SPIN-LATTICE RELAXATION STUDIES ON SEMIQUINONE IONS

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Received July 14, 1972

(Communicated by Prof. B. V. Thosar, F.A.SC.)

ABSTRACT

Electron spin-lattice relaxation times of *p*-benzosemiquinone, durosemiquinone and 2, 5 ditertiary butyl-*p*-benzosemiquinone ions have been measured by the pulsed saturation recovery technique. The relaxation times of the different hyperfine components of a semiquinone ion are the same within the limits of experimental error in disagreement with the findings of Schreurs and Fraenkel.[3] The dependence of T_1 on viscosity does not follow the BPP's theory.

INTRODUCTION

IN 1955[1] it was noticed that in ethanol solutions of certain organic free radicals the ratio of the peak heights of different hyperfine components did not correspond to the ratio of the degeneracies of the components and that the ratio of the peak heights varied with microwave power. A typical example is an ethanol solution of 2, 5-ditertbutyl-*p*-benzosemiquinone ion (DTBPBSQ) where three hyperfine levels, arising from two equivalent protons of the ring have a dnegeeracy ratio of 1:2:1. It was found that the ratio of the peak height of the central hyperfine component ($M_I = \sum_i m_{Ii} = 0$ where m_{Ii} is the projection of the spin angular momentum of the *i*-th proton) to those of the side components ($M_I = \pm 1$) was found to vary from 1·3 to 2·2 as the microwave power was lowered from about a few milliwatts to a few microwatts. These effects were carefully investigated by Schreurs, Blomgren and Fraenkel[2, 3] by measurements of line widths and saturation parameters of the different hyperfine components as a function of the incident microwave power. The samples investigated were ethanol solutions of *p*-benzosemiquinone ion (PBSQ) and 2, 5-ditert-butyl-*p*-benzosemiquinone ion (DTBPBSQ). Stephen and Fraenkel[4,5] developed a theory for the saturation of hyperfine components which showed that motional modulation of the intramolecular electron-nuclear anisotropic dipole-dipole interaction introduces a relation between the saturation parameters of the hyperfine components that varies symmetrically about the center of the spectrum and causes a smaller degree of relaxation for the central components in the central portion of the spectrum, than those in the wings. This relaxation mechanism introduces a greater dependence on the nuclear spin state for radicals with several magnetic nuclei than for radicals with only one such nucleus. It was also shown that a cross term between this dipolar interaction and motional modulation of the anisotropic *g*-tensor introduces a relaxation that varies linearly from one side of the spectrum to the other.

Schreurs, Blomgren and Fraenkel[2, 3] on the basis of the above theory showed that both T_1 and T_2 measured by the continuous saturation technique followed an equation of the form

$$\frac{1}{T_{1,2}} = a_{1,2} + b_{1,2} M_I + C_{1,2} M_I \, . \tag{1}$$

Kivelson[6] also arrives at a similar conclusion from his theory. Further refinements on these theories made by Freed and Fraenkel[7] and Freed[8] have been employed to explain various line width effects found in ESR of solution of organic free radicals.

This paper is a preliminary report on our measurements of spin-lattice relaxation times, T_1, in solutions of three semiquinone ions in ethanol by the saturation recovery method of Jeffries.[9] The sample is irradiated with a pulse of large microwave power and then the return of the population distribution to the thermal equilibrium is followed by monitoring the population difference with a small microwave power.

INSTRUMENT

We have carried out our measurements with an ESR Superheterodyne Spectrometer built in our laboratories operating at about 9300 MHz. A 12-inch Varian Magnet (V-3603) with Fieldial power supply (VFR–2501) was used. The spectrometer (Fig. 1) can be used for both resonance and relaxation studies. For resonance studies the main Klystron is locked to the sample cavity by employing the method of Hirshon and Fraenkel.[10] The local oscillator and the main Klystron are interlocked to obtain an IF of 60 MHz. Operating in the resonance mode, our spectrometer is sensitive enough to observe in DSQ ion, on the oscilloscope itself, satellites due to ^{13}C in natural abundance with a power of about a few mW incident on the sample cavity.

For operation on the relaxation mode we stabilize the main Klystron to an external reference cavity, this part of the stabilization loop does not see the pulse of large microwave power. A switching diode (Philco mount 901A–96 with diode L 4146) is used to obtain the pulse of microwave power. The diode is ordinarily biased with a negative voltage (−20 v) to maintain an attenuation of about 25 dB in the off-cycle. The on-off ratio in attenuation is about 20 dB. The pulse repetition is variable from 1 Hz to 30 Hz. For relaxation studies we have used a wide band (± 4 MHz band width) 60 MHz radar amplifier whose overall recovery time is less than 3μ sec. The output of the detector of the IF amplifier is presented on a Tektronix 585 oscilloscope. The oscilloscope is externally triggered by the incoming pulse.

