

## Study of molecular motions in liquids by electron spin-lattice relaxation measurements, I: Semiquinone ions in hydrogen bonding solvents

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MS received 20 April 1974

**Abstract.** The electron spin-lattice relaxation times ( $T_1$ ) of a variety of semiquinone ions in hydrogen bonding solvents have been measured by the pulsed saturation recovery technique as a function of temperature ( $T$ ) and viscosity ( $\eta$ ) of the solvent. Also linewidths ( $\Delta H$ ) have been measured in suitable cases in such solvents at low radical concentrations ( $\sim 10^{-4} M$ ). It is observed that (i) the temperature and viscosity dependence of  $T_1$  can be fitted to an equation of the form

$$1/T_1 = A(T/\eta) + B \exp(-\Delta E/RT)$$

where  $A$  and  $B$  are constants and  $\Delta E$  is an activation energy of the order of 1 kcal mole $^{-1}$  for these systems; (ii)  $T_1$  is essentially independent of the radical concentration within the range  $10^{-3}$  to  $5 \times 10^{-2} M$ ; (iii) the concentration independent part of the linewidth ( $\Delta H$ ) increases linearly with ( $\eta/T$ ) at sufficiently low temperatures, and (iv) the ( $\eta/T$ ) dependent part of  $T_1$  is sensitive to the size of the semiquinone as well as that of the solvent molecule, whereas the linewidth which is proportional to ( $\eta/T$ ) at high viscosity, low temperature region is not sensitive to the size of the semiquinone and that of the solvent. Based on these observations, it is postulated that in hydrogen bonding solvents, three types of motion contribute significantly to electron spin relaxation:

- (a) A restricted small step diffusional motion, not involving large changes in the orientation of the molecule, leading to the dominant viscosity dependent contributions to  $T_1$  and  $\Delta H$ , due to spin rotation interaction;
- (b) a large amplitude reorientation of the semiquinone, coupled to translational diffusion, resulting in viscosity dependent contributions to  $T_1$  and  $\Delta H$ , through  $g$ -modulation;
- (c) a hindered rotation of the semiquinone within the solvent cage, contributing to  $T_1$  due to spin rotation interaction.

The fact that  $T_1$  is not sensitive to the concentration of the radicals, is ascribed to the formation of the solvent cage that prevents the close approach of radicals, thereby rendering radical-radical interactions to be weak mechanisms for relaxation, even at relatively high radical concentrations.

**Keywords.** Electron spin resonance; spin-lattice relaxation; free radicals; semiquinones; solvent-radical interactions; molecular motions in liquids.

### 1. Introduction

The translational and rotational motions of a free radical in a liquid modulate the position-dependent, orientation-dependent and angular momentum-dependent

terms in the Hamiltonian, which is reflected in the spin-lattice relaxation times,  $T_1$ , and the transverse relaxation times,  $T_2$ , which are related to the unsaturated linewidths,  $\Delta H$ , associated with the electron spin resonance (esr) of the free radical. Since the dominant terms occurring in the expression for  $T_1$  need not be the same as the dominant terms occurring in the expression for  $\Delta H$ , at a particular temperature  $T$ , a combined study of  $T_1$  and  $\Delta H$  as a function of  $T$  is necessary to get a more detailed picture of the molecular motion in liquids.

Earlier Schreurs and Fraenkel (1961) examined the linewidths and saturation behaviour of *p*-benzosemiquinone in ethanol at room temperature on the basis of the theory developed by Stephen and Fraenkel (1960) and obtained an estimate for the reorientation correlation time  $\tau_\theta$ , assuming the modulation of the *g*-tensor to be the dominant mechanism responsible for both  $T_1$  and  $\Delta H$ . Nyberg (1967) pointed out that the contribution from the spin-rotation interaction is necessary to obtain a satisfactory agreement between the theoretically predicted values of  $T_1$  and  $\Delta H$  and the experimentally observed values at room temperature. Recently Leniart (1971) and Connor (1972) have estimated  $T_1$  (by the continuous saturation method) and  $\Delta H$  for *p*-benzosemiquinone and durosemiquinone in ethanol in the temperature region 0° C to -70° C. An explanation of the results on the basis of isotropic small step rotational diffusion model (Debye 1945, Hubbard 1958, 1963) (taking into account both the *g*-tensor and spin-rotational interaction modulation) gives different values for the lattice induced electron spin flip transition probability ( $W_c$ ) depending on whether  $T_1$  or linewidth data are used. No satisfactory explanation for this has been given by Leniart (1971).

In the earlier papers from our laboratory (Lingam *et al* 1972, Rengan *et al* 1972 *a*, 1972 *b*), it was concluded that in semiquinone systems with ethanol as a solvent: (i) the relaxation traces obtained by the pulsed saturation technique were exponential; (ii) the spin-lattice relaxation times,  $T_1$ , for the different hyperfine transitions of a given semiquinone, were the same within the limits of experimental error; (iii)  $T_1$  is insensitive to the variation of the concentration of the semiquinone ion in the range  $10^{-3}$  to  $5 \times 10^{-2}$  *M*; (iv) the activation energy obtained from the temperature dependence of  $T_1$  is not the same as that associated with the temperature dependence of viscosity of the solution. It was suggested that in these systems the contribution from the spin-rotational interaction is the dominant term in the expression for  $1/T_1$  and that the hindered rotation associated with the hydrogen bonding between the alcohols and the semiquinone ions should also be taken into account.

In this paper we present the results of further investigations carried out in our laboratory on these systems where  $T_1$  is measured by the pulsed saturation recovery technique and the linewidths are determined from examining the unsaturated esr spectra. It has been possible by consideration of both linewidths and  $T_1$  data to arrive at a better understanding of the nature of the dominant mechanisms which contribute to spin-lattice relaxation and linewidths in these systems and to explain the paradoxical results of Leniart (1971). A preliminary note about these studies has been published elsewhere (Rengan *et al* 1972 *b*).

## 2. Experimental

Solutions of *p*-benzosemiquinone (PBSQ), tolusemiquinone (TSQ), 2,5-dimethyl-semiquinone (2,5-DMSQ), 2,6-dimethylsemiquinone (2,6-DMSQ), durosemi-

quinone (DSQ), tertiary butylsemiquinone (2-TBSQ), and 2,5-ditertiarybutylsemi-quinone (2,5-DTBSQ) ions were prepared in methanol, ethanol, *n*-butanol and benzyl alcohol and ethanol-glycerol mixtures (Analar, dry) by the air oxidation of the corresponding alkaline alcoholic solutions of the respective hydroquinones (Venkataraman 1956). 2,5-DTBSQ in tetrahydrofuran (THF) was obtained by dissolving the solid semiquinone salt (obtained by distilling off ethanol from a solution of the radical in ethanol in a vacuum line) in THF.

The linewidth measurements were carried out in a 100 KHz field modulated X-band esr spectrometer described elsewhere (Khakhar *et al* 1966). The measurement of spin-lattice relaxation times were carried out at X-band using a pulsed superheterodyne esr spectrometer (Lingam *et al* 1972). The exponential nature of the signal recovery trace was checked by superposing the output of an exponential generator on the signal recovery trace in a dual beam Tektronix 545 oscilloscope. Relaxation times were then measured, by measuring the characteristic time associated with the output of the exponential generator at the corresponding setting, with the help of the standard delay output of the oscilloscope. The precision of measurement of  $T_1$  depends on the signal to noise ratio and at moderate concentrations ( $\sim 10^{-3} M$ ), it is about  $\pm 5\%$ , and hence no attempt was made to recalibrate the standard delay to a greater accuracy. The standard delay was however checked and found to have greater accuracy than the limits mentioned above.

For measurements of  $T_1$  at lower temperatures, when  $T_1$  is longer than 0.1 msec, it was found necessary to correct for the effect of the microwave power level used to monitor the signal recovery after saturation. In a two-level system, the time dependence of the signal recovery trace is given by the time dependence of the population difference ' $n$ '. If  $W$  is the microwave induced transition probability at the microwave power level used for monitoring,

$$dn/dt = (n_0' - n)/T_1' \quad (1)$$

where

$$1/T_1' = W_{\downarrow} + W_{\uparrow} + 2W \simeq 2W_0 + 2W' \quad (2)$$

and

$$n_0' = N(W_{\downarrow} - W_{\uparrow})/(2W_0 + 2W) \quad (3)$$

where  $n_0'$  is the equilibrium population difference in the presence of microwave power,  $N$  is the total number of spins and  $W_{\downarrow}$  and  $W_{\uparrow}$  are the lattice induced transition probabilities in the two directions. Both  $n_0'$  and  $1/T_1'$  tend to approach the conventional definitions of  $n_0$  and  $1/T_1$ , as  $W \rightarrow 0$ , *i.e.*, at very low monitoring power levels. Hence, at low temperature,  $T_1'$  was measured as a function of monitoring power and the linear plot obtained by plotting  $1/T_1'$  against the microwave power level was extrapolated to zero power level to determine  $1/T_1$ .

In order to determine the effects of dissolved oxygen on  $T_1$  and  $\Delta H$ , measurements were made before and after degassing a particular sample and in agreement with the observations of Schreurs and Fraenkel (1961), it was found that  $T_1$  and  $\Delta H$  did not change, within the limits of experimental error, by degassing. Since alkaline solutions of hydroquinones are excellent scavengers of oxygen, it is to be expected that the concentration of dissolved oxygen in alkaline solutions of hydroquinones is always extremely small.

The observations were carried out in the concentration range  $10^{-4}$  to  $5 \times 10^{-2} M$  and an estimate of the concentrations were made by comparing the esr spectra

with that from a standard DPPH sample. It is expected that our concentration estimates are correct to  $\pm 20\%$ . No attempts were made to improve the accuracy since, as will be presented later, the measurements of interest in this paper in alcoholic solutions are essentially concentration independent in this range.

The temperature was varied by varying the temperature of the nitrogen gas passing over the sample and flowing through a quartz dewar inserted into a home-made rectangular cavity operating in the  $TE_{102}$  mode. The temperature of the nitrogen gas was controlled using the Varian V-4540 temperature control accessory. The temperatures were measured using a copper-constantan thermocouple and a type K-3 Leeds and Northrup potentiometer. The temperatures were maintained constant to  $\pm 1^\circ\text{C}$  and consequently the temperature measurements were accurate to this extent. Measurements at liquid nitrogen temperature were carried out using a tunable cylindrical cavity operating in the  $TE_{111}$  mode immersed in liquid nitrogen.

Viscosity measurements on solutions of hydroquinones in ethanol and *n*-butanol were made using an Ostwald viscometer at different temperatures in a thermostat to determine how critically the viscosity depended on the hydroquinone concentration. It was observed that the viscosity of the solvent and the solution were significantly different only for concentrations of hydroquinones higher than  $10^{-2} M$ ; and that the temperature dependence of the viscosity—when expressed in the form  $\eta = \eta_0 \exp(\Delta E/RT)$ —was given by the same value of  $\Delta E$  for both the solvent and solutions up to a concentration of  $10^{-1} M$ . Since most of the measurements were carried out at a hydroquinone concentration less than  $10^{-2} M$ , it was decided to use the viscosity of pure solvents, at different temperatures (Handbook 1971-72) while analysing the data.

### 3. Theory

#### 3.1 Relaxation times

Organic free radicals, whose *g* values measure close to 2.0023, obviously, have their orbital angular momentum mostly quenched. In such orbitally non-degenerate systems, the contributions to spin-lattice relaxation and linewidths in dilute solutions arise from (a) the modulation of the anisotropic part of the *g*-tensor due to the random motions; (b) spin-rotation interaction and (c) the modulation of the anisotropic part of the electron-nuclear hyperfine interaction. At higher concentrations of free radicals two additional interactions, (d) exchange interactions (both chemical and Heisenberg type) and (e) electron-electron dipolar interactions are expected to play a significant role.

The dependence of spin-lattice relaxation times and linewidths on the nuclear spin quantum number associated with the transition, the nature of the solvent, temperature, viscosity and the concentration of the paramagnetic species will indicate as to which of the interactions mentioned above are the dominant ones. In our earlier paper (Rengan *et al* 1972 *a*) we have discussed some of these aspects and here we briefly outline, for the purpose of later discussions, as to how these interactions determine the relaxation behaviour of the free radicals.

