rigid polymer chains should be reduced extensively compared with those of the weak chains, the spin-lattice relax-

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[7] N. Tatsumoto, *J. Chem. Phys.*, **47**, 4561 (1967).

[8] E. V. Goldammer and M. D. Zeidler, *Ber. Bunsenges. Phys. Chem.*, **73**, 4 (1969).

[9] G. Mavel, *J. Phys. et. Radium*, **21**, 38 (1960).

ation rate must increase by a factor of 2 in the present study. On the other hand, in a solution more dilute than 50 mol% of acid, the polymer chains shorten. Moreover, in this concentration region, the polymer-dimer equilibrium may become appreciable, and the fraction of the dimer increases gradually.

Our interpretation does not conflict with the results of the chemical shift studies. The increase in the chain length on dilution is considered to result in the low field shift of the hydroxyl proton, because the fraction of the terminal acetic acid molecules, whose hydroxyl proton resonates at a higher field than that of the acid participating in the hydrogen bonding, decreases.[6] The observed chemical shift is the average of those of the protons in two different sets of circumstances because of the rapid averaging of the shielding effects. Contrary to the shortening of the chain length, the fraction of the dimer may increase in the lower concentration region. The hydroxyl proton of the dimer is considered to resonate at a lower field than that of acid participating in the internal hydrogen bonding of the chains, because the anisotropy of the susceptibility of the carbonyl group contributes more effectively to the hydroxyl proton of the dimer as a result of the cyclic structure of the dimer.[10] Thus, the average proton resonance may be concluded to move to the low field on dilution.

It may be supposed that, if experimental measurements were made on a solution more dilute than a 5—10 mol% acid solution, spin-lattice relaxation behavior due to the predominant dimer structure might be observed. The experimental results that the T_1^{-1} of the methyl, except in a dilute solution, does not follow the changes in the length of the polymer chains described above probably reflects the relatively free rotation of methyl about the C_3 axis. Indeed, Goldammer and Zeidler have shown that the correlation time of the internal rotation of the methyl is very short compared with that of the rotational motion of the whole molecule.

Benzene and Chloroform Solution. In Fig. 2, the plot of the T_1^{-1} of acetic acid in benzene-d_6 *versus* the acid concentration is shown. Contrary to the results on a carbon tetrachloride solution, two distinct maxima are observed in the relaxation behavior of the hydroxyl proton, but that of the methyl decreases linearly on dilution. We attribute the maximum in the high-concentration region to the changes in the polymer length described in the previous section, and that in the low-concentration region, to the relaxation behavior of the dimer and the dimer—monomer equilibrium which is not observed in carbon tetrachloride.

Shimizu[11] has investigated the change in the chemical shift of acetic acid in benzene, and found that the acid concentration at which the minimum of the hydroxyl proton chemical shift occurs is 30—40 mol%, higher than that in carbon tetrachloride. He has interpreted the results in terms of acid-benzene interaction, in which the acid monomer becomes stable and the monomer fraction is appreciable even in the high-concentration region of acid where, in carbon tetrachloride, the monomer scarcely exists at all. The dimer fraction is considered to be predominant at the acid concentration of 30—40 mol%. At almost the same acid concentration, the maximum of the relaxation rate of the hydroxyl proton is observed. Therefore, our consideration described above is considered probably to be true. Davis and Pitzer[12] have also shown evidence for the interaction between benzene and acetic acid by their chemical shift measurements. In