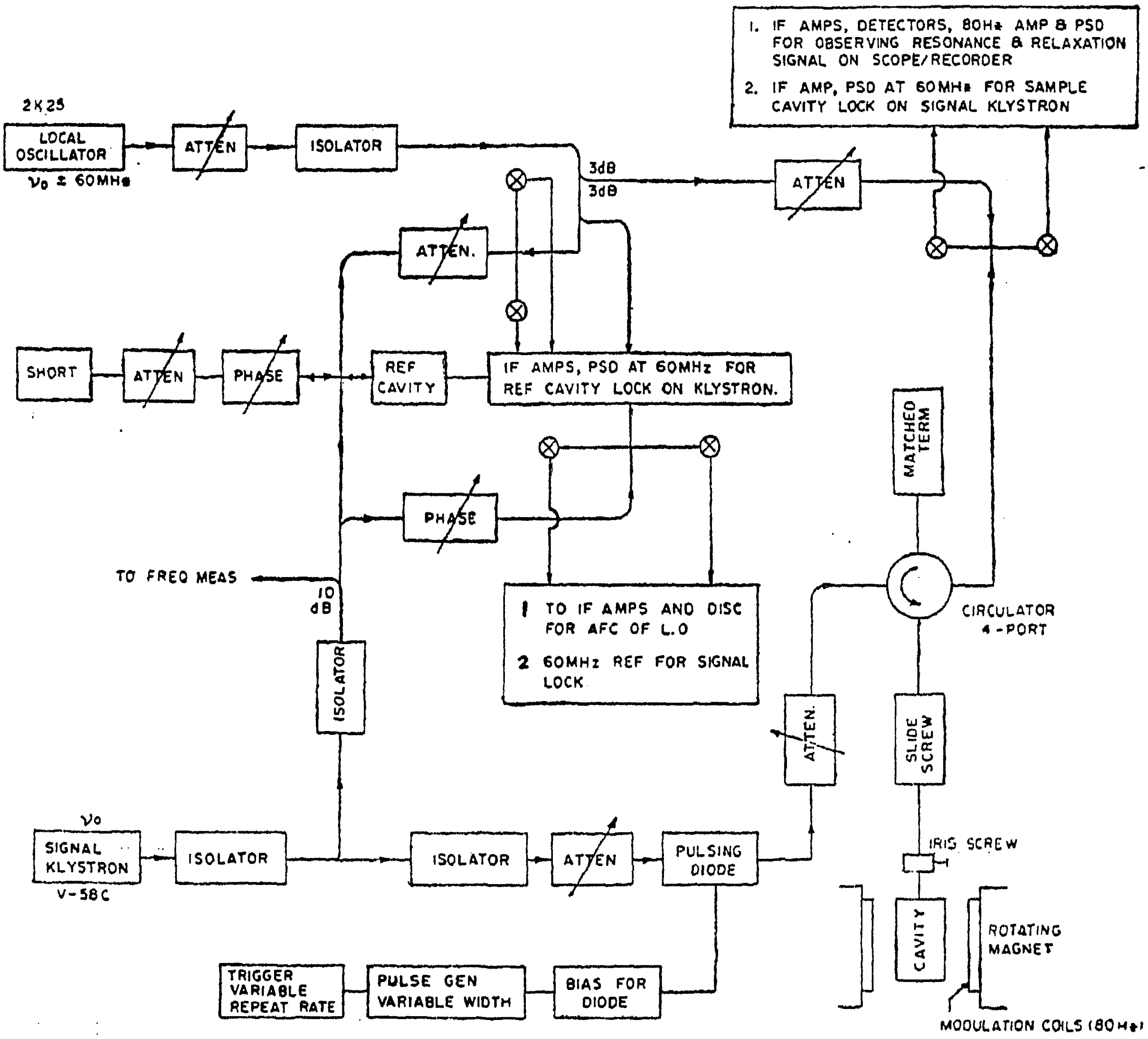

FIG. 1. Block diagram of the pulsed x-band ESR Superheterodyne Spectrometer used for resonance and relaxation studies.

For measurements of the relaxation times and for verifying the exponential character of the recovery, we have employed an exponential function generator whose decay times can be varied from 2 μ sec to 10 m.sec. The exponential generator is also triggered by the scope trigger output, but with a variable delay. The output of the exponential generator and the transient recovery trace of the ESR signal are superimposed and matched by varying the amplitude and decay time of the exponential generator. The decay time of the exponential generator is measured by the usual method. Figure 2 presents the relaxation recovery signals from ethanol solutions of DTBPBSQ. The recovery trace is found to fit to a single exponential.