(a) The *g*-modulation and (b) the spin-rotation interactions: The contribution of these two interactions to the relaxation times are independent of the nuclear spin state and depend upon the correlation times  $\tau_\theta$  and  $\tau_J$ , where  $\tau_\theta$  refers to the

correlation time associated with the angular reorientation and  $\tau_j$  the correlation time associated with changes in angular momentum. For the case of isotropic tumbling motion of the free radical, we have the following expressions (Nyberg 1967):

$$1/T_{1v} = \sum_{i=1}^3 (g_i - g_s)^2 \frac{\omega_0^2}{5g_s^2} \frac{\tau_\theta}{(1 + \omega_0^2 \tau_\theta^2)} \quad (4)$$

$$1/T_{2v} = \sum_{i=1}^3 (g_i - g_s)^2 \frac{2\omega_0^2 \tau_\theta}{15g_s^2} + 1/(2T_{1v}) \quad (5)$$

and

$$1/T_{1SR} = 1/T_{2SR} = \frac{6kT}{9I} \sum_{i=1}^3 (g_i - 2.0023)^2 \tau_j \quad (6)$$

with  $\omega_0^2 \tau_j^2 \ll 1$  and  $\tau_j \ll \tau_\theta$ . Here the subscripts 'g' and 'SR' to  $T_1$  and  $T_2$  represent the contributions to the two relaxation times from these two interactions;  $g_1, g_2$  and  $g_3$  are the principal values of the  $g$ -tensor with  $g_s = (1/3)(g_1 + g_2 + g_3)$ ;  $I$  represents the moment of inertia of the molecule treated as a sphere and  $\hbar\omega_0$  is the energy separation between the electron Zeeman levels giving the esr transitions. The above contributions, mainly, will be independent of free radical concentration unless a resultant viscosity change arises.

(c) The modulation of the anisotropic part of the electron-nuclear hyperfine interaction: The contribution from such an interaction is nuclear spin state dependent and earlier papers (Stephen and Fraenkel 1960, Schreurs and Fraenkel 1961, Kivelson 1960, McConnell 1956) have explained the dependence of linewidths of the different hyperfine lines of a given semiquinone ion on this basis. It has been shown that the contribution of this interaction to spin-lattice relaxation is not significant compared to those from the modulation of the  $g$ -tensor and spin rotational effects (Nyberg 1967, Lingam *et al* 1972, Rengan *et al* 1972 *a* and references 2e, 2f, 4c, 4d, 5b, 5d, 5i, 9 and 19 in it). However, this interaction which is responsible for significant variation in the linewidths among the different hyperfine lines, is not considered while discussing our linewidth data, since only the  $M = 0$  ( $M = \sum_i m_i$ ) line (to whose linewidth this contribution is least) is investigated, and no comparison of linewidths of different hyperfine components is attempted.

(d) Exchange interactions: The theory of exchange interactions as applicable to the studies of relaxation times of free radicals in solutions has been worked out by several authors in detail (Eastman *et al* 1969 and references 8-13 in it). However, the net effect of exchange interaction, if it is strong, is to cause cross-relaxation between the hyperfine levels of a given  $m_s$  state of an electron spin level and we would not be able to observe this cross-relaxation effect in the saturation recovery trace unless both the pulse-widths and the time constant of the spectrometer are less than the cross-relaxation time. In the notation of Eastman *et al* (1969) what we shall be observing is  $T_{1M}(0)$ , *i.e.* the relaxation time, in the absence of exchange; with this characteristic time all the hyperfine levels corresponding to a given  $m_s$  relax together to an equilibrium distribution ( $T_{1M}(0) = 1/2W_e$ ). Also

linewidths have been measured in dilute solutions in a region where they are essentially concentration independent. It is therefore clear that our investigations cannot throw any light on the exchange interactions; however, we do believe that they are very weak even at high concentrations, due to the shielding of the free radicals from one another by a cage of solvent molecules. In such cases where exchange interaction is small, the spin-lattice relaxation will bring out equilibrium faster and hence the exchange effects cannot be detected.

(e) Electron-electron dipolar interactions: When electron dipole-dipole interactions are dominant, a concentration dependence for  $T_1$  is expected and in the absence of such a dependence we are forced to the conclusion that due to the caging effect of the solvents, the electron-electron dipole interactions do not play a dominant role in our studies and hence can be ignored.

### 3.2 Models for molecular rotations in liquids

As mentioned earlier, the random molecular motions in the liquid can be characterised by the correlation times  $\tau_\theta$  associated with the reorientation of the molecule and  $\tau_J$  associated with the changes in the angular momentum. Explicit expressions for  $\tau_\theta$  and  $\tau_J$  depend on the models used to describe the motions. We have considered in this section three simple models for molecular rotations which are used in explaining our results.

(a) Isotropic small step rotational diffusion model: In the isotropic small step rotational diffusion model (Debye 1945) the rotational diffusion takes place in small steps. The reorientational correlation time  $\tau_{\theta s}$  can be expressed in terms of the rotational diffusion constant  $D_r$  as,  $\tau_{\theta s} = 1/6D_r$  (Debye 1945; Bloembergen *et al* 1948). Using the Debye-Einstein-Stokes relationship we can write (Debye 1945):

$$\tau_{\theta s} = 4\pi R^3 \eta_{mr} / 3kT\beta_r \quad (7)$$

where  $R$  is the effective hydrodynamic radius of the molecule equated to a sphere,  $\eta_{mr}$  is the microviscosity seen by the molecule undergoing rotation, and  $\beta_r$  is a parameter, which depends on the coefficient of sliding friction in Sutherland's (1905) theory and is approximately unity. Following Hubbard (1958, 1963), we can write, under the assumption that  $\tau_{\theta s} \gg \tau_{Js}$ ,

$$\tau_{Js} = \frac{I}{6kT} \frac{3kT\beta_r}{4\pi R^3 \eta_{mr}} \quad (8)$$

so that

$$\tau_{Js}\tau_{\theta s} = I/6kT \quad (9)$$

One can expect such a reciprocal relationship between  $\tau_{\theta s}$  and  $\tau_{Js}$  on quite general grounds. If a given value of angular velocity,  $\omega$ , is maintained for a relatively long period, one should expect a large change in orientation during the same period and hence  $\tau_\theta$  will be short. Under the assumptions of equation (9), equation (6) reduces to

$$1/T_{1SR} = 1/T_{2SR} = (1/9) \sum_{i=1}^3 (g_i - 2.0023)^2 \tau_{\theta s}^{-1} \quad (10)$$

(b) Quasi lattice random flight model: This model developed by O'Reilly and Schacher (1963) and O'Reilly (1968), based on the large step random walk theory

of rotational diffusion (Ivanov 1963), assumes that the structure of the liquid up to a few coordination shells can be approximated by a lattice, so that some of the properties of the solid state, such as vacancies and translational diffusion by vacancy migration, are present. It is assumed that the molecule undergoes little or no reorientation at the normal site; but at the time of excitation of the molecule to an interstitial lattice site during the process of translational diffusion, it is to be expected that the molecule will undergo large amplitude reorientation because of the drastic changes in inter-molecular forces. The orientation of the molecule at the new site will not be correlated to the orientation before the translation occurred. If we assume that the reorientation takes place with translational diffusion, the orientation correlation time  $\tau_{\theta t}$  is equal to  $\tau_t$ , where  $\tau_t$  is the correlation time associated with the random flight (Chandrasekhar 1943), and is given by

$$\tau_{\theta t} = \tau_t = \langle d^2 \rangle / 6D_t \quad (11)$$

where  $\langle d^2 \rangle$  is the mean square flight distance and has a value  $(\sqrt{2} V_m)^{2/3}$  ( $V_m$  = molar volume) for a fcc arrangement of the quasilattice and  $D_t$  is the translational diffusion coefficient. Eyring and Ree (1958) have shown, after taking into account the discrete structure of the liquid, that  $D_t$  can be given by a relation similar to Stokes-Einstein relation, leading to:

$$\tau_{\theta t} = \frac{\langle d^2 \rangle \pi R \eta_{mt}}{kT\beta_t} \quad (12)$$

where  $\eta_{mt}$  is the microviscosity seen by the molecule undergoing translational motion and  $\beta_t$  is a parameter in Sutherland's theory (1905) or in Eyring's theory (1958);  $\beta_t$  will depend on the number of nearest neighbours in the quasilattice.

The angular momentum correlation time  $\tau_{Jt}$ , associated with the random flight, can be derived following a treatment similar to that proposed by Brown *et al* (1963). It can be shown (Huang and Kivelson 1972) that  $\tau_{Jt}$  is given by

$$\tau_{Jt} = \frac{I}{6kT} \tau_{\theta t}^{-1} \epsilon_0^2 (1 - \lambda_2)^{-1} \quad (13)$$

where the mean rotational jump angle  $\epsilon_0$  can be expressed in terms of  $\tau_t$ , the mean time for which reorientation occurs, as:

$$\epsilon_0 = \sqrt{\frac{6kT}{I}} \tau_t \quad (14)$$

$\lambda_2$  is a function of  $\epsilon_0$  and depends on the nature and width of the distribution of jump angles. Since spin-rotational interaction is the dominant term contributing to  $1/T_1$  at all temperatures, the quasilattice random flight model would predict that

$$1/T_{1SR} = 1/T_{2SR} = (1/9) \sum_{i=1}^3 (g_i - 2 \cdot 0023)^2 \epsilon_0^2 (1 - \lambda_2)^{-1} \tau_{\theta t}^{-1} \quad (15)$$

However, one should recognize that the molecule in the normal site will not be at rest, but undergoes small amplitude angular oscillations most of the time without changing its mean position. These oscillations can be treated in the same manner as in the small step diffusion model and our postulate is that even though a quasilattice random flight may take place, the contributions to  $1/T_{1SR}$  may arise mostly from these small amplitude oscillations. In these situations, the dependence of  $1/T_{1SR}$  on various experimental parameters should be understood in terms of eq. (10) alone, in which case it will not be possible to decide between the two

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From eqs (7), (12), (17) and (18) we have for the angular reorientation correlation time  $\tau_\theta$ , in the two models considered above,

$$\tau_{\theta s} = \frac{1}{9} \frac{\eta\pi}{kT\beta_t} \frac{R^6}{a^3} \quad (19)$$

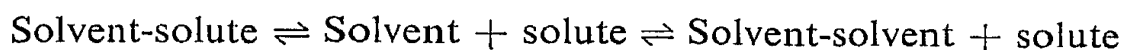
and

$$\tau_{\theta t} = \frac{1}{2} \frac{\langle d^2 \rangle \pi\eta}{kT\beta_t} \frac{R^2}{a} \quad (20)$$

For the reasonable assumption that  $\langle d^2 \rangle \simeq (2a)^2$ ,

$$\tau_{\theta t} \simeq \frac{2\pi\eta}{kT\beta_t} R^2 a \quad (21)$$

(c) Hindered rotation: Another type of motion which is of interest to us, when using hydrogen bonding solvents is similar to the model proposed by Brown *et al* (1963). Here, the molecule undergoes free rotation for an average time  $\delta$  and the free rotation is absent during an average time  $\tau_r$ . This situation can be imagined to be arising from a chemical equilibrium of the type:



where - indicates bonding. Taking the specific example of semiquinones in alcohols, the semiquinone is hydrogen bonded to the neighbouring alcohol molecules through its oxygens, for an average period  $\tau_r$  during which it is not free to rotate. The breaking of the hydrogen bonds leading to a situation when the semiquinone and its neighbours are free, requires an activation energy  $\Delta E_r$ . But this activated state is unstable. A stable situation can be obtained when the neighbouring alcohol molecules form hydrogen bonds between themselves leaving the semiquinone free to rotate in the solvent cage for an average time  $\delta$ . This free rotation is stopped when the neighbouring solvent molecules break the hydrogen bonds between themselves which requires an activation energy  $\Delta E_\delta$  enabling the solvent molecules to form bonds with the semiquinone. The number of times the oxygens of the semiquinone come across the solvent hydrogen bonding sites while the semiquinone is freely rotating is proportional to the frequency of rotation. Thus using  $I_a \omega_a^2 = kT$  for the rotation about an axis (denoted by  $a$ ), we can write

$$\delta = C \sqrt{\langle I \rangle / kT} \exp(\Delta E_\delta / RT) \quad (22)$$

and

$$\tau_r = \tau_0 \exp(\Delta E_r / RT) \quad (23)$$

where  $C$  is a constant factor. The hindered rotation can also be described in a slightly different way.

