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T_{1e} and T_2 Relaxation Times of Some Free Radical Solutions as Function of the Radical Concentration

by

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T_{1e} and T_2 Relaxation Times of Some Free Radical Solutions as Function of the Radical Concentration

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T_{1e} and T_2 relaxation times of diphenyl, tetracyanoethylen (TCNE) and α, α'-dipyridyl radicals prepared in THF in various concentrations have been measured by using a double resonance weak-field spectrometer, constructed in this laboratory. The theory and technique of measurement have been given, and the results obtained have been discused.

INTRODUCTION

The variation of the electron polarization in a sulution, which contains electron and nuclear spins affects the nuclear polarization. This effect is known as Overhauser-effect [1], [2]. As a result of the Overhauser -effect the dynamic nuclear polarization arises and the species and the strength of this polarization depend on the origin of the spins, magnetic field strength and the saturation degree of the electron spin resonance. In the steady state, for the dynamic nuclear polarization, the following equation can be written [3].

$$\frac{P_z}{P_o} = 1 + \rho f s \frac{\gamma_s}{\gamma_I} \qquad (1)$$

where, P_z is the excited nuclear polarization and P_o is the nuclear polarization in the thermal equilibrium. The parameters which are shown in the equation have the following meanings: ρ, is a coupling parameter which depends on the origin of the interactions between nuclear and electron spins. In the case of the sufficiently rapid molecular motions ($\omega^2_s \tau^2_c \ll 1$) ρ can be taken as 1/2 for dipolar and 1 for scalar coupling. f, is the distribution factor which depends only on the nuclear relaxation. The value of f is in between O and 1, and it can be expressed as

$$f = \frac{T_1}{T_1'} = \frac{T_{10}}{T_1' + T_{10}} = 1 - \frac{T_1}{T_{10}} \tag{2}$$

where, T_1 is the total nuclear relaxation time of the radical solution, T_1' is the relaxation time arising from the coupling of the electron spins and T_{10} is the relaxation time which is originated from the other mechanisms in the pure solvent. s is the saturation parameter which depends only on the properties of the electron spins, such as electron spin relaxation and the shape of the resonance curve and it is defined as

$$s = \frac{\Pi_0 - \Pi_z}{\Pi_0} \qquad 0 \leqq s \leqq 1 \tag{3}$$

where Π_z is the electron spin polarization excited with the resonance and Π_0 is the value of the same quantity in the thermal equilibrium. γ_s, γ_I are the gyromagnetic ratios of the electron and nucleus respectively.

By using the representation,

$$F = \rho f \frac{\gamma_s}{\gamma_I} \tag{4}$$

equation (1) can be written as

$$\frac{P_z}{P_o} = 1 - Fs \tag{5}$$

In this equation F is the extrapolated enhancement factor and it can be determined by extrapolating of the saturation curve (s = 1). It is evident that for the pure dipol - dipol coupling the value of the enhancement factor of the nuclear polarization $(P_z - P_o) / P_o$ is equal to -330.

The state of a radical in a magnetic field can be expressed by a wave function Ψ_m and for a magnetic quantum number m, electron polarization leads to

$$\Pi_z = -\frac{1}{S} \sum_m (m | S_z | m) \frac{N_m}{N} \tag{6}$$

[4], [5]; where S_z is the component of the spin operator S (S_x, S_y, S_z) in the z direction and N_m is the population in the Ψ_m state. The summation is made all over the states in order to find the total electron polarization in the same direction.

A high frequency field excites some transitions between the energy levels of the magnetic dipol, if the frequency of the magnetic field is near the appropriate transition frequency of the system. Hence the polarization given by the equation (6) will be affected by these transitions. By calculating the transition probability for absorption or emission in the unit time by means of the perturbation theory, the following equation can be obtained,

$$W_{ik} = 2\pi\gamma_s^2 H_1^2 g(\omega - \omega_{ik}) \, |(m_i | S_x | m_k)|^2 \tag{7}$$

The shape function $g(\omega - \omega_{ik})$ which is shown in this equation, is normalized as,

$$\int_{-\infty}^{+\infty} g(\omega - \omega_{ik}) \, d\omega_{ik} = 1 \tag{8}$$

and the function reachs its maxima for the value $g(0) = \frac{T^{ik}}{\pi}$

This relation gives also the theoretical definition of the transversal relaxation time T_2^{ik}.

The population which is changed in any energy state m, due to the transitions, is given by a differential equations system,

$$\frac{dN_m}{dt} = \sum_m [-N_m (W_{mn} + w_{mn}) + N_n (W_{nm} + w_{nm})] \tag{9}$$

where, w_{mn} , w_{nm} are the upward and downward transitions probabilities for the stimulated transitions and they are exactly equal each other according to the equation (8), and W_{mn} and W_{nm} are the relaxation transition probabilities per spin per unit time due to the spin - lattice coupling. The relation between these probabilities can be given as,

$$\frac{W_{nm}}{W_{mn}} = e^{\frac{-\hbar\omega_{nm}}{kT}} \tag{10}$$

By using equations (3), (6), (8), and (9), s which describes the properties of the electron spin system can be obtained [4]. The value of s depends on the shape of the ESR spectrum. If $S = \frac{1}{2}$ and $I = 0$, the hyperfine structure can not be expected, that means, there is only one ESR line in the spectrum. In this case s has the following form,

$$s = \frac{\sigma g\,(\omega - \omega_o)}{1+\sigma g\,(\omega-\omega_o)} \tag{11}$$

where,

$$\sigma = \pi\gamma_s^2\, H^2_1\, T_{1e} \tag{12}$$

and ω_o is the transition frequency. When $\sigma g \gg 1$, s approachs 1. In this case, by measuring P_z / P_o , the value of F can be calculated by means of the equation (5). By using F and P_z / P_o value measured under the condition of $\sigma g \ll 1$, s can be found from the same equation, but in this case equation (11) becomes,

$$s = \sigma g\,(\omega - \omega_o) \tag{13}$$

Therefore the value of σ can be easily determined. Hence using this result and the equation (12) T_{1e} can be found. On the other hand the shape of $g(\omega-\omega_o)$ renders possible to evaluate T_2.

