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Electric Field Induced Changes of Spin Lattice Relaxation Time T_1 in Polar Liquids

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T_1 was found to change linearly with applied electric field for the liquids nitrobenzene, chlorobenzene, ether and dioxane; no change was observed in hexane and cyclohexane. These substantial reductions in T_1 are explained in terms of quasi-crystalline structures in the liquid.

1 INTRODUCTION

Whenever an electric field E is applied to a polar liquid there will be a partial alignment of the dipoles in the direction of the field. The ordering effect of the field will be in competition with the randomizing influence of thermal motion.[1] The degree of ordering is usually expressed in terms of $\langle \cos \theta \rangle_E$ where θ is the angle between the dipole and the field direction. This ordering effect is central to studies such as non-linear dielectrics,[2] electric birefringence, etc.[3]

The effect of applied electric fields on nuclear magnetic dipole-dipole coupling for polar molecules has been considered by a number of workers.[3–6] The earliest attempts to detect electric field effects in an NMR spectrum were made by Buckingham and McLauchlan[7] and Deutch and Waugh[8] using continuous wave techniques. The former authors[7] reported a spectral shift for p-nitrotoluene, whereas the latter workers were unable to detect any effect in the materials they investigated. A subsequent detailed theoretical and experimental investigation using pulse techniques was made by Sears and Hahn.[9,10] Sears and Hahn[10] measured a spectral shift in *p*-nitrotoluene of approximately 25% of that reported in Ref (7). Electric field effects involving quadrupolar nuclei have been reported by McLean and his co-workers[11,12] In all of these NMR studies the theory has involved changes in the ensemble averages for the various terms of the dipolar Hamiltonian as a function of the applied electric field interaction with the electric dipole; much of the discussion has centered on various local field models, Onsager, Lorentz, etc. Sears and Hahn[9] expected the changes in T_1 to be quadratic in field and of the order of, or less than, one part in ten thousand and hence did not investigate the existence of such an effect.

Pajak and Pislewski in a brief conference report[13] some two years later, however, describe significant changes in T_1 due to an electric field for a number of polar liquids namely nitrobenzene, thiophene, furan and diethyl ether. Application of large electric fields to non-polar solvents (cyclohexane, cyclopentane, hexane and benzene) failed to give any effect. The sample cell used was of glass with platinum electrodes the samples being degassed using the freeze-thaw technique. The possible importance of impurities was studied by measuring benzene samples which were dry degassed, dry non-degassed and moist degassed; while the absolute value of T_1 was different for each sample, in none of these cases was a field effect seen.

The present paper is a preliminary report of measurements of the spin lattice relaxation time T_1 which have been made in a number of polar and non-polar solvents. The observed effects are similar to those observed by Pajak and Pislewski.[13] The explanation of these effects is not possible in terms of the previous theories,[9] as the changes are much larger than predicted and are not quadratic in field. The measured linear dependence on E suggests the possible formation of small areas of an ordered state, perhaps analogous to liquid crystalline structures.

2 EXPERIMENTAL

Measurements of the spin lattice relaxation time T_1 have been made using the 180°–90° pulse method. The studies were made at 40 MHz and a temperature of 20 ± 0.1°C. The sample cell consisted of a glass tube containing brass or copper electrodes, and a teflon insert which acted to separate the electrodes and to restrict the sample to the volume between the electrodes which was in turn at the centre of the sample coil. The effect was insensitive to the direction of the electric field. The electrodes were typically 5 mm apart and fields of up to 3×10^6 V m^{-1} were applied to the sample.

The samples were obtained from BDH Ltd. All samples were doubly distilled and dried before use. The sample tube was evacuated and the liquids degassed by the freeze-thaw technique before the measurements were taken. Measurements were taken for increasing and decreasing fields.

3 RESULTS

Measurements of T_1 were made on the solvents cyclohexane, hexane, dioxane, diethyl-ether, chlorobenzene and nitrobenzene. T_1 was found to be independent of field for the non-polar solvents cyclohexane and hexane in all cases. T_1 on the other hand was found to decrease with increasing field E for the other liquids, the effect increasing in magnitude in going from dioxane to ether to chlorobenzene to nitrobenzene. In the case of nitrobenzene T_1 decreased from 6.4 secs at $E = 0$ to 3.0 secs at $E = 6 \times 10^5$ V m^{-1}. (This is comparable to the change observed by Pajak and Pislewski.)[13] The results are presented in a form of a graph of $T_1^{E=0}/T_1^E$ against E in Figure 1. Table I shows the values of $T_1^{E=0}$ together with various derived quantities which will be discussed in the next section. The error in $T_1^{E=0}/T_1^E$ is 10% and in E 5%.