The start of the free rotation is brought about by the simultaneous breaking of the hydrogen bonds between the solvent and solute and formation of the bonds between the solvent and solvent, the activation energy required for this process being  $\Delta E_r'$ , the difference in the two hydrogen bonding energies. The free rotation will stop when the semiquinone ion forms bonds with any other neighbouring solvent molecule which is free. This does not require any activation energy. Thus in this picture

**Table 1.** The dependence of  $\tau_\theta$ ,  $\tau_j$ ,  $T_1$  and  $T_2$  on the experimental parameters as predicted by the different models for molecular motion.

	Small step rotational diffusion model	Quasilattice random flight model	Hindered rotation
	is proportional to	is proportional to	Independent of $\eta$ ; Exponential dependence on temperature
$\tau_\theta$ ..	$(R^6/a^3), (\eta/T)$	$R^2a, (\eta/T)$	
$\tau_j$ ..	$(a^3/R^6), (1/\eta)$	$\{(a^3/R^6), (1/\eta)^*\}$ $\{(R^2a)^{-1}, (1/\eta)^\dagger\}$	
$1/T_{1SR} = 1/T_{2SR}$ ..	$(a^3/R^6), (T/\eta)$	$\{(a^3/R^6), (T/\eta)^*\}$ $\{(R^2a)^{-1}, (T/\eta)^\dagger\}$	
$1/T_{1E} (\omega_0^2 \tau_\theta^2 \gg 1)$	$(a^3/R^6), (T/\eta)$	$(R^2a)^{-1}, (T/\eta)$	
$1/T_{2E} (\omega_0^2 \tau_\theta^2 \gg 1)$	$(R^6/a^3), (\eta/T)$	$R^2a, (\eta/T)$	
	* Corresponding to the small amplitude oscillations in the normal site. † Corresponding to the reorientation by random flight.		

$$\delta = C' \sqrt{(I/kT)} \quad (24)$$

and

$$\tau_R = \tau_0 \exp(\Delta E_R'/RT) \quad (25)$$

In this hindered rotation model,  $\delta^2/\tau_R$  takes the place of  $\tau_j$  and  $\tau_R$  takes the place of  $\tau_\theta$  used in the discussions of viscosity dependent motion. If the hindered rotation takes place about an axis 'a' the contribution to  $T_1$  and  $T_2$  from the spin-rotational interaction will be

$$1/T_{1SR}^h = 1/T_{2SR}^h = \frac{2kT}{3I_a} (g_a - 2.0023)^2 \frac{\delta^2}{\tau_R} \quad (26)$$

when  $\omega_0^2 \delta^2 \ll 1$  and  $\delta \ll \tau_R$ ;  $g_a$  is the  $g$  value along the axis of rotation. Using the expressions for  $\delta$  and  $\tau_R$ , we have

$$1/T_{1SR}^h = 1/T_{2SR}^h = \frac{2C_0}{3\tau_0} (g_a - 2.0023)^2 \exp(-\Delta E/RT) \quad (27)$$

where  $C_0 = C^2$  or  $C'^2$  and  $\Delta E = (\Delta E_R - 2\Delta E_\delta)$  or  $\Delta E_R'$  depending on the description of the hindered rotation.

Table 1 sums up our discussions on the models for molecular motions by comparing the predicted dependence of the correlation times and the relaxation times on the physical parameters varied in the experiments.

#### 4. Results

As stated earlier, the spin-lattice relaxation times of *p*-benzosemiquinone ion (PBSQ), toluosemiquinone ion (TSQ), 2,5-dimethylsemiquinone ion (2, 5-DMSQ), 2,6-dimethylsemiquinone ion (2,6-DMSQ), durosemiquinone ion (DSQ), mono-tertiarybutylsemiquinone ion (2-TBSQ) and 2,5-ditertiarybutylsemiquinone ion

(2, 5-DTBSQ) have been measured as a function of temperature in the hydrogen bonding solvents methanol, ethanol and *n*-butanol. The dependence of  $T_1$  on the viscosity of the solvent has been determined in the case of 2,5-DMSQ, 2-TBSQ and 2,5-DTBSQ by using mixed solvents of ethanol and glycerol in different proportions. In suitable cases, the dependence of  $T_1$  on the concentration of the radical has been investigated. Linewidth studies have been made on PBSQ and DSQ in methanol, ethanol, *n*-butanol and benzyl alcohol as a function of temperature at low radical concentrations ( $\sim 10^{-4} M$ ).

In all the spin-lattice relaxation experiments mentioned above, in agreement with earlier reports from our laboratory, the signal recovery traces at the end of the saturating pulse were exponential. The dependence of  $T_1$  on the nuclear magnetic quantum number associated with the hyperfine transition was reinvestigated in the case of PBSQ in ethanol and *n*-butanol, DSQ in ethanol and 2,5-DTBSQ in methanol, ethanol and *n*-butanol. It was observed that  $T_1$  was the same for all the hyperfine transitions of the semiquinone within the limits of experimental error ( $\pm 5\%$ ) confirming the earlier reports from our laboratory (Lingam *et al* 1972, Rengan *et al* 1972 *a*).

Connor (1972) has investigated some of the above systems by continuous saturation technique and table 2 compares our data with his  $T_{1M}(0)$  (for  $M = 0$  line) for PBSQ, 2,5-DMSQ and DSQ in ethanol. It is observed that the two sets of data, presented in table 2, agree reasonably well at higher temperatures. We believe our results to be superior, due to the directness of the method of measurement and the inherent difficulty in the continuous saturation method, of measuring  $H_1$ , the strength of the oscillating magnetic field at the site of the sample; further

Table 2. Comparison of  $T_1$  data obtained by continuous saturation technique† (i) and saturation recovery technique\* (ii), for PBSQ, 2,5-DMSQ and DSQ in ethanol.  $T_1$  is expressed in  $10^{-6}$  sec.

Temperature °C	$T_1$ of PBSQ in ethanol		$T_1$ of 2, 5-DMSQ in ethanol		$T_1$ of DSQ in ethanol	
	by (i)	by (ii)	by (i)	by (ii)	by (i)	by (ii)
0	2.77	..	..	5.80	7.24	7.75
-10	3.02	3.05	5.60	7.00	8.49	8.65
-20	3.14	4.0	6.07	8.40	8.59	10.1
-30	4.28	5.05	7.64	10.20	9.69	11.9
-40	5.05	6.50	8.02	12.1	12.00	13.8
-50	6.51	8.40	8.95	14.3	12.00	16.2
-60	7.11	10.7	9.49	16.8	13.90	19.0
-70	9.32	13.8	..	19.7	12.80	22.0
-80	9.94	18.2	..	23.0	..	25.1

† Data from Connor (1972).

\* Present work

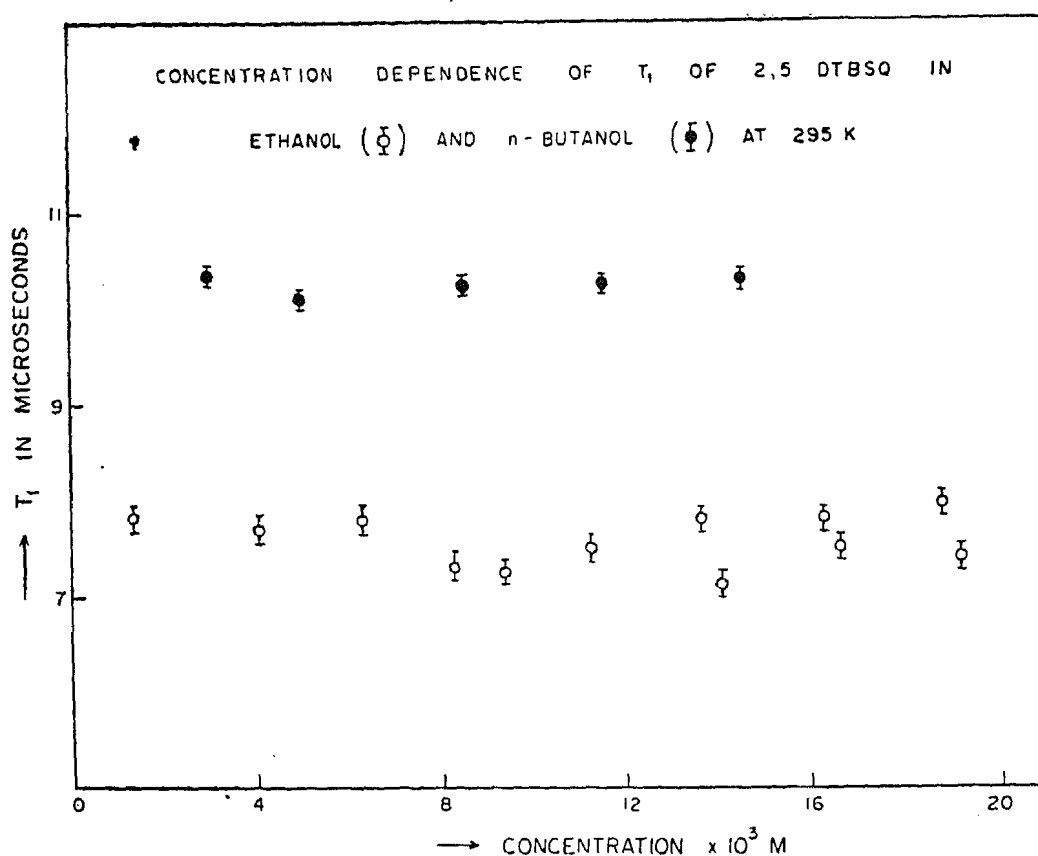


Figure 1. Concentration dependence of  $T_1$  of 2,5-DTBSQ in ethanol ( $\circ$ ) and *n*-butanol ( $\bullet$ ) at 295 K, in the radical concentration range  $3 \times 10^{-3}$  to  $3 \times 10^{-2}$  M

in this method,  $T_1$  is dependent on the assumed line shape function. We shall now summarise our observations on the dependence of  $T_1$  upon the different experimental parameters varied during our current investigations.

#### 4.1 Concentration dependence of $T_1$

The relaxation times,  $T_1$ , have been measured as a function of free radical concentration in the range  $3 \times 10^{-3}$  to  $3 \times 10^{-2}$  M in ethanol and *n*-butanol for 2,5-DTBSQ at 295 K. Figure 1 shows the measured values of  $T_1$  for 2,5-DTBSQ as a function of radical concentration in ethanol and *n*-butanol and it is clear that  $T_1$  is not sensitive to the radical concentration. This behaviour has been qualitatively verified at different temperatures and for other semiquinones.

The negligible dependence of  $T_1$  on concentration suggests that radical-radical interactions are not the dominant relaxation mechanisms that contribute to spin-lattice relaxation in these solvents. This behaviour is to be expected if we assume that the free radical is caged by the solvent molecules preventing the radicals from approaching close to one another for these interactions to play a dominant part. Such an assumption is justified later in this section.