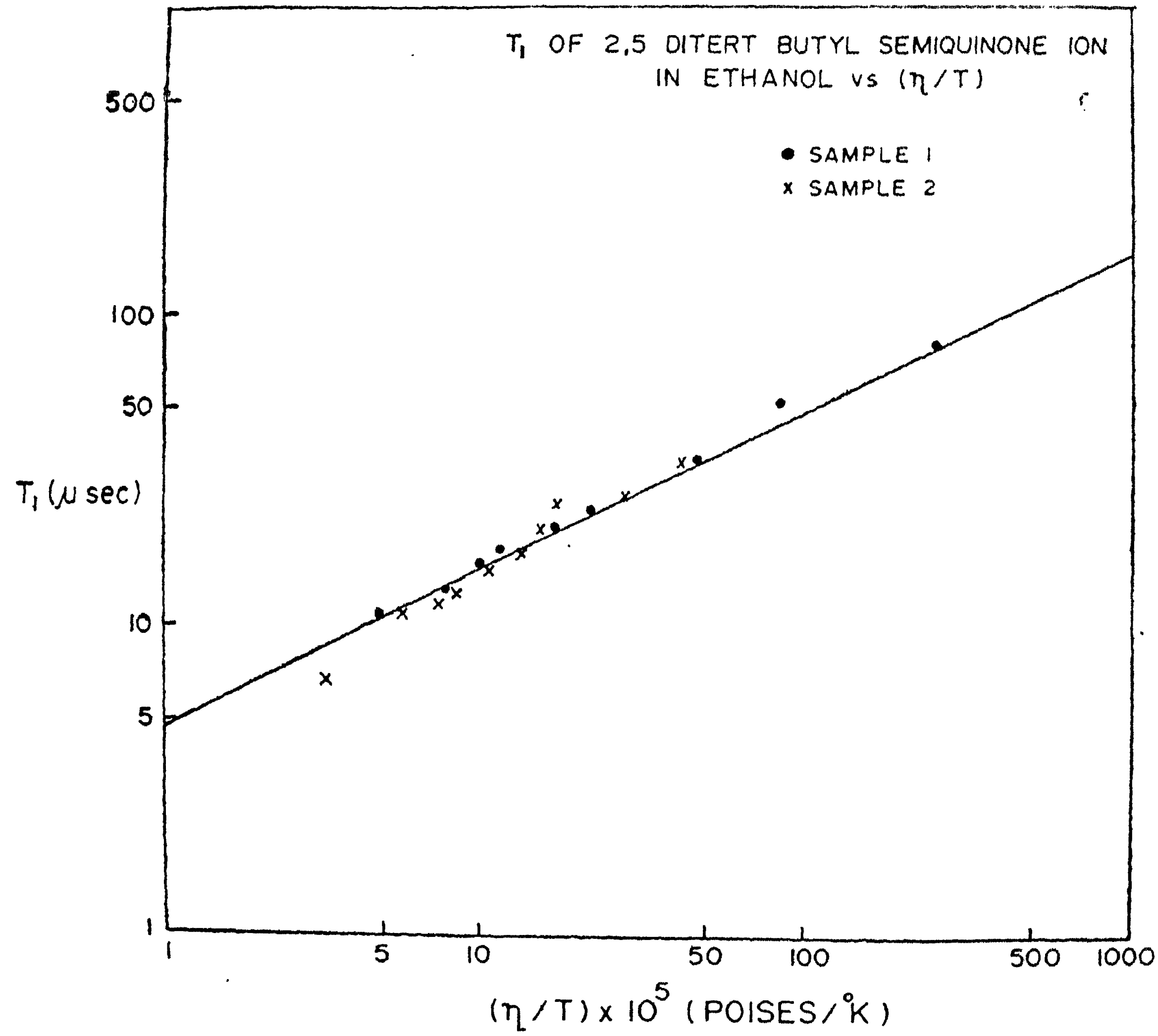

FIG. 3. A log-log plot of T_1 *vs.* η/T for the central hyperfine component of DTBPBSQ on in ethanol. Radical concentration estimated to be 10^{-2} M in sample 1 and 2×10^{-3} M in sample 2.

A Varian variable temperature accessory (V-4540) was used to control the temperature of the sample. The temperatures were measured using a copper-constantan thermocouple placed at the site of the sample before and after relaxation measurements at a particular temperature setting. The temperature regulation (± 3° C) was not satisfactory enough for this purpose especially below −30° C where the variation in viscosity of the solvent is large for small fluctuations of temperature. We are at present engaged in improving this system.

It was found that the operation of the spectrometer in relaxation mode was found to be optimum near 9300 MHz on account of the band width of the isolator we had used. Proper locking of the signal klystron to the reference cavity is obtained only when the stabilizing loop saw very little of the high microwave power during pulsing and these conditions were obtained around 9300 MHz. A gold-plated variable temperature TE_{102} X-band rectangular cavity was fabricated to have a resonating frequency of 9300 MHz when a home made quartz variable temperature insert is placed inside it. This gave us very good operating conditions at sufficiently high monitoring power required for studies near room temperature. The monitoring power was decreased at lower temperatures with the help of an attenuator.

The dependence of the measured relaxation times on the monitoring microwave power and pulse widths (variable in five steps of 16, 26, 140, 1500 14000 μ sec.) was always checked and these parameters were kept in the region where they had little effect on the relaxation times and at the same time gave maximum signal to noise ratio.