If there is separated hyperfine structure in the spectrum, s can be given as,

$$s = \sum_{ik} \frac{\sigma_{ik}\; g\,(\omega - \omega_{ik})}{1 + \sigma_{ik}\; g(\omega - \omega_{ik})}\; h\,(\omega_{ik}) \tag{14}$$

where the summation is made all over ik transitions and,

$$\sigma_{ik} = 4\pi \gamma_s^2 H_1^2 T_{1e}^{ik} \,|\,(m_i \,|\, S_x \,|\, m_k)\,|^2 \tag{15}$$

and

$$\sum_{ik} h\ (\omega_{ik}) = 1 \tag{16}$$

where $h(\omega_{ik})$ is a correction factor for ESR line. Generally there are too many lines in a ESR spectrum and usually these lines are not separated. Therefore it is possible to write the summation in the equation (14) as an integral form

$$s = \int_{-\infty}^{+\infty} \frac{\sigma_{ik}\ g\ (\omega - \omega_{ik})}{1 + \sigma_{ik}\ g(\omega - \omega_{ik})}.\ h\ (\omega_{ik})\ d\omega_{ik} \qquad 17$$

where

$$\int_{-\infty}^{+\infty} h\ (\omega_{ik})\ d\omega_{ik} = 1 \tag{18}$$

The equation (17) can be used for the ESR lines which are broadened inhomogeneously. The evaluation of this integral is not difficult, if the inhomogeneous brodening is larger than the line-width of a single ESR line or if the local field distribution has a Lorentz form.

In the first case, the broadening must not be resulted from the saturation. This condition can be fulfilled by using sufficiently weak H_1 during the measurement of ESR - line. If $g(\omega - \omega_{ik})$ has a Lorentz form, this function can be writen as

$$g\ (\omega - \omega_{ik}) = \frac{T_2^{ik}}{\pi} \ \frac{1}{1 + (\omega - \omega_{ik})^2\ (T_2^{ik})^2} \tag{19}$$

and in this case all the T_{1e}^{ik} are equal to the T_{2e}^{ik} in the ESR-line frequency interval. According to this result, equation (17) gives

$$s = \frac{\sigma\ h\ (\omega)}{\sqrt{1 + \frac{\sigma}{\pi} T_{2e}}} \tag{20}$$

In the second case, the local field dustribution has a Lorentz form,

$$h\,(\omega_{ik} - \omega_o) = \frac{\tau_o}{\pi} \cdot \frac{1}{1 + (\omega_{ik} - \omega_o)^2\, \tau^2_o} \qquad (21)$$

and the equation (17) gives

$$s = \frac{\frac{\sigma}{\pi}}{\sqrt{1 + \frac{\sigma}{\pi} T_{2e}}} \cdot \frac{\tau}{1 + (\omega_{ik} - \omega_o)^2\, \tau^2} \qquad (22)$$

where τ is given by the folllowing equation,

$$\frac{1}{\tau} = \frac{1}{\tau_o} + \frac{1}{T_{2e}} \sqrt{1 + \frac{\sigma}{\pi} T_{2e}} \qquad (23)$$

In order to determine T_{1e}, it is necessary to measure the dependence of P_z / P_o on the ESR frequency for $\frac{\sigma}{\pi} T_{2e} \ll 1$. Hence, in the first case h (ω) and in the second case the line width parameter $\tau\,(H_1)$ of the Lorentz curve can be found. When the inhomogeneous broadening is large, s can be determined by means of F using a P_z/P_o value measured in the sufficiently weak H_1. It is possible to determine σ from the equation (20) by using the calculated value of s and T_{1e} can be found.

It is convenient to use the equation (22) for the high H_1. In this case, there is no importance of the shape function because of the existing saturation, and F can be obtained from the saturation curve. If a series of $P_z / P_o\,(H_1)$ measurements are performed for $\omega = \omega_o$, a limited P_z/P_o value can be determined by extrapolating H_1 to infinity. Under these conditions s is equal to 1, hence F can be easliy calculated.

EXPERIMENTAL

A. Spectrometer

The system used in the present work is a double resonance weak field spectrometer. The block diagram of this spectrometer is shown in Fig. 1.