#### 4.2 Viscosity and temperature dependence of $T_1$

In our earlier paper (Rengan *et al* 1972 *a*), the temperature dependence of  $T_1$  of the different semiquinones in alcoholic solvents have been analysed assuming that  $T_1$  follows an equation of the form:

$$T_1 = AT^{-n} \exp(E/RT) \quad (28)$$

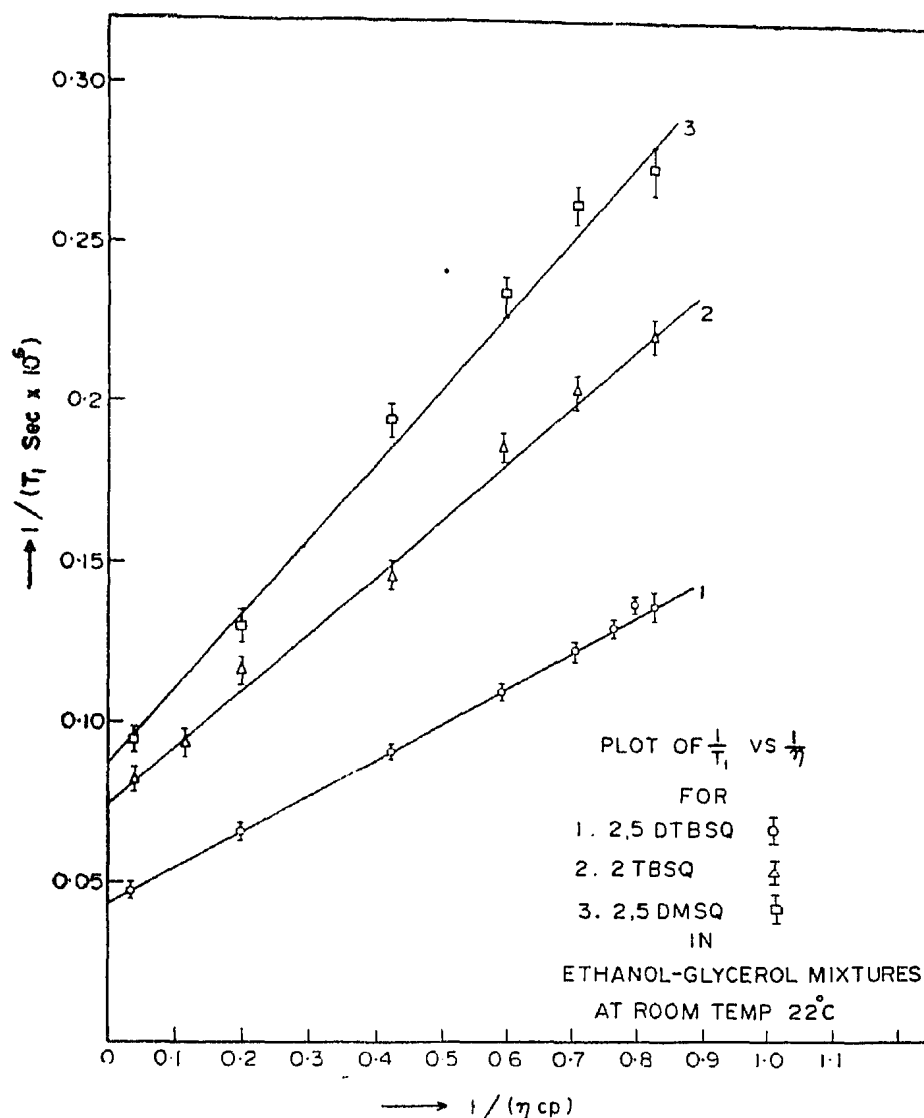


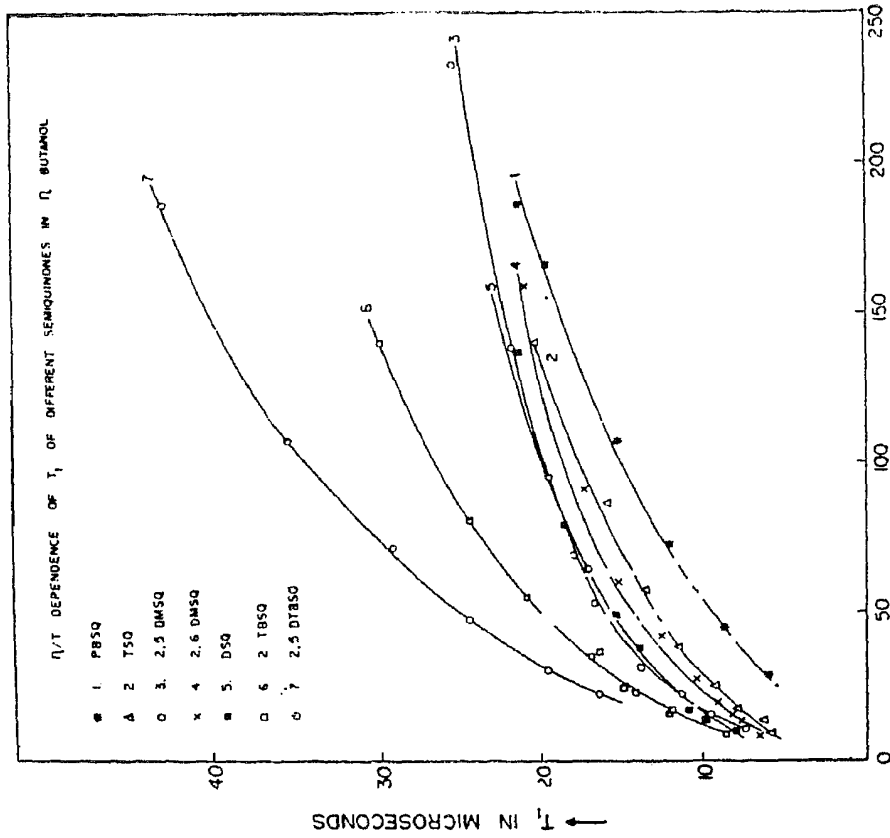
Figure 2. A plot of  $(1/T_1)$  versus  $(1/\eta)$ , for 2,5-DMSQ ( $\square$ ), 2-TBSQ ( $\triangle$ ), and 2,5-DTBSQ ( $\circ$ ), in ethanol-glycerol mixtures at 295 K.

with  $n = 0, \frac{1}{2}$  and 1. It was found that the activation energy  $E$  associated with the temperature dependence of  $T_1$  was different from that associated with the viscosity of the solvent. This suggested that the dominant term in the expression for the spin-lattice relaxation time is not dependent on the viscosity of the solvent in these systems. However, the fit obtained was not very good. The role, played by the viscosity-dependent motion in the spin-lattice relaxation, has been examined by measuring  $T_1$  for 2, 5-DMSQ, 2-TBSQ and 2, 5-DTBSQ in a mixture of ethanol and glycerol at 295 K. The viscosity of the mixed solvent was varied by varying the proportion of glycerol from 0% to 25% by volume, in the mixture. Figure 2 shows a plot of  $(1/T_1)$  versus  $(1/\eta)$  for these semiquinones. The viscosity values for the different mixtures were taken from literature (Timmermans 1959).

It can be seen that the variation of  $T_1$  with viscosity follows an equation of the form:

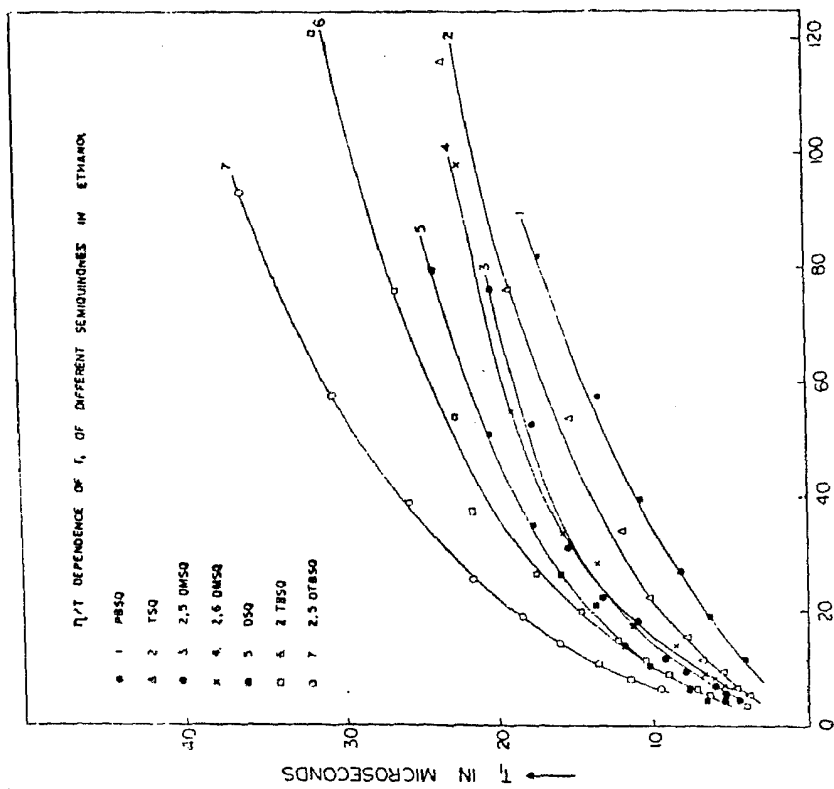
$$(1/T_1) = (A'/\eta) + B' \quad (29)$$

where  $A'$  and  $B'$  are constants at a given temperature  $T$ . This equation clearly shows that a viscosity-dependent motion also contributes to the spin-lattice relaxation process. Since the correlation times associated with the viscosity dependent



$$\rightarrow (\eta_{cp}/T^2 K) \times 10^3$$

Figure 3 (b).  $T_1$  is plotted against  $(\eta/T)$  for different semiquinone ions in *n*-butanol: PBSQ, TSO, 2,5-DMSQ, 2,6-DMSQ, DSO, 2-TBSQ and 2,5-DTBSQ [solid lines are computed using equation (30) with  $A$ ,  $B$  and  $\Delta E$  values quoted in table 3].



$$\rightarrow (\eta_{cp}/T^2 K) \times 10^3$$

Figure 3 (a).  $T_1$  is plotted against  $(\eta/T)$  for different semiquinone ions in ethanol: PBSQ, TSO, 2,5-DMSQ, 2,6-DMSQ, DSO, 2-TBSQ and 2,5-DTBSQ [solid lines are computed using equation (30) with  $A$ ,  $B$  and  $\Delta E$  values quoted in table 3].

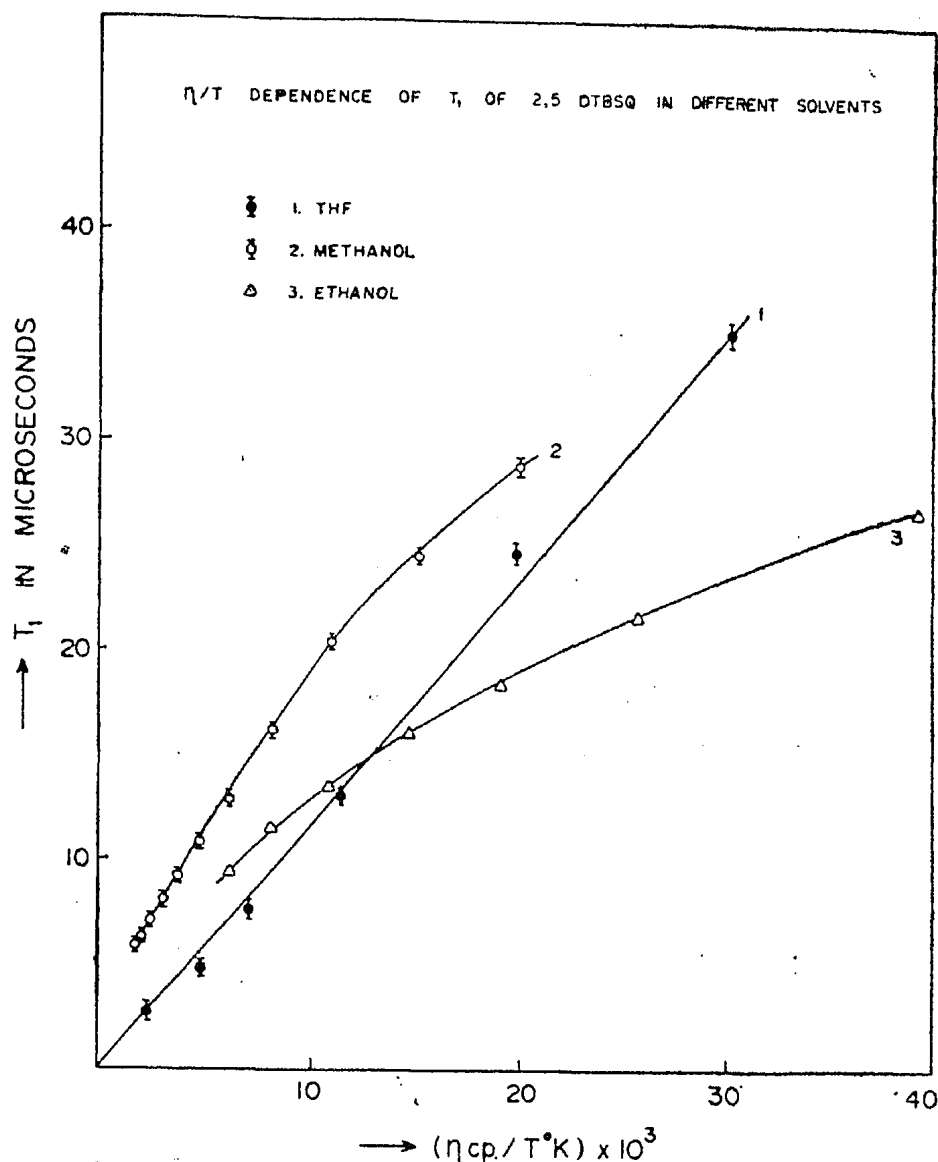


Figure 3(c).  $T_1$  is plotted against  $(\eta/T)$  of 2,5-DTBSQ in different solvents: methanol, ethanol and THF [solid lines are computed using equation (30) with  $A$ ,  $B$  and  $\Delta E$  values quoted in table 3].

motions are expressed in terms of  $\eta/T$ , we expect  $A'$  to vary linearly with temperature. Writing  $A' = A \cdot T$ , the temperature dependence of  $B'$  of PBSQ and other substituted semiquinones in alcoholic solvents was examined by analysing the  $T_1$  data at various temperatures.