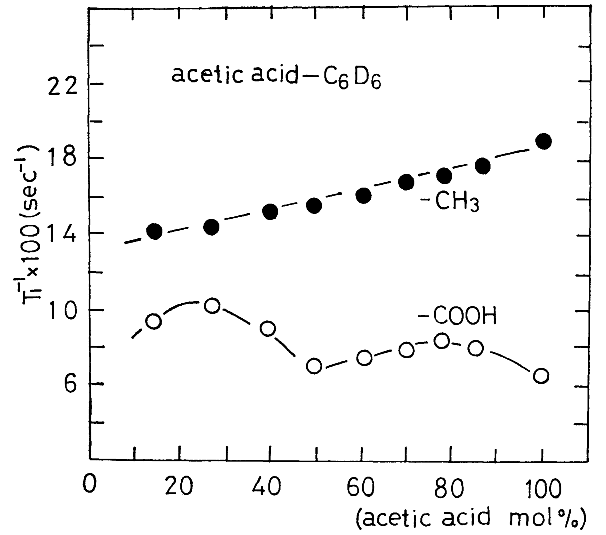

Fig. 2. Plots of $1/T_1$'s of the hydroxyl (○) and methyl (●) protons of acetic acid in benzene-d_6 *vs.* apparent mole fraction of acetic acid.
The number density of protons is constant; $N=41.65\times10^{20}$. Apparent mole fraction of acetic acid was varied by addition of acetic acid-d_4.

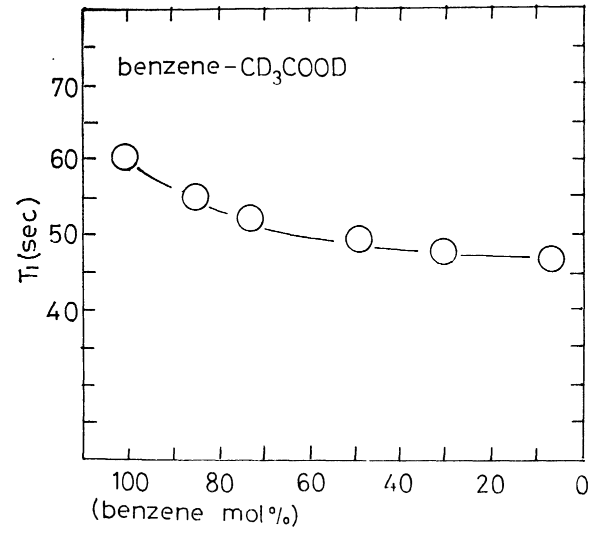

Fig. 3. Plot of $1/T_1$'s of benzene in acetic acid-d_4 *vs.* apparent mole fraction of benzene.
The number density of protons is constant; $N=40.5\times10^{20}$. Apparent mole fraction of benzene was varied by addition of benzene-d_6.

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[10] N. Nakagawa, *Kagaku no Ryoiki*, **15**, 665 (1961).

[11] H. Shimizu, *Nippon Kagaku Zasshi*, **81**, 1025 (1960).

[12] J. C. Davis, Jr., and K. S. Pitzer, *J. Phys. Chem.*, **64**, 886 (1960).

Fig. 3, the T_1's of benzene in acetic acid-d_6 are shown *versus* the mole fraction of benzene. It is clear that the spin-lattice relaxation of benzene is affected by the presence of acetic acid. This implies that the interaction between benzene and acetic acid exists and influences the microdynamic molecular motion to the degree of changing the spin-lattice relaxation behavior.

It has been well known that the dimer form of acetic acid is considerably stable. For example, Reeves and Schneider[5] have shown that, even in the gaseous state, the acetic acid dimer exists. Therefore, we consider that the decrease in the microdynamic molecular mobility and the relaxation rate of the dimer should be greater than those of the monomer and the less stable polymers. This expectation can be clearly verified from Fig. 2. Recently, Rothschild[13] has studied the translational molecular motion of neat acetic acid and discussed the possibility that the dimeric form is stable and can perform the translational jumps as a unit. The relaxation rates of the polymers in benzene are smaller than those in carbon tetrachloride, and the position of the maximum in the former deviates to a higher acid-concentration region than that in the latter. It is suggested that the polymer chains become less stable and weak through the acid-benzene interaction and show a tendency to shorten in the higher-acid-concentration region.