4 DISCUSSION

Pajak and Pislewski[13] explained their results in terms of what they termed a quasi-crystalline phase. This term has been used rather diversely by different authors[14] and it would appear that Pajak and Pislewski are using the term in a somewhat loose sense to denote a phase of the liquid different from the bulk. They envisaged two distinct spin lattice relaxation times for the bulk and for the quasi-crystalline states which they denote T_1^l and T_1^q respectively.

Assuming the correlation times to be much shorter than the life-time of the molecules in the quasi-crystalline phase, and the fraction of molecules in this phase to be α then,

$$\frac{1}{T_1^E} = \frac{\alpha}{T_1^q} + \frac{1-\alpha}{T_1^l} \tag{1}$$

α will be made up of two parts, one corresponding to quasicrystalline structures produced by the applied electric field (α_E), and the other due to the ionic electric fields (solvation shells) denoted by α_0; hence

$$\alpha = \alpha_E + \alpha_0 \tag{2}$$

The value of α_0 will of course depend on the number of ions in the liquid.

In the presence of a d.c. field (even a small field compared to the lowest fields applied here) a substantial number of ions will be removed. Let the coefficient corresponding to this situation be α_0. If on the other hand $E = 0$ then a larger number of ions will be in solution increasing α_0 to α_0' say and reducing the value of T_1. Extrapolation of the high field data to zero field would in effect give us the situation corresponding to α_0, but at zero field.

The nature of the quasi-crystalline phase is not clear at the present time. However, it is quite conceivable that small elements of a phase similar to those in liquid crystals is involved. Measurements of the spin lattice relaxation time T_1 as a function of temperature have been carried out for well known liquid crystalline materials near the transition temperature from the isotropic to the anisotropic phase. Runyan and Nolle,[15] for instance, found that T_1 began to decrease several degrees above the accepted transition temperature. They conclude that these pretransitional changes in the isotropic liquid phase are due to the formation of clusters of the anisotropic phase. For molecules in such clusters certain thermal orientations are hindered and the correlation times are modified, hence changing T_1. The existence of similar small volumes of ordered molecules due to the application of a large electric field in the polar solvents studied here could well account for the effect.

Assuming that the amount of the quasi-crystalline phase formed is proportional to the degree of orientation;

$$\alpha_E = |C\langle\cos\theta\rangle_E| \tag{3}$$

where C is the constant of proportionality and

$$\langle\cos\theta\rangle_E = L(y) \tag{4}$$

where $L(y)$ is the Langevin function and $y = \mu E/kT$. μ is the electric dipole moment of the molecule, k Boltzman's constant and T the temperature.

Now

$$L(y) = \frac{\mu E}{3\,kT} - \frac{\mu^3 E^3}{45\,k^3 T^3} + \cdots \tag{5}$$

Since for the dipoles and fields used here $y \ll 1$ it is a good approximation to write

$$\langle\cos\theta\rangle_E = \mu E/3\,kT \tag{6}$$

hence

$$\alpha_E = C\mu|E|/3\,kT \tag{7}$$

Using equations (1), (2) and (7) and assuming that $\alpha \ll 1$ gives

$$\frac{T_1^{E=0}}{T_1^E} = \frac{T_1^{E=0}}{T_1^q}\frac{C\mu}{3\,kT}|E| + \frac{T_1^{E=0}}{T_1^l} + \frac{\alpha_0 T_1^{E=0}}{T_1^q} \tag{8}$$