RESULTS

2, 5-*ditert butyl-p-benzosemiquinone ion* (*DTBPBSQ*).—Among the two semiquinone ions investigated by Schreurs, Blomgren and Fraenkel[2] the 2, 5-ditert butyl-*p*-benzosemiquinone ion is found to be more stable and hence was chosen by us for detailed investigations. Further they had deduced from their line width and peak height measurements at different power levels that $T_1 (M_I = \pm 1)/T_1 (M_I = 0) = 0 \cdot 65$ for this substituted semiquinone and it was also known from earlier work[1] that this semiquinone exhibited greater degree of saturation behaviour. It was expected that any dependence of T_1, as measured by our saturation recovery technique, on M_I, should be greater in this compound.

The problem of producing a stable radical with sufficient concentration of DTBPBSQ was resolved by the controlled oxidation of a degassed solution of DTBPBSQ in alkaline ethanol. The degassing of two separate solutions of alkaline ethanol and DTBPBSQ in ethanol were carried out separately *in vacuo*. After mixing the solutions *in vacuo* a controlled a mount of oxygen was admitted into the system. The samples were then sealed and the radical has been found to stay for months. A small decrease in concentration (a factor of about 2) was observed in five months.

DTBPBSQ has two equivalent ring protons which are known to have a hyperfine splitting constant of 2·13 gauss[1] (Fig. 2). The protons of the tertiary butyl groups are known to have a splitting of the order of 60 mG. At the concentrations we have employed (estimated to be 10^{-2} M for sample and 2×10^{-3} M for sample 2) the further splittings due to the protons of the tertiary butyl groups cannot be seen. We have chosen these concentrations purposefully to wipe out this hyperfine structure and to get good signal to noise ratio for relaxation traces.

Table I presents the data on the relaxation times of the different hyperfine components as a function of temperature. In both the samples it was found that on the average the central component has a slightly longer relaxation time than that of the side components at temperatures where the different components are well separated. However, we are unable to say with certainty that the two relaxation times are different. No noticeable trends have been found between the $M_I = +1$ and $M_I = -1$ component and we have taken an average of the measured values for these two components. We do no definitely notice the 35% difference found by Fraenkel and co-workers[2] from their determination of the saturation parameters.

Following Bloembergen, Purcell and Pound[11] we have plotted T_1 against η/T. The values of η were obtained from *the Handbook of Physics and Chemestry* (35th Ed.; 1953 54). Figure 3 depicts a straight line for the log-log plot except for deviations at lower temperatures. If we are in the region $\omega\tau \gg 1$ BPP's theory predicts that the slope should be $+1$. However, the slope is far fiom it and all that we can say at present is that the viscosity model for the rotation of molecules used in BPP's theory does not give the correct temperature dependence.

p-*Benzosemiquinone ion* (*PBSQ*).—Unlike DTBPBSQ solutions PBSQ solutions in ethanol were too unstable for careful investigations even when prepared under controlled conditions *in vacuo*. Our variable temperature control insert does not allow a flow system for obtaining steady state concentrations to be used. It was observed that the radical stayed considerably longer if it was prepared by adding a dr opof dilute alcoholic potassium hydroxide to the ESR sample tube containing a sample of 0·01 M hydro-