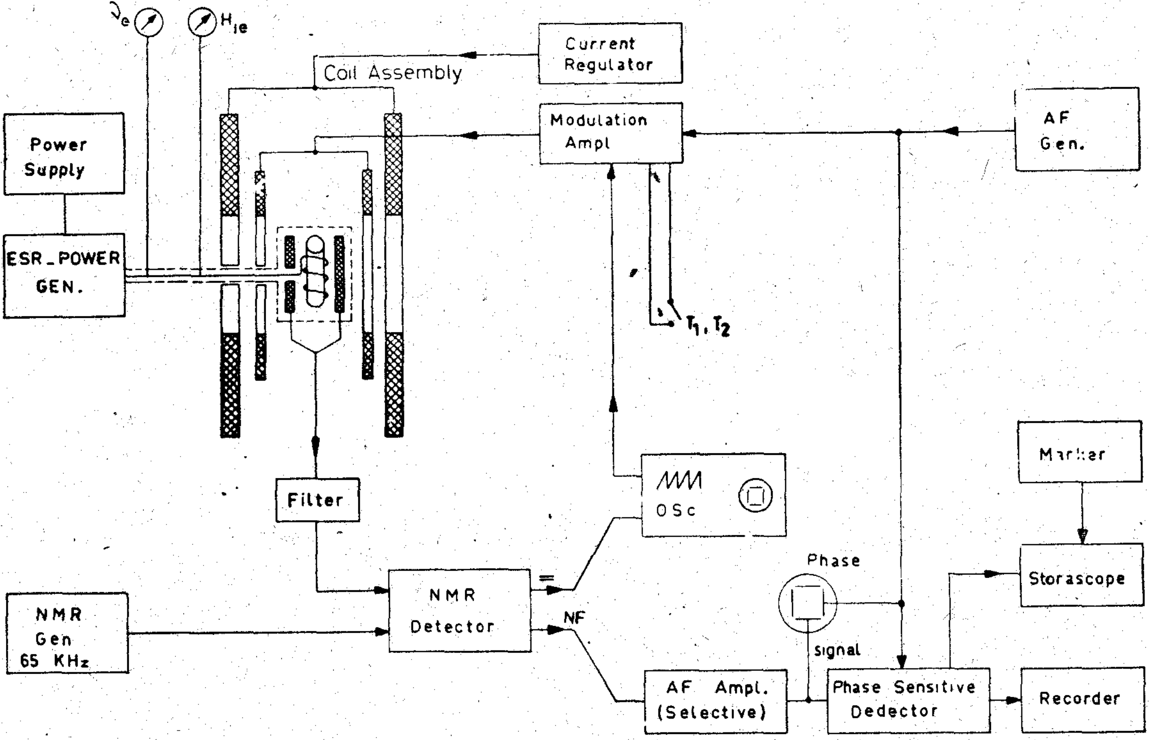
ν_e
H_{1e}
Current Regulator
Coil Assembly
Power Supply
ESR_POWER GEN.
Modulation Ampl
AF Gen.
T_1, T_2
Filter
OSc
Marker
Storascope
Phase
NMR Gen 65 KHz
NMR Detector
=
NF
signal
AF Ampl. (Selective)
Phase Sensitive Dedector
Recorder

Fig. 1

The static magnetic field H_0 (= 15 oe) of this spectrometer has been obtained by a Helmholtz coils system of 300 - 300 turns and 80 cm in diameter, with a stabilized current of 2 amps. Another Helmholtz field modulation system which has 300-300 turns has been placed coaxially between the static field coils. These coils have been fed by a sawtooth or a sin - voltage generator according to the type of modulation needed. The sawtooth and alternating field modulations have been produced by means of an oscilloscope Tektronix 534A and an audio frequency generator Hewlett Packard 200AB respectively. A modulation amplifier has been used either for DC sawtooth or AC modulation field currents.

The sharp absorption signal and the number of wiggles observed on the scope, in the case of DC modulation, is a measure of the homogeneity of the H_0 which is extremely important for the sensitivity of the spectrometer (Fig. 2.) As a further precaution, a small permenant magnet has been used to change the field gradient in the vicinity of the sample head to obtain the possible field homogeneity in the spectrometer.

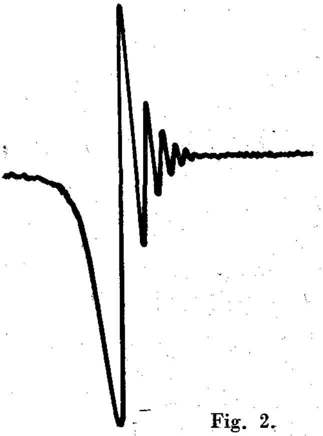

Fig. 2.

The rapid modulation technique (modulation frequency$\gg$ linewidth) has been used for the measurements [6] and the spectrometer system have been adjusted for the modulation frequency of 93 cps.

The sample head which is just placed in the middle of the axis of the coils systems consists of two small coils which are wound one over the other. Common axis of these coils is perpendicular to that of the field coils. The inner one which is called ESR coil was made from silver coated copper wire and it has only four turns. This coil has been used to produce high frequency field H_{1e} .

ESR spectrum has been obtained by using a high frequency voltage generator, Wandel and Goltermann Type LMS-68 with an out put of max 10 V_{eff}. Special matching boxes have been constructed working in the successive intervals of the frequencies between 20 - 80 Mc and they have been used to transfer by amplifying the out put voltage of the generator to the ESR coil. Even if the coupling boxes are used, the saturation of the samples were not possible. Therefor, a special oscillator has been made and used for the measurements which were taken in the vicinity of the saturation. The output of this generator was about 300 V_{eff} around 43 Mc.

The outer coil of the sample head is the nuclear resonance coil which has about 350 turns. This coil was connected through a high frequency filter to the NMR detector which is fed by a quartz genenerator of 65 Kc. This frequency corresponds to the proton resonance frequeny for the static field of the spectrometer used in the present work.