The spin-lattice relaxation times  $T_1$  of different semiquinones in ethanol and *n*-butanol are plotted against  $(\eta/T)$  in figure 3a and figure 3b respectively. Figure 3c depicts similar plots for 2, 5-DTBSQ in methanol, ethanol and tetrahydrofuran (THF). The data could be fitted to the equation

$$1/T_1 = A (T/\eta) + B \exp(-\Delta E/RT) \quad (30)$$

(where  $A$  and  $B$  are constants), in cases where alcohols were used as solvents. In the case where THF (which is not a hydrogen bonding solvent) was used as solvent the second term in eq. (30) was absent and  $T_1$  was proportional to  $(\eta/T)$ . Different values of  $\Delta E$  varying from  $0.5 \text{ kcal mole}^{-1}$  to  $1.5 \text{ kcal mole}^{-1}$  were assumed and  $A$  and  $B$  values were obtained using the least squares fit procedure. It was found that the parameter  $A$  was not very sensitive to the changes in  $\Delta E$  and the minimum percentage error in the least squares fitting could be obtained for  $\Delta E$  values in

Table 3.  $T_1$  data analysed as  $(1/T_1) = A(T/\eta) + B \exp(-\Delta E/RT)$  for different semiquinones in different solvents.  $A$  and  $B$  values for  $\Delta E = 1$  kcal mole $^{-1}$ .  $A$  is expressed in units of  $10^4$  P. sec $^{-1}$ . K $^{-1}$ .  $B$  is expressed in units of  $10^6$  sec $^{-1}$ .

Solvent	Semiquinone							
	PBSQ	TSQ	2,5-DMSQ	2,6-DMSQ	DSQ	2-TBSQ	2,5-DTBSQ	
Methanol	$A =$	..	..	..	..	..	..	0.000244 $\pm 0.000012$
	$B =$	..	..	..	..	..	..	0.269 $\pm 0.012$
Ethanol	$A =$	0.00240 $\pm 0.00036$	0.000828 $\pm 0.000041$	0.000483 $\pm 0.000039$	0.000676 $\pm 0.000060$	0.000370 $\pm 0.000030$	0.000535 $\pm 0.000026$	0.000385 $\pm 0.000014$
	$B =$	0.410 $\pm 0.012$	0.519 $\pm 0.021$	0.540 $\pm 0.016$	0.505 $\pm 0.020$	0.469 $\pm 0.019$	0.347 $\pm 0.010$	0.268 $\pm 0.007$
<i>n</i> -Butanol	$A =$	0.00360 $\pm 0.00010$	0.001162 $\pm 0.000080$	0.000640 $\pm 0.000026$	0.000875 $\pm 0.000043$	0.000578 $\pm 0.000056$	0.000753 $\pm 0.000025$	0.00060 $\pm 0.00002$
	$B =$	0.267 $\pm 0.005$	0.381 $\pm 0.016$	0.383 $\pm 0.004$	0.404 $\pm 0.008$	0.404 $\pm 0.012$	0.260 $\pm 0.005$	0.174 $\pm 0.006$
THF	$A =$	..	..	..	..	..	..	0.00090 $\pm 0.00002$
	$B =$	..	..	..	..	..	..	0.0



**Table 4.** Comparison of  $A$  and  $B$  values obtained from the  $T_1$  data of 2,5-DMSQ, 2-TBSQ and 2,5-DTBSQ: (i) Temperature dependence study in ethanol, and (ii) Viscosity dependence studies in ethanol-glycerol mixtures.

Semiquinone	$A$ ( $10^4$ P. sec. $^{-1}$ K $^{-1}$ )		$B$ ( $10^6$ sec. $^{-1}$ )	
	(i)	(ii)	(i)	(ii)
2,5-DMSQ	0.000483 $\pm 0.000039$	0.00079 $\pm 0.00005$	0.540 $\pm 0.016$	0.461 $\pm 0.025$
2-TBSQ	0.000535 $\pm 0.000026$	0.00060 $\pm 0.00005$	0.347 $\pm 0.010$	0.395 $\pm 0.022$
2,5-DTBSQ	0.000385 $\pm 0.000014$	0.00038 $\pm 0.00002$	0.268 $\pm 0.007$	0.232 $\pm 0.010$

the range 0.9 kcal mole $^{-1}$  to 1.1 kcal mole $^{-1}$ , for all the semiquinones studied. The value of  $B$ , however, was quite sensitive to changes in  $\Delta E$ , as expected. The parameters  $A$  and  $B$  obtained for different semiquinones in alcohols for  $\Delta E = 1$  kcal mole $^{-1}$  are given in table 3.

It can be seen that eq. (30) reduces to eq. (29), at constant temperature  $T$  (illustrating the inherent consistency of these equations). The constants  $A'$  and  $B'$  of eq. (29) are related to  $A$ ,  $B$  and  $\Delta E$  as

$$A' = AT \quad (31)$$

$$B' = B \exp(-\Delta E/RT) \quad (32)$$

Assuming  $\Delta E = 1$  kcal mole $^{-1}$ , the values of  $A$  and  $B$  were also obtained from the values of  $A'$  and  $B'$  obtained from the  $T_1$  data of semiquinones in ethanol-glycerol mixtures (figure 2). These are compared in table 4 with those obtained from the study of temperature-dependent behaviour (table 3) in ethanol. The agreement is fairly good, considering the fact that the character of the solvent changes, from one solvent composition of ethanol-glycerol mixture to another.

In figure 4,  $T_1$  is plotted (in logarithmic scale) as a function of  $(1/T)$  for 2,5-DTBSQ in ethanol and  $n$ -butanol and the data points extend beyond the freezing points of the solvents (indicated by arrows in figure 4) and it can be seen that there is no discontinuity at the freezing points of the solvents. Below the freezing point  $\log T_1$  varies linearly with respect to  $(1/T)$  and hence the relationship between  $T_1$  and  $T$  is expressible as

$$1/T_1 = B \exp(-\Delta E/RT) \quad (33)$$

with the same values of  $B$  and  $\Delta E$  obtained in our analysis of the data above the freezing point (*i.e.*, in the liquid state). Also eq. (33) is consistent with eq. (30), since the latter reduces to the former when  $\eta$  tends to sufficiently large values, so that the contribution from the first term can be neglected.

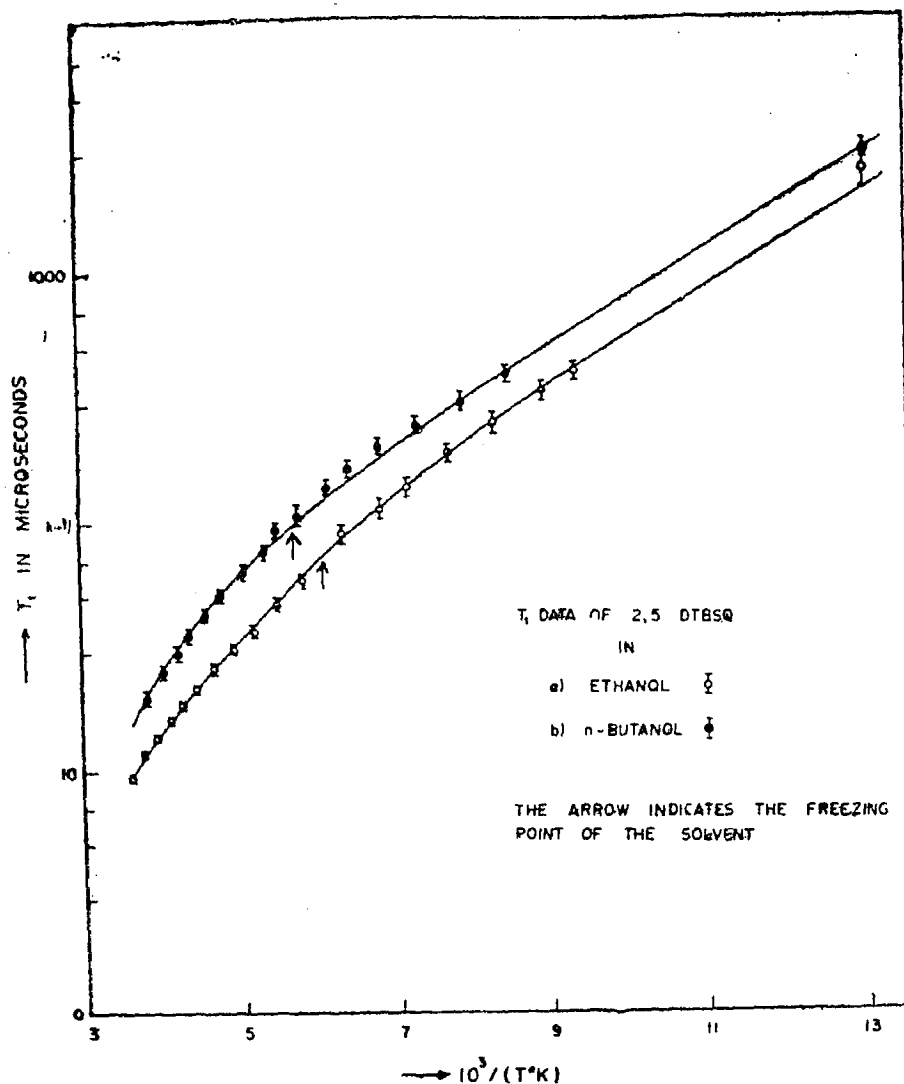


Figure 4. A plot of  $T_1$  (logarithmic scale) versus  $10^3/T$  for 2,5-DTBSQ in ethanol and *n*-butanol. The data points extend beyond the freezing points of the solvents indicated by the arrows.

#### 4.3 Linewidth studies

For studies on linewidths, it is desirable to choose the well-resolved hyperfine lines of PBSQ and DSQ rather than others, which have poorly resolved or inhomogeneously broadened lines. The linewidths of PBSQ and DSQ were measured as a function of temperature in methanol, ethanol, *n*-butanol and benzyl alcohol. The samples were prepared under vacuum, to improve the radical stability and the estimated concentrations were of the order of  $10^{-4} M$ . The spectra did show the expected linewidth dependence on  $M$ , the quantum number of the hyperfine transition. Since the linewidths are more sensitive than  $T_1$ , to concentration changes, two different samples whose concentrations did not differ by more than a factor of two were examined for each semiquinone in these solvents, except for DSQ in methanol and benzyl alcohol. This was done to ensure that we are very close to the concentration ranges, where exchange and dipolar effects may be neglected.