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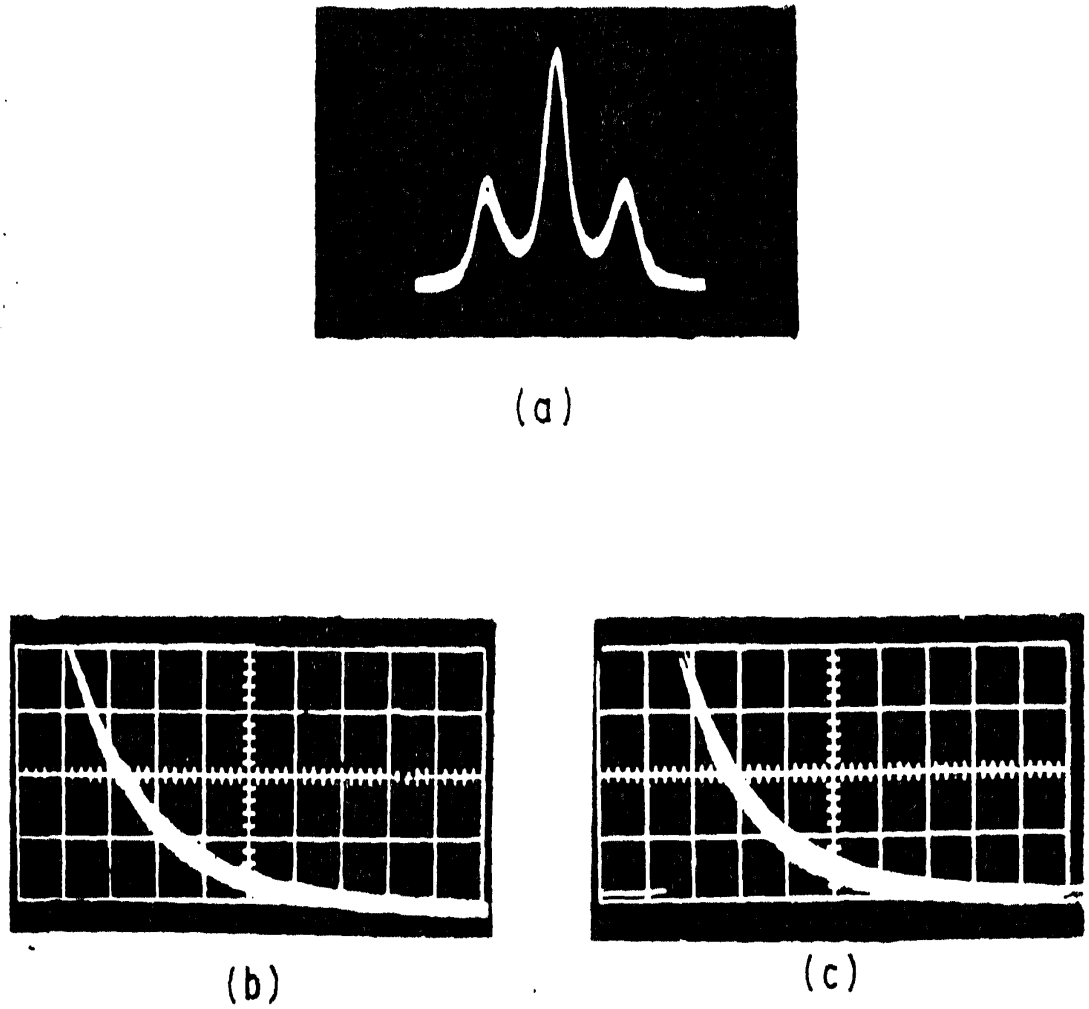

(a)

(b) (c)

FIG. 2. (*a*) ESR of 2, 5-ditert-butyl-*p*-benzosemiquinone ion (DTBPBSQ) showing the triplet hyperfine spectrum due to the two ring-protons. (*b*) and (*c*) The characteristic recovery from saturation of the central hyperfine component of DTBPBSQ and the output of an exponential generator as seen on a dual beam oscilloscope. In (*b*) the 2 traces are matched to show the exact exponential character of the recovery from saturation. In (*c*) the output of the exponential generator is slightly displaced. ($T_1 = 16 \cdot 2\ \mu$ sec. at 248° K).

TABLE I

Spin-lattice relaxation times of the hyperfine components of 2, 5 *ditert butyl*-p-*benzosemiquinone ion in ethanol*

T (°K) (± 3° K)	Relaxation Times (T_1) μ sec. (± 10%)				
	Central Components $M_I = 0$		Side components $M_I = \pm 1$		
	Sample 1	*Sample* 2	*Sample* 1	*Sample* 2	
300	..	7·6	..	6·3	
298	7·0	..	6·9	..	
278	11·6	11·0	10·7	10·8	
269	..	12·5	..	11·2	
266	13·9	..	12·7	..	
263	..	13·7	..	12·3	
258	15·5	..	15·5	..	
256	..	15·4	..	15·0	
249	..	17·2	..	17·5	
248	17·5	..	17·5	..	
241	..	21·5	..	19·4	
237	20·8	..	20·8	..	
232	..	24·0	..	24·7	
229	23·8	..	23·8	..	
222	..	28·6	..	24·5	
211	..	34·3	..	33·7	
209	35·0	..	33·8	..	
195	52	..	..	..	Hyperfine components are overlapped
189	..	45·4	..	..	
174	80	..	..	..	
166	..	79·4	..	..	

quinone solution in ethanol (not degassed). The radical concentration stayed at convenient level (about 0·005 M) for at least half an hour. PBSQ ion has 5-hyperfine lines with a degeneracy ratio of 1:4:6:4:1 arising from four equivalent protons. Table II presents the measured relaxation times of the central component as a function of temperature and measurements at temperatures lower than − 80° C were not possible on account