A sample placed in sample head causes an absorption, for each modulation cycle, and an absorption signal can be detected through Q -meter, high frequency amplifier and demodulation parts of the NMR detector. This absorption signal can be taken directly on a scope when DC modulation was used, by making the connections in Fig. 1. The out put of the detector is connected to a narrow band amplifier equiped a filter for 93 cps which is used as modulation frequency. Using audio frequency AC modulation, the signal can be taken again on a scope, by connecting the out put of the narrow band amplifier and the modulation generator vertical and horizontal plates respectively.

The signal can be recorded by connecting the out put of a phase sensitive detector to the recorder. The signals have been registered by using either a Hartmann and Braun Minicomp LB recorder or a Wandel and Goltermann BLS 218 storascope.

B. Determination of the field constant of ESR coil

The measurement of T_{1e} is a little complicated and depends on the determination of some other quantities. High frequency field H_{1e} which is produced by the ESR coil has a special importance for this measurement. H_{1e} should be precisely calculated by using V_{1e} and therefore the proportionality constant between H_{1e} and the other measured values should be determined.

The experimental method, which is more favourable than the theoretical way, has been used to determine this constant.

H_{1e} can be found by measuring the relaxation time T_{1e} and by calculating σ for a sample from the equation (12). For this purpose $(SO_3)_2\ NO^{--}$ ions, which are prepared by solwing $K_2(SO_3)_2\ NO$ in water and in the nitrogen atmosphere, were used.

ESR frequency dependence of $|P_z / P_o| + 1$ quantity of these ions is shown in Fig.3. This measurement has been performed in a constant H_{1e} (eff) and especially far from the saturation. The transition frequencies of these ions have been already observed [3], [4]. The curve shown in Fig. 3. is the hyperfine structural line of these ions and corresponds to $m = -\frac{1}{2} \rightarrow +\frac{1}{2}$ transition around 68.6 Mc. This curve has a Lorentz shape and T_{2e}, which is equal to T_{1e} in this case, can be easily determined from its line width

$$\frac{1}{T_{2e}} = \Delta\omega = 2\pi . \Delta\nu$$

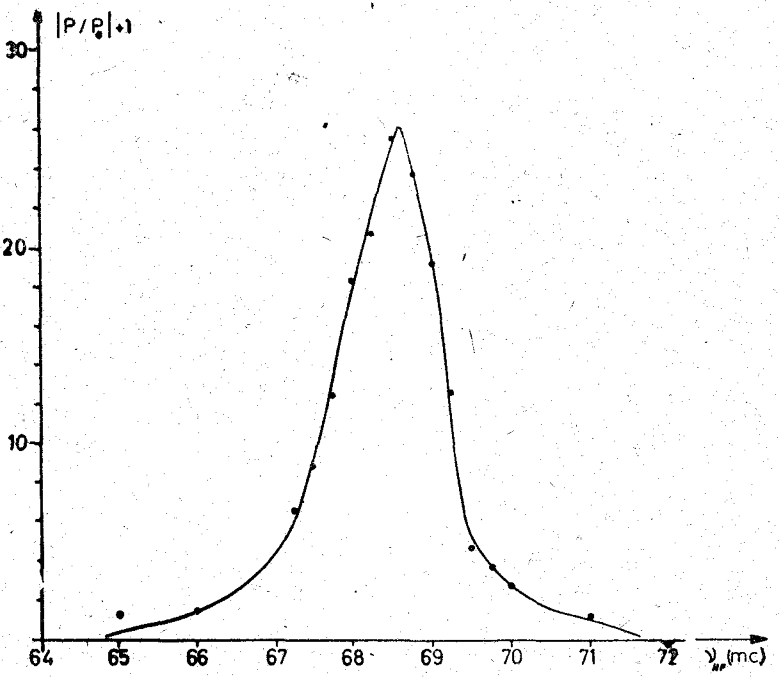

Fig. 3.

This equality is only valid, if there is no oxygen in the solution [7] and in the absence of saturation broadining.Hence T_{1e} has been found as 2.2 10^{-7} sec. On the other hand F has been determined from P_z / P_o (H_{1e}) measurement for the same frequency. The result of these measurements are shown in Fig. 4. The value of F has been estimated as 48.8 by extrapolating H_{1e} to the infinity and s has been calculated as 9.74 10^{-2} by using P_z / P_o measurement, for very weak H_{1e} (V_{1e} = 16 volts), and the enhencement factor F. Equation (19) gives 7.00 10^{-8} sec for g (ω_o) in the case of $\omega = \omega_o$ as the curve has a Lorentz shape. By using these results σ has been found as 1.39 10^6 $\sec^{-2}$ from the equation (13) and H_{1e} have been calculated as 8.11 10^{-2} oe from the equation (12).