In figure 5 the linewidths  $\Delta H$  of  $M = 0$  line of PBSQ in ethanol (as measured between the points of extreme slope) are plotted against  $(\eta/T)$ . These values agree well with those reported by Leniart (1971). It can be seen that  $\Delta H$  decreases with increase in  $(\eta/T)$  for small values of  $(\eta/T)$ , reaches a minimum and then increases being proportional to  $(\eta/T)$  for large values of  $(\eta/T)$ . The data could be fitted reasonably well to an equation of the form

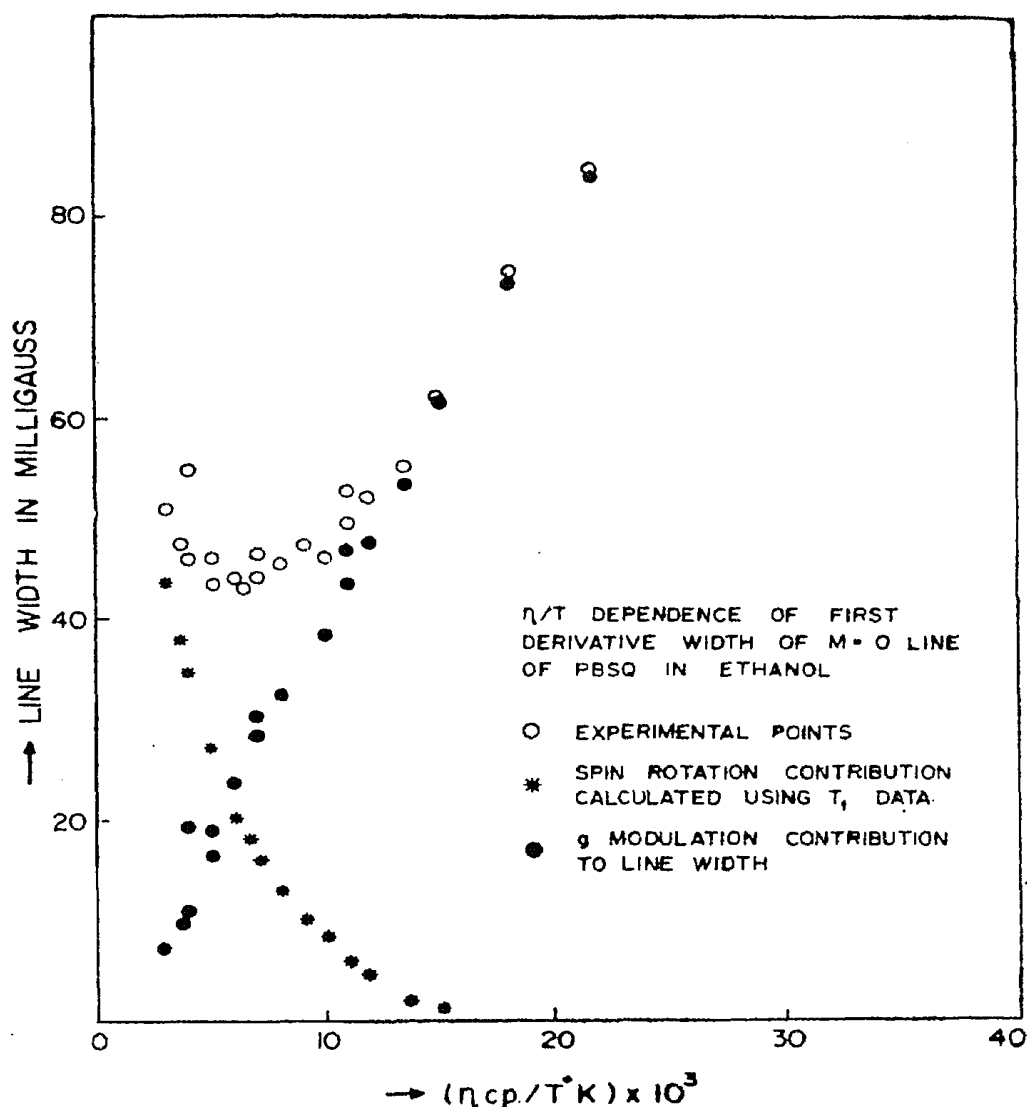


Figure 5. Plot of linewidth (distance between points of extreme slopes) versus  $(\eta/T)$ , of  $M = 0$  line of PBSQ in ethanol. The resolution of the observed linewidth into two separate contributions  $1/T_{2SR}$  and  $1/T_{2g}$  is also shown.

$$1/T_2 = 1/T_1 + K \cdot (\eta/T) \quad (34)$$

where  $K$  refers to the slope of the curve for large values of  $(\eta/T)$ . Figure 5 also shows the resolution of the linewidths into two such components. In figures 6 *a*, 6 *b*, 6 *c* and 6 *d* the linewidths of  $M = 0$  line are plotted as a function of  $(\eta/T)$  for PBSQ and DSQ in methanol, ethanol, *n*-butanol and benzyl alcohol, respectively. In these cases also  $\Delta H$  is proportional to  $(\eta/T)$  in the low temperature high viscosity region. The slopes  $K$  for the various systems studied are given in table 5.

## 5. Discussion

### 5.1 Dominant interactions responsible for the spin-lattice and transverse relaxations

It has been mentioned earlier that in the absence of radical-radical interactions, only spin rotational effects and the  $g$ -modulation contribute significantly to the spin-lattice relaxation and the linewidth of the  $M = 0$  line. A combined examination of  $T_1$  and  $\Delta H$  enables us to come to definite conclusions regarding the relative contributions of each of these effects. Referring to figure 5 and eq. (34) (for the case of PBSQ in ethanol) we realise that there is a contribution to  $1/T_2$ , equal to

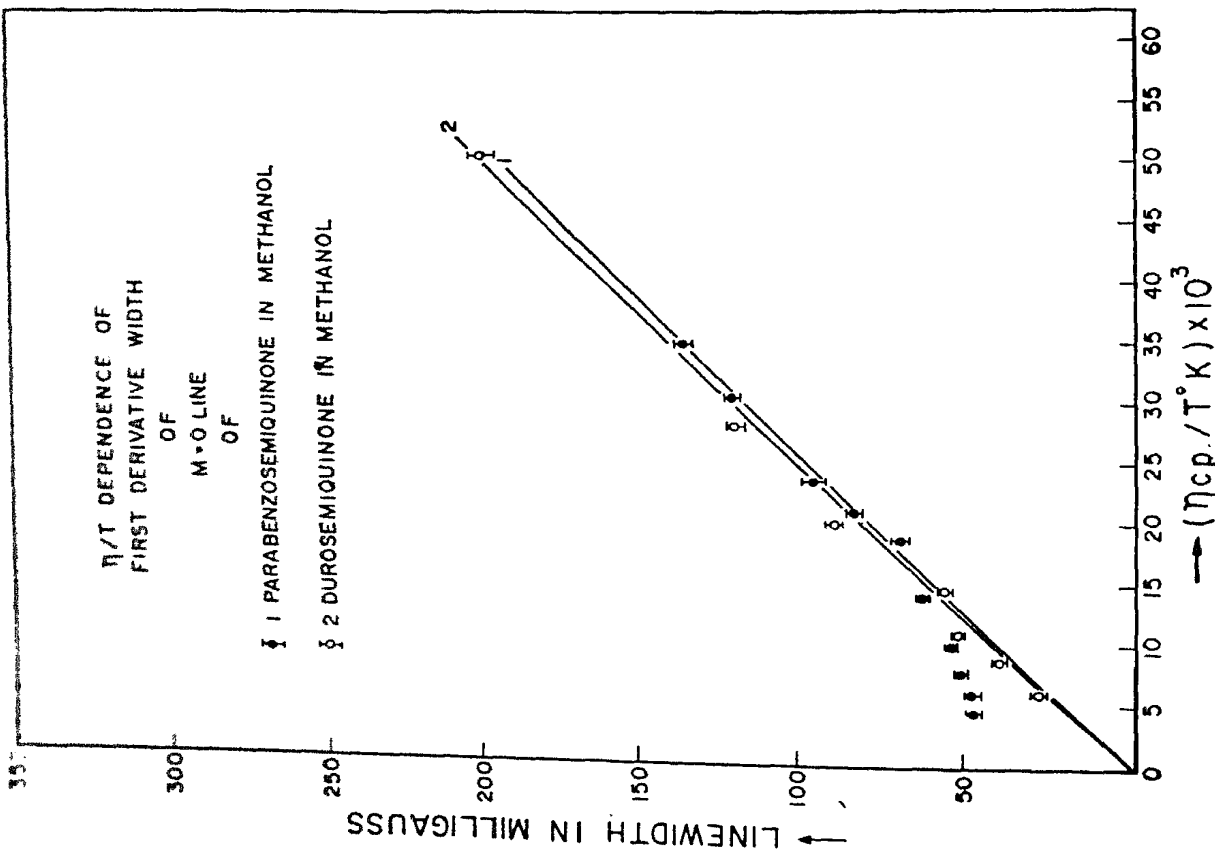


Figure 6 (a). Plot of linewidth (distance between points of extreme slopes) versus  $(\eta/T)$  of  $M = 0$  line of PBSQ and DSQ in methanol; (the concentration is about  $10^{-4} M$ ).

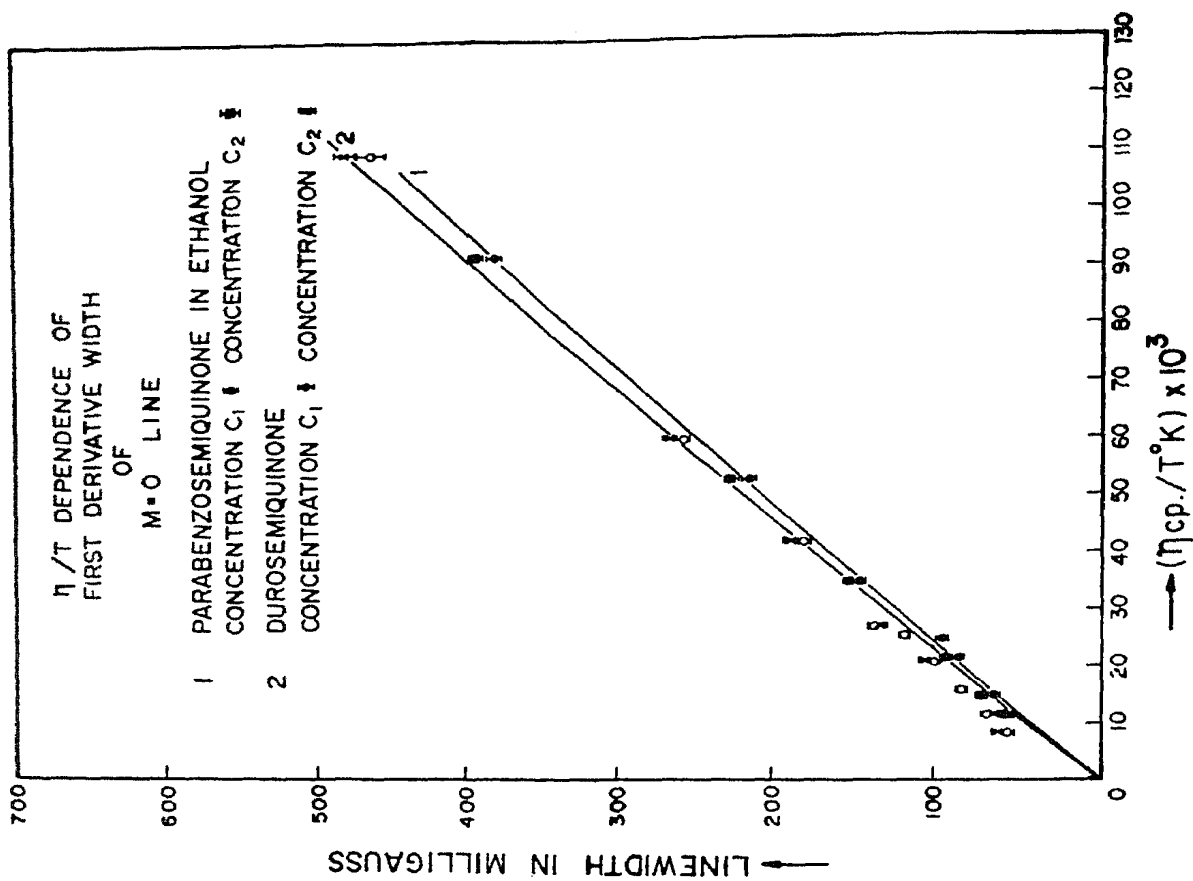


Figure 6 (b). Plot of linewidth (distance between points of extreme slopes) versus  $(\eta/T)$ , of  $M = 0$  line of PBSQ and DSQ in ethanol at two different concentrations  $C_1$  and  $C_2$ ; (the low concentration is about  $10^{-4} M$ ).