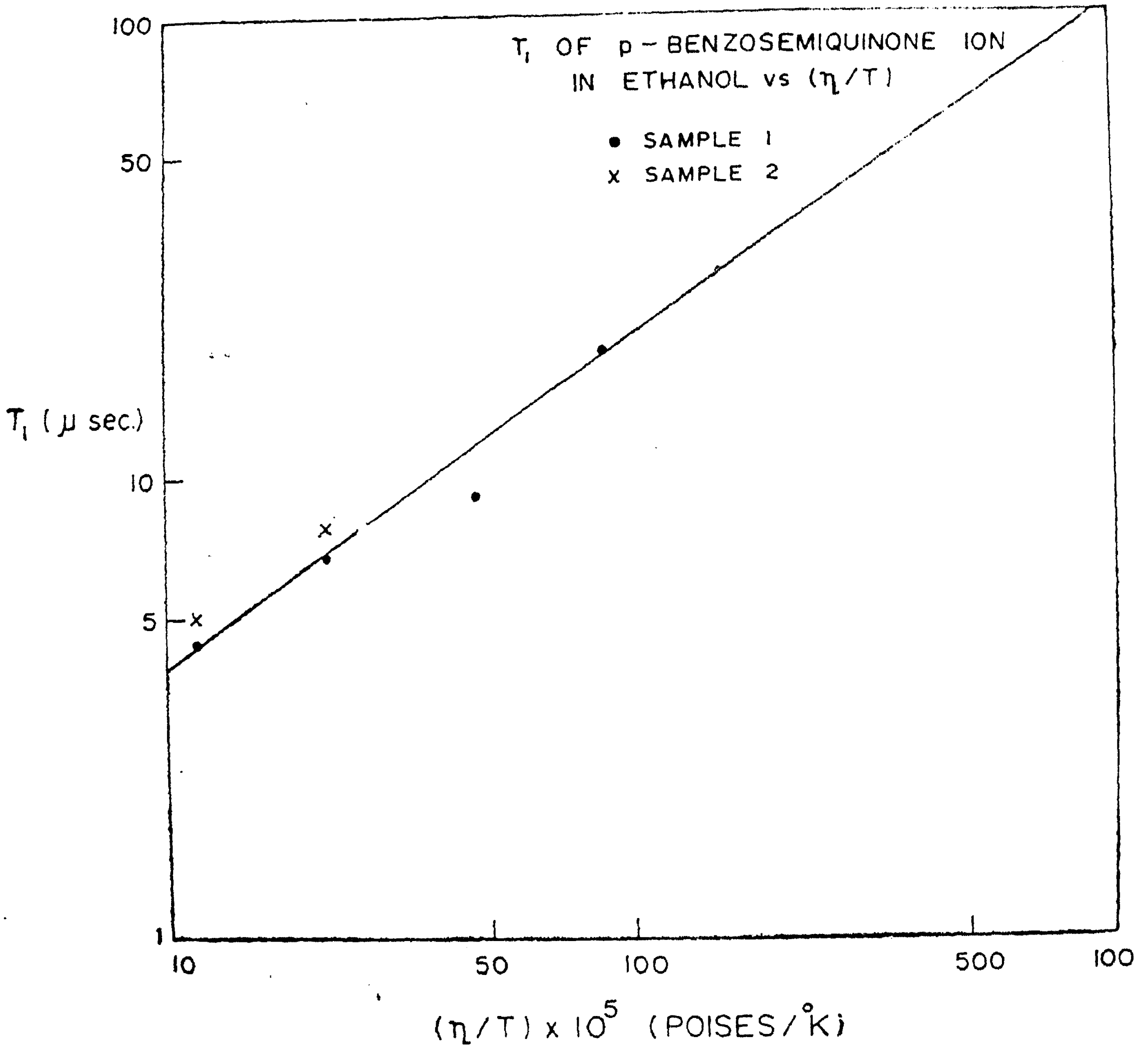

FIG. 4. A log-log plot of T_1 *vs.* η/T for the central hyperfine component of durosemiquinone ion in ethanol.

of the considerable broadening of the lines due to overlap and consequent decrease in signal intensity. A log-log plot of T_1 against η/T (Fig. 4) again gives a straight line with a slope not equal to 1.

A comparison can be made here with the results of Schreurs and Fraenkel[8] on this compound. At about 25° C where all their measurements have been conducted, they obtain for T_1 a value of $1 \cdot 66 \pm 0 \cdot 20\,\mu s$ for the central component and a decrease of about 7% for the $M_I = \pm 1$ components and of

TABLE II

Spin-lattice relaxation times of the central hyperfine component of p-*benzosemiquinone ion in ethanol*

T (°K) (± 3° K)	Relaxation Time (T_1) μ sec. (± 10%) of the central hyperfine component $M_I = 0$		
	Sample 1	Sample 2	
298	less than 1 μ sec.		
266	less than 2·2 μ sec.		
248	4·4	5·0	
229	6·7	7·8	
209	9·1	..	
195	18·8	..	Line width variations among the different hyperfine components seen very well. Low field components are broadened

about 13% for the $M_I = \pm 2$ components. Our values for T_1 at room temperature show that $T_I \sim 2\mu$ sec. and we cannot measure relaxation times less than 3μ sec., our amplifier recovery time. At lower temperatures preliminary results on $M_I = 0$ and $M_I = \pm 1$ components did not show any dependence of T_1 on M_I value of the hyperfine component, which can be definitely placed beyond the experimental errors. Even if there is to be a dependence of the order found by Schreurs and Fraenkel[3] for their saturation parameters, it is just within our experimental errors to be easily observed. Intensity of $M_I = \pm 2$ hyperfine components was too low in these samples for good determinations of their relaxation times.