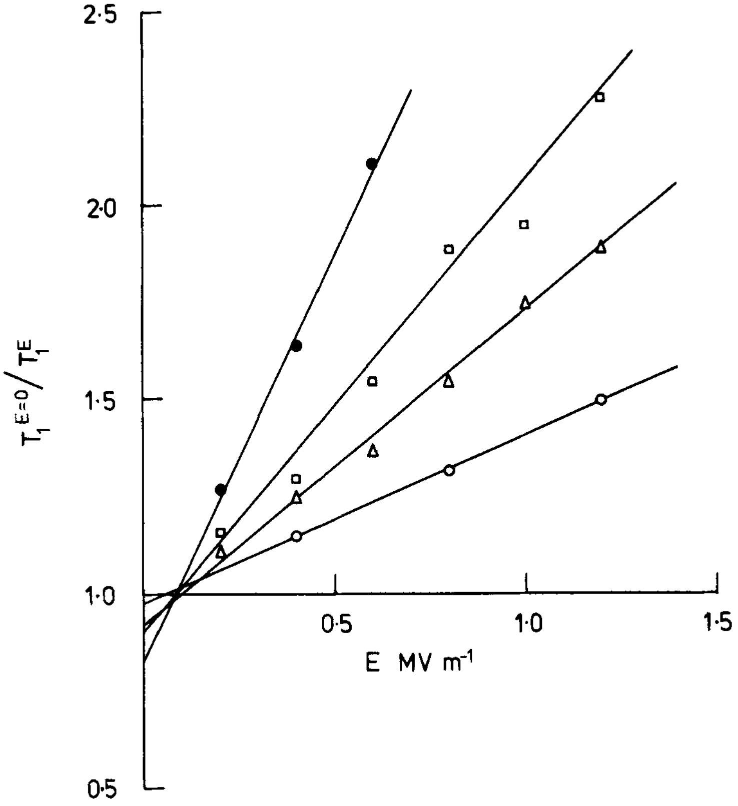

FIGURE 1 Plot of $T_1^{E=0}/T_1^E$ against field in MV m^{-1} at 40 MHz and 293 K. Open circles, dioxane; triangles, diethyl-ether; squares, chlorobenzene; closed circles, nitrobenzene.

According to this treatment a plot of $T_1^{E=0}/T_1^E$ against E should give a straight line the slope of which will depend directly on μ and inversely on T and T_1^q. Previous discussion of α_0 and α_0' means that the point at $E = 0$ should be neglected in determining this slope.

The data for dioxane, ether, chlorobenzene and nitrobenzene are shown plotted in this way in Figure 1. The data for cyclohexane and hexane are not shown in this figure but would correspond to a horizontal line at $T_1^{E=0}/T_1^E = 1$. The lines drawn in Figure 1 correspond to a least squares fit determination neglecting the point at $E = 0$ as discussed previously. The points are seen to be good fits to straight lines as evidenced by the coefficients of determination which vary from 0.98 for chlorobenzene to 1.00 for dioxane.

It would appear that in general terms the model adopted here is acceptable; certainly the changes in relaxation time are linearly dependent on the field, and not quadratically dependent as predicted from previous considerations.[9]

TABLE I

Dipole moment and spin lattice relaxation data for polar molecules in study

Liquid	Dipole moment (cm)	T_1^q (ms)	$T_1^{E=0}$ (s)	T_1^E by extra polation (s)
Dioxane	3.33×10^{-31}	0.3	4.5	4.6
Diethyl-ether	3.90×10^{-30}	4.8	12.1	13.2
Chlorobenzene	5.82×10^{-30}	5.2	12.1	13.4
Nitrobenzene	1.43×10^{-29}	3.5	6.4	7.8

Extrapolation of the lines to zero field give the T_1 values corresponding to the partial removal of ions by the field; the values quoted are those derived numerically from the least-squares analysis.

Interpretation of the slopes of these curves in terms of molecular parameters is speculative at this stage. However, if it is assumed that $C = 1$ then values of T_1^q can be determined. Taking $T = 293$ K, Boltzmanns' constant $k = 1.38 \times 10^{-23}$ J K^{-1}, and using the vapour phase dipole moments of the molecules as listed in Table I,[16] T_1^q can be calculated and is given in the table. (The effective dipole moment of dioxane in the liquid state is a matter of dispute[17] and the value listed here is somewhat arbitrary). The values of T_1^q are seen to be about 4 ms except for dioxane. The T_1^q value for dioxane depends obviously on the μ chosen, but in any case is certainly much less than for the other liquids.

Measurements using different samples and or different electrode materials, while giving different absolute values of T_1 due to impurities, etc., all gave substantially the same dependence on electric field as shown here.

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