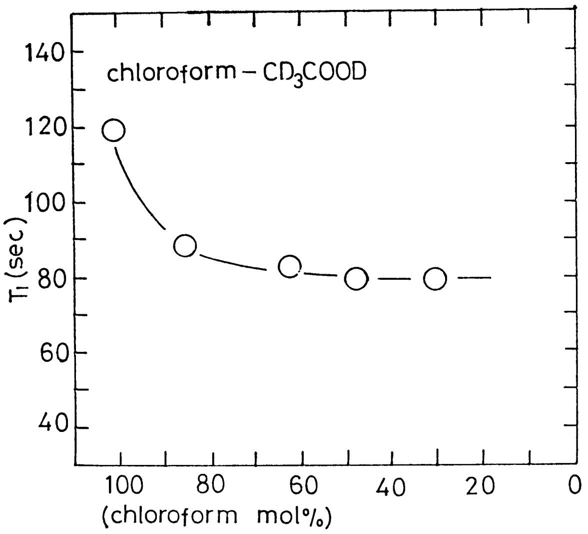

Fig. 5. Plot of $1/T_1$'s of chloroform in acetic acid-d_4 *vs.* apparent mole fraction of chloroform.
The number density of protons is constant; $N = 29.8 \times 10^{20}$. Apparent mole fraction of chloroform was varied by addition of chloroform-*d*.

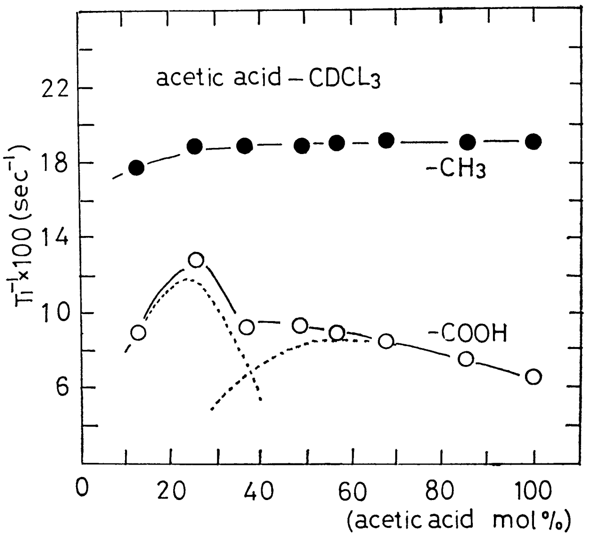

Fig. 4. Plots of $1/T_1$'s of the hydroxyl (○) and methyl (●) protons of acetic acid in chloroform-*d* *vs.* apparent mole fraction of acetic acid.
The number density of protons is constant; $N = 41.65 \times 10^{20}$. Apparent mole fraction of acetic acid was varied by addition of acetic acid-d_4.

In Fig. 4, the plot of T_1^{-1} of acetic acid in chloroform-*d* is shown *versus* the acid concentration. It seems reasonable to decompose the curve thus obtained into two relaxation curves. In chloroform, there exist two maxima, just as in benzene. The one appearing at the low acid concentration is considered to reflect the relaxation behavior of the predominant dimer, while the other, at the high concentration, may be due to the relaxation of the polymers. Except for the position of the maximum at the high concentration, the other relaxation behavior, such as the relaxation rate and the position of the maximum at the low concentration, is almost identical with that in benzene. The small difference between the two cases may arise from the difference in the acid-solvent interactions. Chloroform interacts with acetic acid, and the spin-lattice relaxation is affected by the chloroform-acid interaction, as is shown in Fig. 5.

It was found that the self-association of acetic acid exerts a pronounced effect on the spin-lattice relaxation of the hydroxyl proton, and that the relaxation behavior largely depends upon the concentration of acid and the kind of solvents. The spin-lattice relaxation study may provide useful information about the microdynamic molecular motion of acid and may, together with the chemical shift and infrared measurements, allow us to infer the mechanism and the nature of the self-association of acetic acid.

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[13] W. Rothschild, *J. Chem. Phys.*, **53**, 3265 (1970).