H_{1e} is proportional to the HF current, so,

$$H_{1e} = K I_{1e} \cdot$$

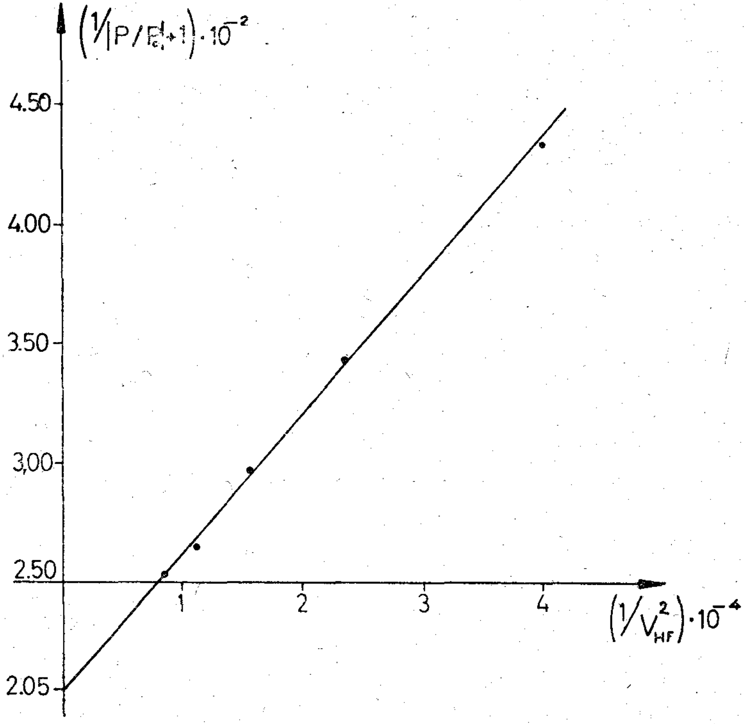

Fig. 4.

can be written. Omiting the resistance of the coil of four turns which is made of copper wire of 3 mm in diameter,

$$H_{1e} = K' \frac{V_{1e}}{\nu}$$

can be writen, where ν is the frequency of V_{1e} and K'is the ESR coil constant. K'has been found as 1,16 10^3 C. G. S. by using the calculated data.

C. The measurement of the nuclêar relaxation time T_2 and the determination of the concentrations of the free radical solutions

To measure nuclear relaxation time T_2, the side bands must be just separated from the central line of the NMR signal obtained by the rapid moulation technique [6]. This separation can be obtained by adjusting the modulation parameter and H_{1e}. ($\gamma H_m / \omega_m$ is called modulation parameter, where γ is the gyromagnetic ratio of the nuclei, H_m is modulation field amplitude and ω_m is the modulation frequency). After the nuclear magnetization has built up in the magnetic field between the upper side band and the central line, adiabatic fast passage brings the DC static field to the center of the central line [8]. The decay of the transverse magnetization can be mesaured by the dispertion signal by using a storascope (Fig. 5.). For this curve

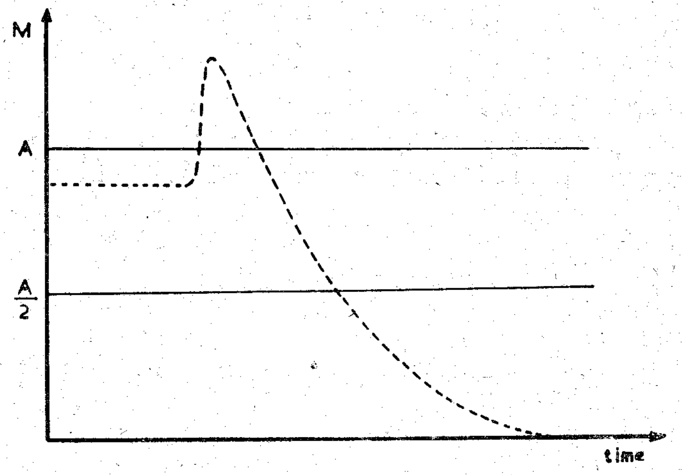

Fig. 5.

$$A \sim e^{-t_1/T_2} \tag{24}$$

as the nuclear magnetization increases or decreases exponantially. Where A is an arbitrary ordinate and T_2 is a constant which characterizes the decay of the magnetization. This constant is called as transversal relaxation time. For A/2

$$\frac{A}{2} \sim e^{-t_2/T_2} \tag{25}$$

can be written . Using equations (24) and (25)

$$T_2 = \frac{t_2 - t_1}{\ln 2} \tag{26}$$

can be obtained. When intensity of the the beam of the storascope was modulated with a frequency f_m, the time interval of $t_2 - t_1$, which corresponds to abscissa interval of A and A/2 can be determined by counting the spots on the screen. Hence the equation (26) becomes.

$$T_2 = 1.44 \frac{n}{f_m}$$

By using this method, the determination of transversal nuclear relaxation times T_{20} of the pure solvent and T_2 of the radical solution are possible, and using these values, from the relation:

$$\frac{1}{T_2} = \frac{1}{T'_2} + \frac{1}{T_{20}}$$

the transversal nuclear relaxation time T_2' which is arising from the interaction with the electron spins can be determined. It is known on the other hand that $1/T'_2$ is proportional to the radical concentration [5].

D. Preparation of the radical solutions and determination of radical concentration

In this study, the concentration of diphenyl radical ions which were prepared in THF and nitrogen atmosphere have been found by measuring T_2 as described above and then by using the graph which is given in ref. [5].The concentrations of TCNE /THF radical ions have been determined by using a S band spectrometer [10]. T_2 relaxation times of the same samples were also determined by using NMR spectrometer. The concentrations of α, α' dipyridyl free radical ions which were prepared in the same solvent, have been determined by using a Q band EPR spectrometer. For this purpose special twin cells on which identical capillary tubes joined were used. The reason of using identical capillaries is to avoid the volume corrections during the concentration measurements. The used cells were calibrated volumetrically, and solid DPPH which was weighted very precisellly was put in one of twin cells and then THF was distiled on it in the nitrogen atmosphere. Hence, a sample, which can be used as a reference, was prepared. Then the free radical solution, approximately about the same concentration was prepared in THF by using the second cell. An ample amount of radical solutions were sent to capillaries and they were cut off by a flame [9]. By comparing these samples at the Q band EPR spectrometer the unknown concentration was determined [10]. T_2 relaxation time of the same sample was also determined by using the double resonance NMR spectrometer.