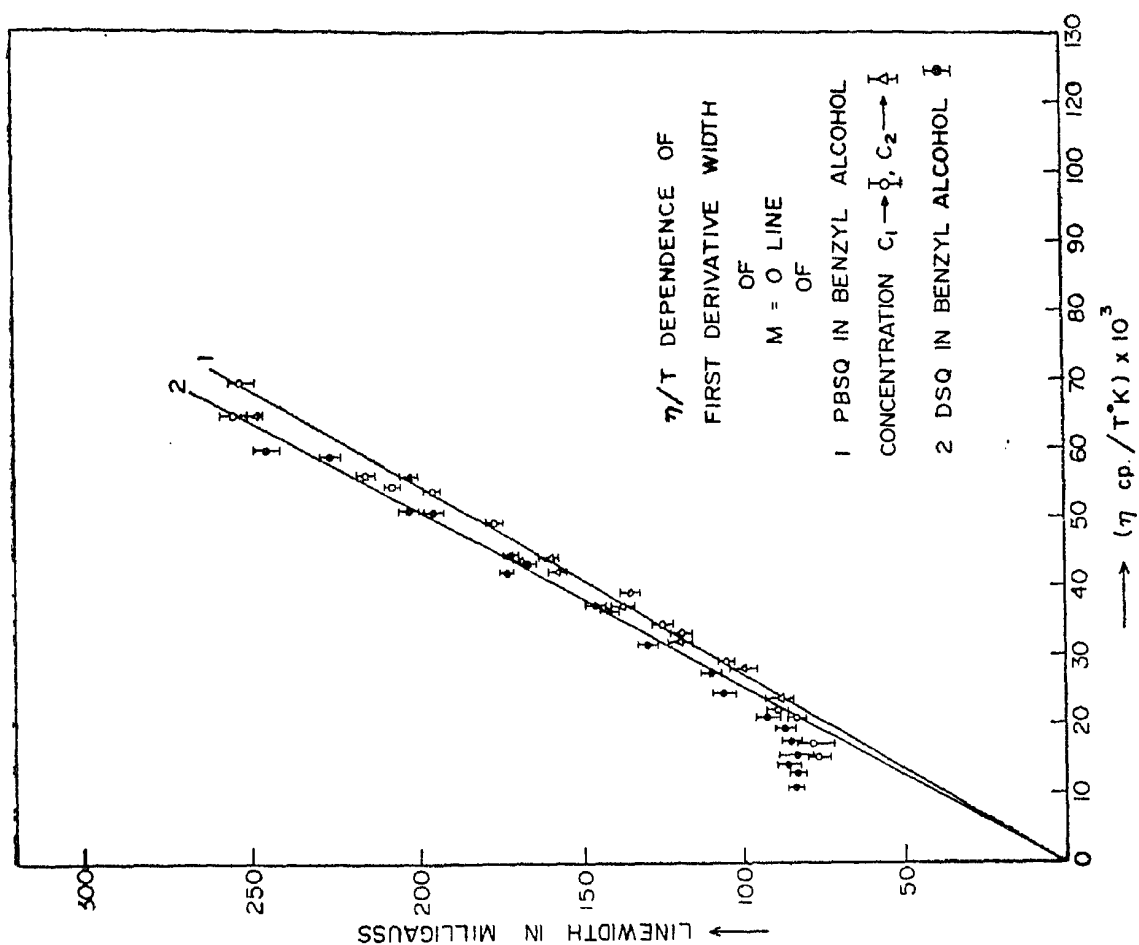


Figure 6 (d). Plot of linewidth (distance between points of extreme slopes) versus  $(\eta/T)$ , of  $M = 0$  line of PBSQ and DSQ in benzyl alcohol (PBSQ at two different concentrations  $C_1$  and  $C_2$ ) (the low concentration is about  $10^{-4} M$ ).

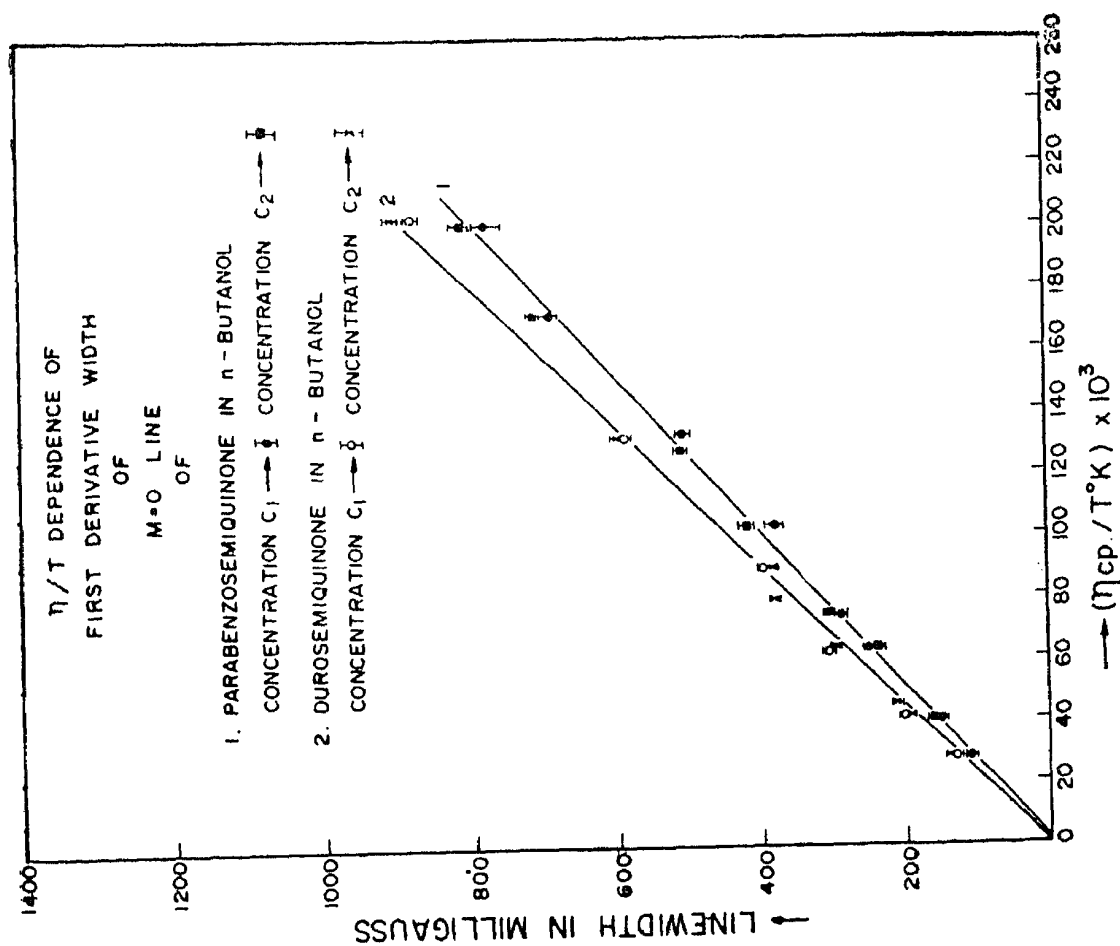


Figure 6 (c). Plot of linewidth (distance between points of extreme slopes) versus  $(\eta/T)$ , of  $M = 0$  line of PBSQ and DSQ in *n*-butanol at two different concentrations  $C_1$  and  $C_2$  (the low concentration is about  $10^{-4} M$ ).

**Table 5.** The slopes ( $K$ ) of linewidth *versus* ( $\eta/T$ ) plots at low temperature high viscosity range, for  $M = 0$  line of PBSQ and DSQ in methanol, ethanol, *n*-butanol and benzyl alcohol, in units of  $10^5 \text{ mG. P}^{-1} \text{ K}$ .

Solvent	PBSQ	DSQ
Methanol ..	3.84	3.96
Ethanol ..	4.12	4.36
<i>n</i> -Butanol ..	3.92	4.44
Benzyl alcohol ..	3.66	3.95

$1/T_1$ . Noting that  $1/T_{1\text{SR}} = 1/T_{2\text{SR}}$ , we come to the conclusion that the term  $1/T_1$  in eq. (34) and the spin-lattice relaxation are essentially due to the spin rotational effects. Thus, we can identify the second term in eq. (34) as due to  $g$ -modulation.

Taking a typical temperature ( $-30^\circ \text{C}$ ) and using eq. (5) we calculate the reorientation correlation time  $\tau_\theta$  (using  $g_1 = 2.0029$ ,  $g_2 = 2.0033$  and  $g_3 = 2.0073$ ) (Leniart 1971) from the linewidth data to be  $\sim 3.0 \times 10^{-10} \text{ sec}$ . Using this value of  $\tau_\theta$ , the contribution to  $1/T_1$  from  $g$ -modulation ( $1/T_{1g}$ ) is calculated to be  $\sim 5.0 \times 10^3 \text{ sec}^{-1}$ . This value is about 2.5% of the measured value  $2.0 \times 10^5 \text{ sec}^{-1}$  (corresponding to  $T_1 = 5.0 \times 10^{-6} \text{ sec}$ ). This confirms the above conclusion that the spin-lattice relaxation is mainly due to spin rotational effects. On the other hand, the transverse relaxation of the  $M = 0$  line is predominantly due to spin rotational effects in the high temperature low viscosity region, and in the low temperature high viscosity region the contribution to  $1/T_2$  comes mainly from the  $g$ -modulation.

### 5.2 Dominant molecular rotational motions responsible for the spin-lattice and the transverse relaxations

In section 3.2 we have discussed three simple models for molecular rotations in liquids. The predicted behaviour of  $\tau_\theta$  and  $\tau_J$  as a function of  $T$ ,  $\eta$ , the solvent size ( $a$ ) and the solute size ( $R$ ), are different for different models. In the following discussion we make the reasonable assumption that the anisotropic  $g$ -tensors of all the semiquinones used in our experiments are very nearly the same and that they do not vary much with the solvent or the temperature, so that the behaviour of  $T_1$  and  $T_2$  essentially reflects the behaviour of  $\tau_\theta$  and  $\tau_J$  [see eqs (19) and (21)]. Hence the measured  $T_1$  and  $T_2$  as a function of the experimental parameters will give us information about the molecular motions in the solution.

(a) Viscosity dependent motions: It has been argued above that the contribution to  $1/T_1$  comes dominantly from the spin rotation interaction and consequently contains information about  $\tau_J$ . Since  $1/T_1$  is expressed as a sum of two terms in eq. (30), it is clear that the angular momentum is modulated by two types of motion, one of which is viscosity dependent and the other is a hindered rotation. An examination of the  $A$  values from table 3 shows that this viscosity-dependent motion is sensitive to the size of the solute molecule. Table 6 gives the  $(A/V_m)$  values for the various semiquinones in alcohols,  $V_m$  being the molar volume of the solvent. The constancy of  $(A/V_m)$  for a particular semiquinone shows that  $A$  is

Table 6.  $(A/V_m)$  values for different semiquinones in alcohols in units of  $10^{-2}$  P. sec. $^{-1}$  cm. $^{-3}$ . K $^{-1}$ 

Semiquinone	Methanol	Ethanol	<i>n</i> -Butanol
	$V_m = 40.45$ cc	$V_m = 58.39$ cc	$V_m = 91.50$ cc
PBSQ	..	41.10	39.30
TSQ	..	14.70	12.69
2,5-DMSQ	..	8.27	7.00
2,6-DMSQ	..	11.57	9.56
DSQ	..	6.34	6.32
2-TBSQ	..	9.16	8.23
2,5-DTBSQ	6.02	6.59	6.55

proportional to  $a^3$  ( $a$  is the effective radius of the solvent molecule approximated to a sphere). These observations are consistent with the expression for  $\tau_j$  in the small step diffusion model [eq. (19)]. The effective radius  $R$  for the typical case of PBSQ in ethanol [using the  $T_1$  value at  $-30^\circ$  C and eqs. (10) and (19)] is found to be 3.1 Å, which is reasonable.