At lower temperatures line width effects could be easily seen on the spectrum and the low field lines were definitely broader in agreement with a negative proton hyperfine coupling constant. ^{13}C satellites could be easily seen above 220° K.

Durosemiquinone ion (DSQ).—DSQ ion also presented a problem of obtaining stable solutions and the only method that succeeded and gave a radical ion whose concentration decreased only by a factor of about 2 in about 24 hours was the addition of a drop of dilute alcoholic KOH into an ESR sample tube containing 0·01 M solution of Durohydroquinone in ethanol (not degassed). The radical concentration is estimated to be about 0·005 M initially. Durosemiquinone ion has twelve equivalent protons

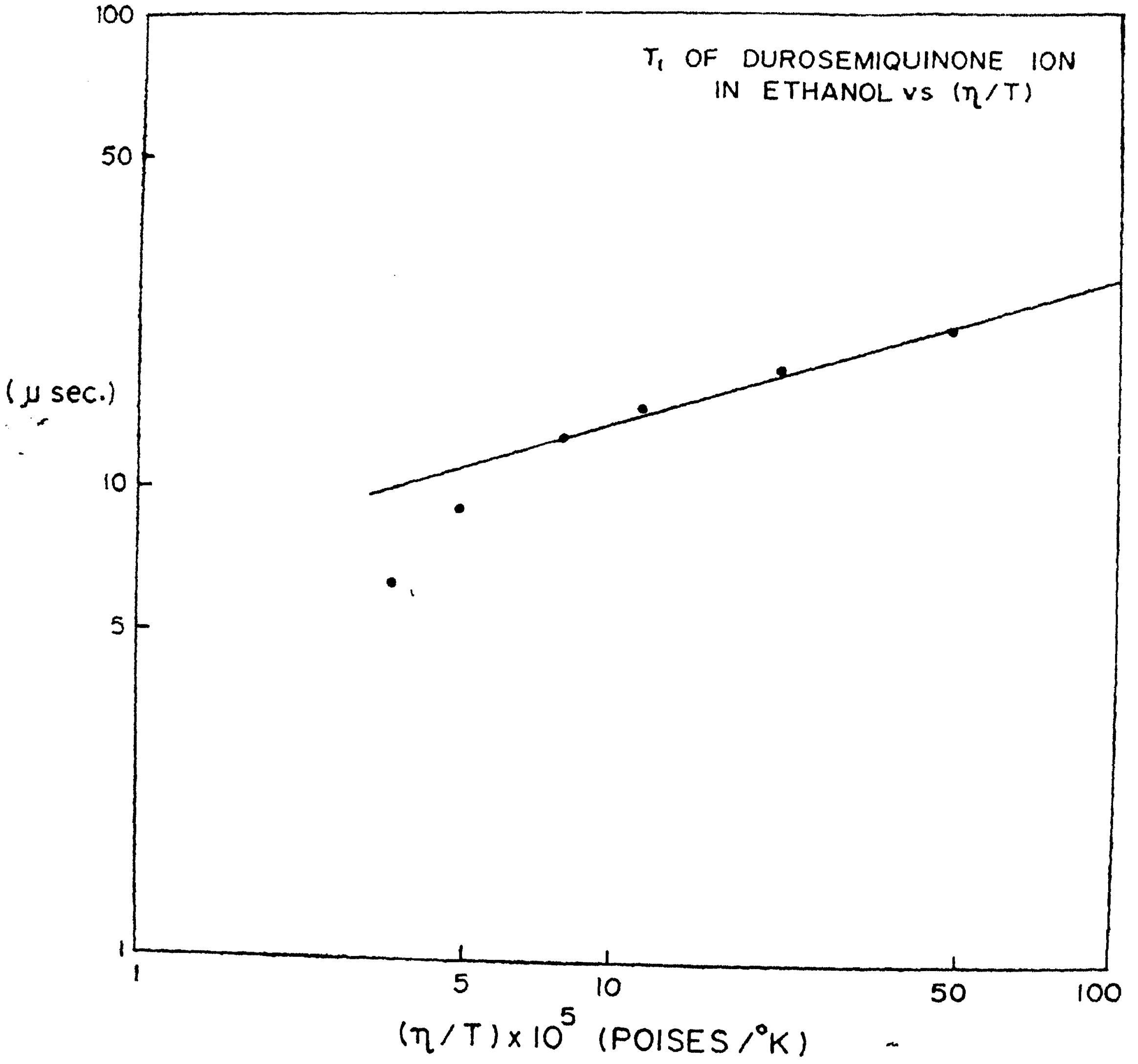

FIG. 5. A log-log plot of T_1 *vs.* η/T for the central hyperfine component of *p*-benzosemiquinone ion in ethanol. Samples 1 and 2 were two identically prepared samples.

arising from four methyl groups and gives a spectrum of 13 equally spaced hyperfine components. In Table III are listed the relaxation times, T_1, as a function of temperature for the $M_I = 0$ and $M_I = \pm 1$ components. There seems to be a trend for the low field component to have a longer T_1 than the other two; however we need better statistics to confirm this preliminary observation. A log-log plot of T_1 *vs.* η/T (Fig. 5) is again a straight line with a slope not equal to + 1. For the DTBPBSQ and DSQ solutions (Figs. 3 and 5) the temperature points deviate from this straight line and we have no explanations to offer for this observation. Near about − 40° C the lines are so narrow (~ 40 mG) that the ^{13}C satellites arising from the three inequivalent positions of carbon and their line width effects could be seen clearly on the oscilloscope.