A series of measurements were made for TCNE and α, α'-dipyridyl and the graph shown in Fig. 6. was obtained. The other concentration values of these free radicals were determined from this graph.

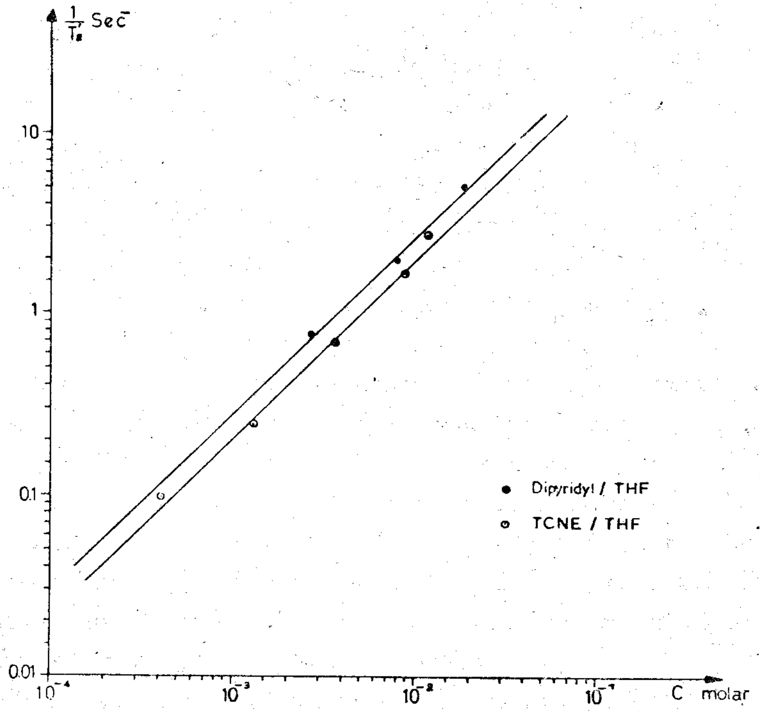

Fig. 6.

E. Determination of the relaxation times T_{1e} of the free radicals

The relaxation times T_{1e} of diphenyl, TCNE and α, α' - dipyridyl free radical solutions, which were prepared in THF in different concentrations, were determined by the methode which has been explained in detail in the introduction. Firstly the concentration of each sample was determined. Then $| P_z / P_0 | + 1$ values were found depending on ESR frequency. This gives the ESR spectrum of the radical which is under examination. Some spectra belonging to these three radicals are shown in Fig. 7, Fig.8, Fig.9. By integrating this curve the value of h (ω) has been obtained. Then the saturation curve was drawn and finally for a known value of H_{1e} under the condition of $\sigma g \ll 1$, $| P_z / P_0 | + 1$ was measured. These measurements, repeated for each concentration, wére made at room teperature and finally the T_{1e} has been determined.

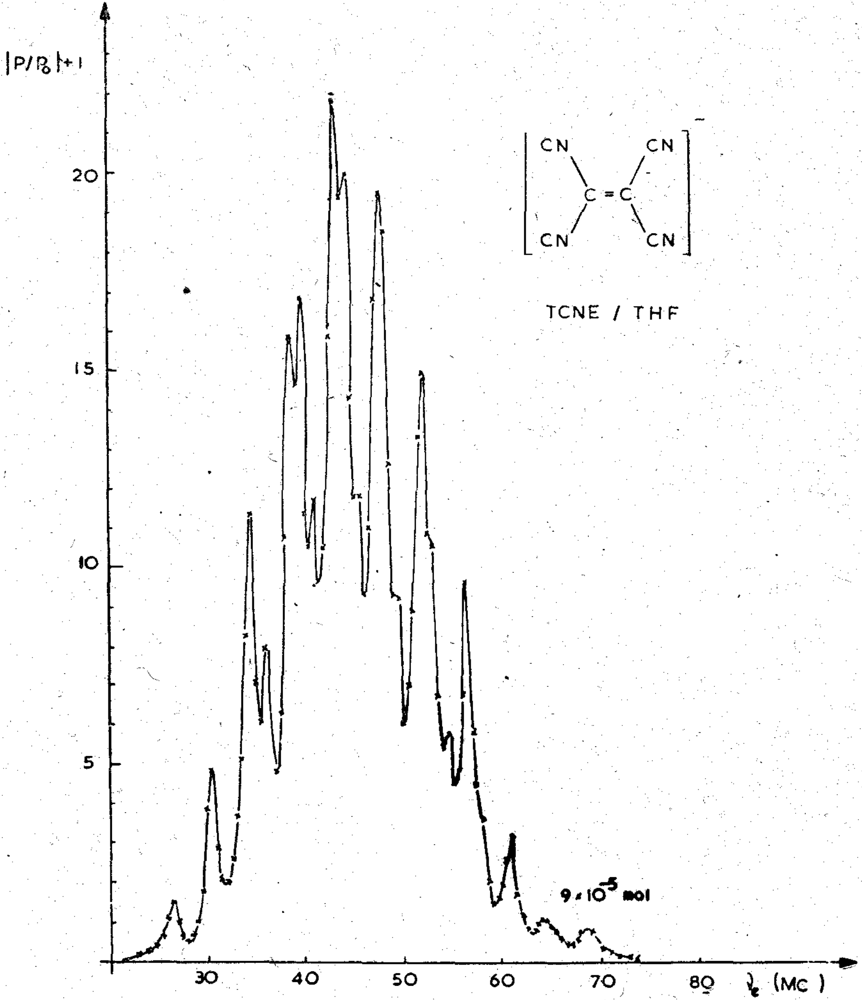
|P/P₀|+1
20
15
10
5
30
40
50
60
70
80
ν_e (Mc)
CN
CN
C = C
CN
CN
TCNE / THF
9·10⁻⁵ mol