However, the second term  $K(\eta/T)$  occurring in eq. (34) for  $1/T_2$  is not very sensitive to the size of the solute or that of the solvent molecule as can be seen from the  $K$  values given in table 5. This term gives the contribution of  $g$ -modulation to  $1/T_2$  and involves the reorientation correlation time  $\tau_\theta$ . Thus the viscosity dependent motion associated with the reorientation of the molecule is not sensitive to the size of the solute or that of the solvent molecule. This would be more consistent with the expression for  $\tau_{\theta t}$  rather than  $\tau_{\theta s}$ . It should also be mentioned that the expressions, given in eqs (19) and (21) for  $\tau_{\theta s}$  and  $\tau_{\theta t}$  respectively, have been obtained assuming the molecules to be spherical. Though this would be a good approximation while describing the rotational motion, it will be a poor approximation for the description of translational motion. (It is assumed that reorientation of the molecule is coupled to translation in the model used to obtain  $\tau_{\theta t}$ .) Thus, it is not surprising that the behaviour of  $K$  does not agree very well with that predicted by eq. (21) for  $\tau_{\theta t}$ . On the basis of the arguments given above, we conclude that the viscosity-dependent reorientation of the molecule is associated with random flight, as described in the quasi lattice random flight model in section 3.2. The effective radius  $R$  for the typical case of PBSQ in ethanol is calculated [from the linewidth contribution  $K(\eta/T)$  at  $-30^\circ$  C, using equations (5) and (21)] to be 3 Å, which is quite reasonable.

The experimental results mentioned above definitely show that the viscosity dependent small step diffusional motion, which modulates the angular momentum, does not bring about the reorientation of the solute as efficiently as the random flight motion. If the small step diffusional motion were unrestricted, we would expect this motion also, to bring about a reorientation, the correlation time associated with this reorientation being  $\tau_{\theta s}$ . Using  $\tau_{\theta s}\tau_{js} = (I/6kT)$ , and the value

of  $A(T/\eta)$  at  $-30^\circ\text{C}$ , for the typical case of PBSQ in ethanol we get  $\tau_{\theta s} \sim 1.7 \times 10^{-11}$  sec, which is much smaller than the value  $\tau_{\theta} = 3.0 \times 10^{-10}$  sec, calculated directly from the  $g$ -modulation part of the linewidth. Thus, if the small step diffusion motion associated with  $\tau_J$  were unrestricted, it would have brought about the reorientation much faster than the observed rate. This argument leads us to conclude that the small step diffusional motion is restricted to a narrow region around a particular orientation before it changes its orientation by a random flight. This type of motion is similar to the oscillations about the mean position.

The constancy of  $A/V_m$  for a particular semiquinone, when the solvent is varied, suggests that the term involving  $\tau_{Jf}$  does not contribute significantly to spin-lattice relaxation compared to  $\tau_{Js}$ . For PBSQ in ethanol at  $-30^\circ\text{C}$ , using a typical value of  $I = 10^{-37}$  c.g.s. units we get  $\tau_{Js} \sim 2.8 \times 10^{-14}$  sec. Unfortunately we cannot estimate a similar correlation time associated with random flight, *viz.*,  $\tau_{Jf}$ , since we do not have any knowledge of the distribution of jump angles. It can be pointed out at this stage that both the types of viscosity dependent motions are consistent with the quasilattice random flight model as described in section 3.2.

(b) Hindered rotation: Equation (30) for  $1/T_1$  can be explained by stating that the solute undergoes restricted small step diffusional motion for a fractional period  $\tau_r/(\tau_r + \delta)$  ( $\approx 1$  for  $\delta \ll \tau_r$ ) giving the first term and undergoes free rotation for a fractional period  $\delta/(\tau_r + \delta)$  ( $\approx \delta/\tau_r$  for  $\delta \ll \tau_r$ ) giving the second term. Thus we can identify the second term with the hindered rotation. It has been pointed out that the activation energy  $\Delta E$  is of the order of 1 kcal mole $^{-1}$  and is not very sensitive to the substitution of H by  $\text{CH}_3$  or tertiarybutyl groups, in the aromatic ring. This suggests that the activation energy is not associated with steric factors, but is associated with some sort of bonds with the oxygens. The absence of the second term in a non-hydrogen bonding solvent like THF indicates that the oxygens of the semiquinone are hydrogen bonded to solvent molecules in alcoholic solvents. This statement is consistent with the observation of Zandstra (1964). The observed activation energy  $\sim 1$  kcal mole $^{-1}$  is then to be associated with the differences in the solvent-solute and solvent-solvent hydrogen bonding energies as described in section 3.2. Such a hindered motion has also been postulated in the solid state for semiquinones in matrices of hydroquinone and biphenyl (Krishnamoorthy and Venkataraman 1967).

An examination of the  $B$  values occurring in eq. (30), tabulated in table 3 (assuming  $\Delta E = 1$  kcal mole $^{-1}$ ), shows no regular pattern. It has already been mentioned that small variations in  $\Delta E$  alter significantly the calculated values of  $B$ . Thus it will not be wise to draw any conclusions from the listed values of  $B$ . However, one can see that  $B$  is not very sensitive to the size of the semiquinone ( $R$ ), as would be expected from eq. (25). For the typical case of PBSQ in ethanol at  $-30^\circ\text{C}$  the value of  $\delta^2/\tau_r$  calculated from eq. (25) is  $\sim 10^{-13}$  sec, using  $g_x = 2.0029$  (Leniart 1971).

### 5.3 Additional evidence for the hindered rotation about the axis perpendicular to the aromatic ring in frozen solutions

From a linewidth study of PBSQ in ethanol it is possible to estimate the value of the  $g$ -tensor components (Schreurs *et al* 1961, Leniart 1971). Leniart (1971) gives the values  $g_x = 2.0073$ ,  $g_y = 2.0033$  and  $g_z = 2.0029$  in consistent with



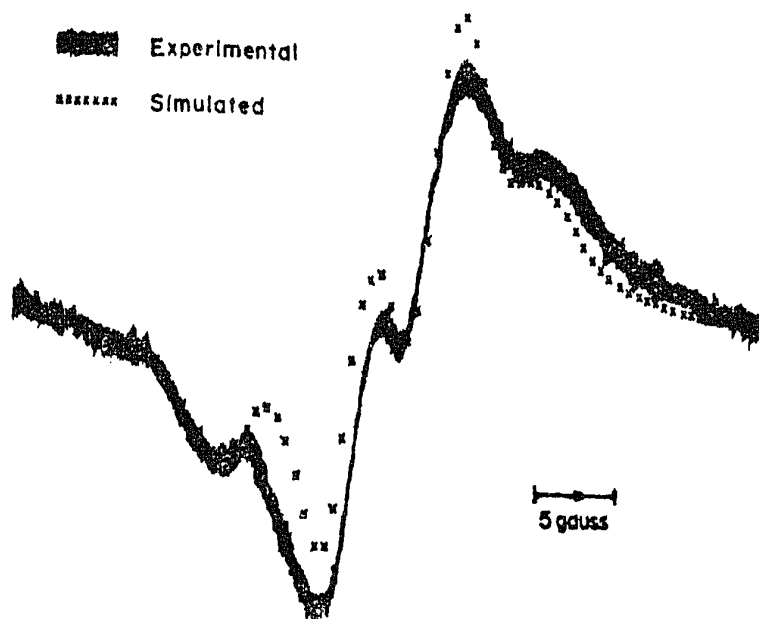


Figure 7. Frozen solution spectrum of PBSQ in ethanol at 148 K; crosses indicate the computed powder spectrum with  $g_{\parallel} = 2.0030$ ,  $g_{\perp} = 2.0052$ ,  $A_{\parallel} = 0.8$  G and  $A_{\perp} = 3.2$  G.

theoretical predictions (Zandstra 1964), which requires the  $z$ -axis to be perpendicular to the aromatic ring. The frozen solution spectrum should then correspond to  $g_{\parallel} = 2.0073$  and  $g_{\perp} \simeq 2.0031$ , in which case  $g_{\parallel} > g_{\perp}$ . However, the experimentally observed spectrum of PBSQ in frozen ethanol (figure 7) at 148 K can be explained with  $g_{\parallel} = 2.0032$  and  $g_{\perp} = 2.0053$ ;  $A_{\parallel} = 0.8$  G and  $A_{\perp} = 3.2$  G (*i.e.*,  $g_{\parallel} < g_{\perp}$ ). This paradoxical difference between the two results can be explained if we say that the molecule undergoes predominantly isotropic tumbling in the liquid state and in frozen solutions, however, the hindered rotation about the  $z$ -axis persists, giving an axial symmetry about this axis, leading to  $g_{\parallel} = 2.0029$  and  $g_{\perp} = (2.0073 + 2.0033)/2 = 2.0053$ . The fact that this hindered rotational motion is not detected in the linewidth studies requires that the conditions  $\tau_R \gg \tau_{\theta r}$  and  $\tau_R \gg \delta$  be satisfied in the liquid state.

It was also observed that the linewidths of the frozen solution spectra increased as the temperature was lowered. This is expected from the slowing down of the hindered rotation as the temperature is lowered. It should be mentioned that similar observations have been made for other semiquinones also.

## 6. Conclusion

The study of spin-lattice and transverse relaxation times of semiquinone alcohol systems have shown that the semiquinone molecule undergoes (i) free rotation for a fractional period  $\delta/(\delta + \tau_R)$  [ $\approx \delta/\tau_R$  when  $\delta \ll \tau_R$ ], and (ii) viscosity-dependent motions for a fractional period  $\tau_R/(\delta + \tau_R)$  [ $\approx 1$  when  $\delta \ll \tau_R$ ].

It is postulated that the semiquinone is hydrogen bonded to the alcohol molecules and resides in a cage of solvent molecules. The free rotation of the semiquinone, within this cage, is postulated to occur about an axis perpendicular to the plane of the aromatic ring, when the bonds between the semiquinone and alcohol molecules break. It is suggested that the solvent cage prevents the close approach of

two radicals, leading to the contribution to  $T_1$  from radical-radical interactions to be very weak, so that  $T_1$  in such solvents is essentially concentration independent (in the ranges studied in our experiments). In THF, which is a non-hydrogen bonding solvent, it was noticed that the dependence of  $T_1$  on  $(\eta/T)$  did not require postulating the hindered rotation.

The viscosity-dependent motions detected in  $T_1$  studies are sensitive to the size of the solvent molecule and that of the semiquinone, whereas the viscosity dependent motion detected in linewidth studies in the high viscosity low temperature region, is not sensitive to the size of the solvent molecule or that of the semiquinone ion. These observations are consistent with the quasilattice random flight model, where the restricted small step diffusional motion (postulated to be small angular oscillations about the mean position) contribute to the spin-lattice relaxation through spin rotation interaction. The linewidth,  $\Delta H$ , especially in the high viscosity low temperature region, is primarily dependent on the reorientation correlation time associated with the large amplitude reorientation accompanying the translation from one lattice site to another. The observation that the measured  $T_1$  values were the same for all the hyperfine lines can now be understood, since the dominant mechanism responsible for spin-lattice relaxation comes from the spin rotational effects due to the above said oscillations (about the mean position) and hindered rotation. The observation of Leniart (1971) that  $W_0$ , obtained from  $\Delta H$  studies are an order of magnitude less than that obtained from  $T_1$  studies is also explained, when we recognise that the motion contributing dominantly to transverse relaxation is not the motion contributing dominantly to spin-lattice relaxation. (Actually  $T_1$  is determined by two types of motion.)

The solvent dependence of  $A$  values has shown that the modified micro-viscosity picture of Gierer and Wirtz (1953) is appropriate while describing the viscosity dependent motions of molecules in liquid. The solvent dependence of  $A$  values could have also been explained by arbitrarily assuming the effective hydrodynamic radius  $R$  to be different in various solvents, or by introducing an arbitrary parameter  $\chi$ , as used by Huang and Kivelson (1972), to take into account the anisotropic motion of the molecules in liquids. However, the agreement between the predicted behaviour and the experimental results makes us prefer the microviscosity picture of Gierer and Wirtz (1953).

### Acknowledgements

The authors are grateful to P W Atkins for valuable discussions, during the preparation of this manuscript.

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