TABLE III

Spin-lattice relaxation times of the hyperfine components of durosemiquinone ion in ethanol

T (° K) (± 3°K)	Relaxation Times (T_1) μ sec. (± 10%)			
	Central component $M_1 = 0$	Components nearest to the central line $M_I = \pm 1$		
		High field component	Low field component	
298	5·6	5·6	5·0	
278	9·0	8·6	9·5	
266	12·7	12·7	12·9	Narrow lines of the order of 40 mG linewidth. The hfs due to the 3 inequivalent ^{13}C and line width effects of them could be seen easily.
248	14·9	13·8	19·1	
229	17·8	15·7	23·8	
209	..	19·5	..	Line gets broadened and the signal strength is poor

DISCUSSION

The spin-lattice, or longitudinal relaxation times T_1 introduced by Bloch[12] as a parameter to measure the presumed exponential decay of the component of the microscopic magnetization along the external magnetic field, determines the saturation behaviour for a two level system.[11] It has also been shown by Solomon[13] that there is an exponential decay of the component of macroscopic magnetization along the external magnetic field direction for all systems, which can be described by a single relaxation time. A multi-level equally spaced system, arising from a single spin $I > \frac{1}{2}$, also behaves in many respects like a two-level system. However, in cases of systems with n equivalent nuclei of $I = \frac{1}{2}$, Stephen and Fraenkel[5] describe the saturation behaviour in terms of a saturation parameter, Ω, which in general need not be simply related to a parameter that can be identified with T_1.

$$\Omega_{ij} = 2\,(W_R)_{ij}^{-1} \tag{2}$$

where Ω_{ij} is the saturation parameter for the (i, j) transition and $(W_R)_{ij}$ is the relaxation probability. If, however, it can be demonstrated that the approach to equilibrium can be described by an exponential law, *i.e.*, exp. $(-t/T_1)$ Kubo and Tomita[14] have shown that even in a complex system there exists a simple relation between T_1 and the transition probabilities induced by relaxation,

$$T_1 = D_i \Omega_{ij} \tag{3}$$

where D_i is the degeneracy of the i-th (j-th) level. Since all our relaxation recoveries to equilibrium have been shown to be exponential within the limits of our exactness of superimposing the output of an exponential generator over the relaxation trace, we feel we are justified in assuming that the relationship (3) should hold for our systems. Our observation that the different hyperfine components have the same relaxation times 'T_1' within the limits of experimental error is in disagreement with the findings of Schreurs and Fraenkel.[3] In the continuous saturation technique employed by these authors, the measurement of T_1 depends on the measurement of T_2 and the microwave field at the sample and the errors in the measurements of these enhance the errors in T_1; whereas in the technique used by us T_1 is measured directly. Thus whenever there are unresolved hyperfine structures (which lead to erroneous measurement of T_2) as in the case of DTBPBSQ, the saturation recovery technique gives better values for T_1 than the continuous saturation technique.

It should also be pointed out that the saturation recovery technique used by us required high concentration of the radicals. In this concentration range the exchange effects are likely to complicate the interpretation of results. The other drawback in our method of T_1 measurements is the limitation to relaxation times longer than a few microseconds.

An interesting observation is the difference between the spin-lattice relaxation times at the same temperature of the three semiquinone ions studied here (*e.g.*, T_1 at 248° K for PBSQ $= 4 \cdot 7\,\mu$ sec.; for DSQ $= 14.9\,\mu$ sec.; for DTBPBSQ $= 17 \cdot 5\,\mu$ sec.). There is an increase in T_1 with increasing molecular weight which is to be expected if the Stoke's relation for the correlation time $\tau_c = 4\pi\eta\, a^3/3kT$, is assumed to be valid and the effective radius '*a*' is assumed to increase with increasing complexity and molecular weight of semiquinone.

SUMMARY

It has been shown that in suitable circumstances we can measure the spin-lattice relaxation times of free radicals in solutions by the saturation recovery technique and the results obtained by this are more precise than the continuous saturation technique. The variation of T_1 with temperature does not follow the BPP's theory. The interpretation of this behaviour will be published in a subsequent paper.

ACKNOWLEDGEMENTS

The authors acknowledge with gratitude the assistance of Mr. R. B. Singh and Mr. V. R. Bhagat in solving many problems connected with electronics and the assistance of Miss M. P. Khakhar in preparation of samples.

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