Fig. 7.

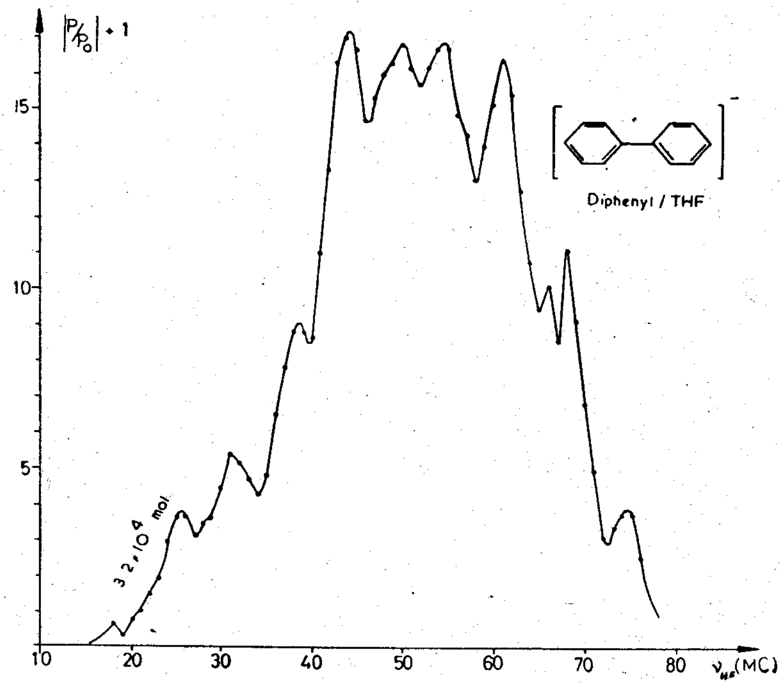
$|P/P_0| + 1$
15
10
5
10
20
30
40
50
60
70
80
ν_{HF}(MC)
3,2 x 10⁴ mol
Diphenyl / THF

Fig. 8.

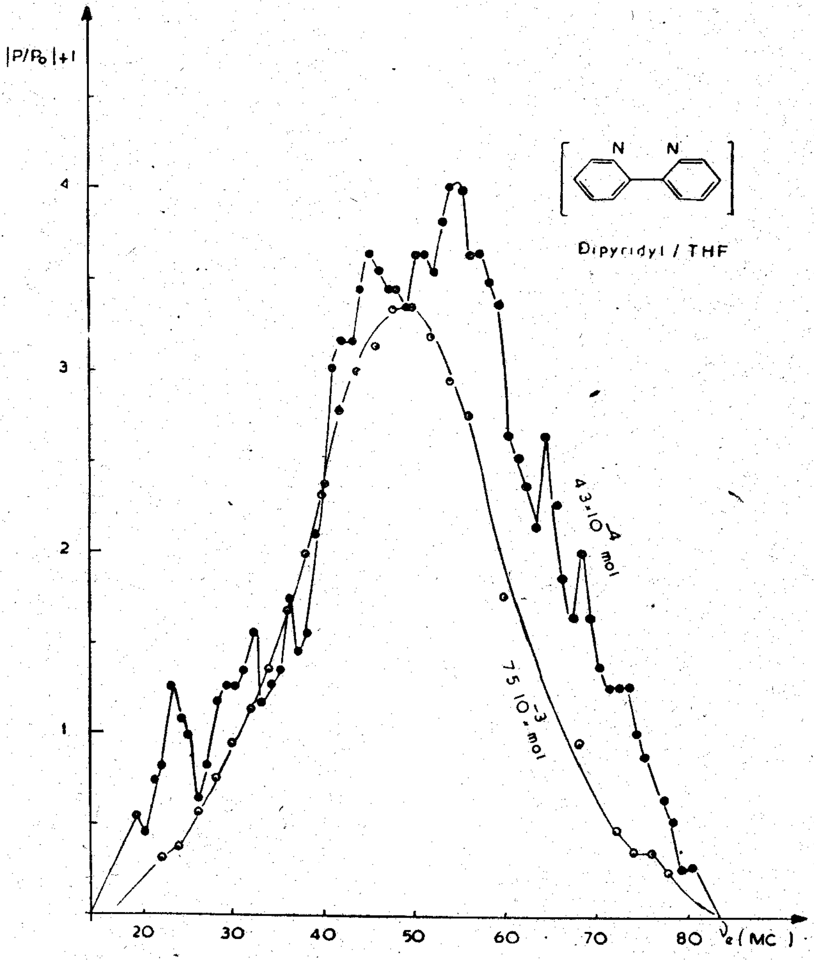
|P/P₀|+1
4
3
2
1
20
30
40
50
60
70
80
ν_e (MC)
N
N
Dipyridyl / THF
4 3·10⁻⁴ mol
75 10⁻³ mol

Fig. 9.

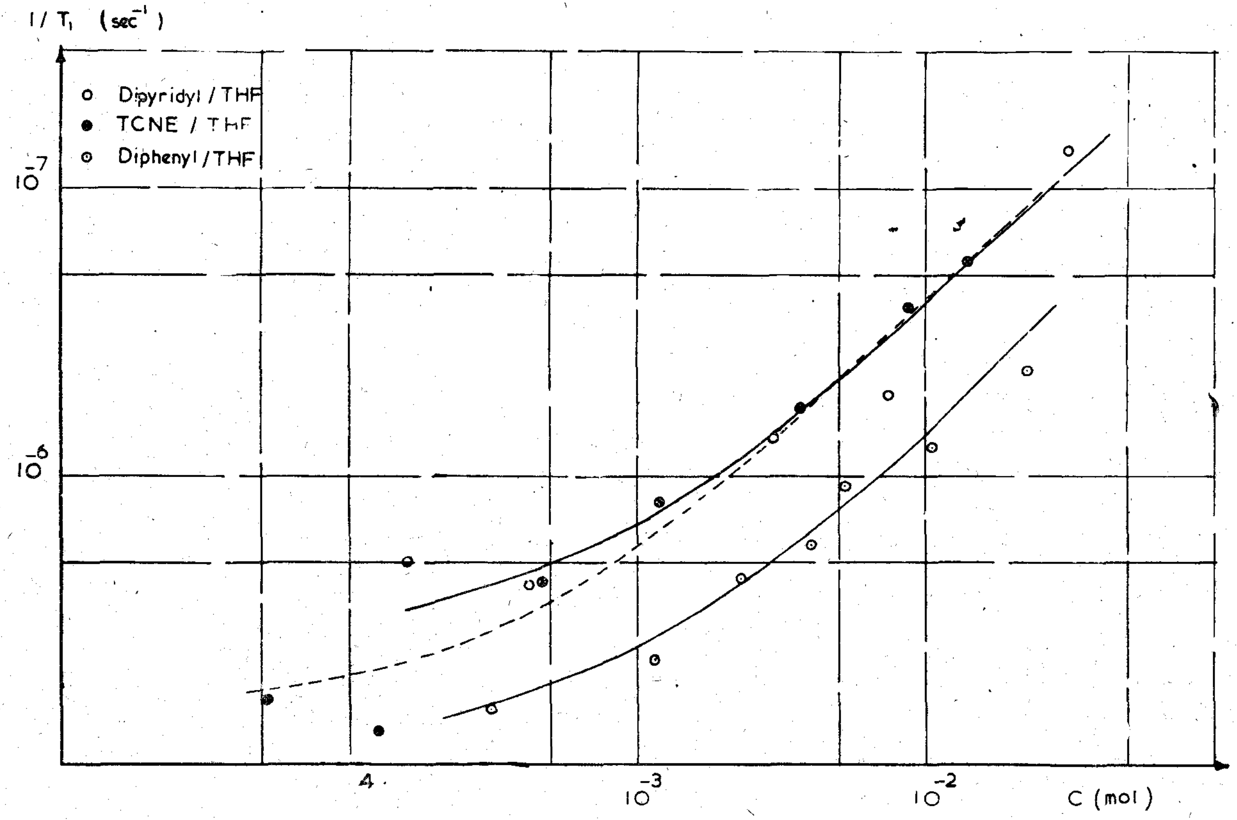
1/ T₁ (sec⁻¹)
○ Dipyridyl / THF
● TCNE / THF
⊙ Diphenyl / THF
10⁻⁷
10⁻⁶
4
10⁻³
10⁻²
C (mol)

Fig. 10.

DISCUSSION OF RESULTS

$1/T_{1e}$ has been ploted against the concentration, for three radical solutions in Fig. 10.It is seen in these graphs that $1/T_{1e}$ is proportinal to the concentration, in the high concentrations region. This result can be attributed to the relaxation of magnetic dipol - dipol interaction [11].The results which have been found experimentally are satisfying and in accordance with the theory. It is accepted in the theory that, the solvent molecules and the radical ions have the completely free motins each others. So it could be only possible to explain the relaxation mechanism in the high concentration region. Therefore there is no association between solvent molecules and radical ions.

It is seen in Fig. 10. that another mechanism affects the relaxation in the case of the low concentrations. An activation by temperature $(\frac{1}{T_{1e}} \backsim e^{V_a/kT})$ is not observed, therefore the relaxation can not be the result of any type of dipolar coupling. In a previous study [4] a type of spin-orbit coupling is proposed, but it is not prooved. It is necessary to take a series of the temperature dependence measurements to see the spin-orbit coupling.

Acknowledgments

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ÖZET

Difenil, TCNE ve α, α'- dipiridil'in THF içinde, farklı konsantrasyonlarda hazırlanan radikallerinin T_{1e} ve T_2 relaksasyon zamanları, bu laboratuarda kurulan bir çift rezonans, zayıf alan spektrometresi ile ölçüldü. Çalışmada teori ve ölçü tekniği hakkında gerekli bilgi verilerek T_{1e} nin konsantrasyona bağlı olarak değişimi tefsir edildi.

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