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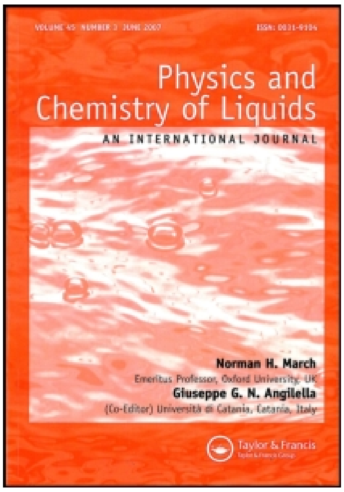

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AN EPR ANALYSIS OF NITROXIDE SPIN PROBES IN ETHYL ALCOHOL AND TETRAHYDROFURAN

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The solutions of 2,2,6,6-tetramethylpiperidinyloxy (TEMPO), 4-hydroxy-TEMPO (TEMPOL) in ethyl alcohol and tetrahydrofurane (THF), 4-amino-TEMPO (TEMPAMINE) in THF were prepared in a concentration range of 0.1 - 10 mM. The EPR (0.3 T) spectra of these samples were recorded at room temperature. Experimental spectra were simulated using high field approximation. For this purpose a FORTRAN program was written and by the use of this program hyperfine coupling constants and intrinsic line widths were determined. Electronic correlation times of the samples were calculated from the line widths and their dependence on the solvent was discussed.

Keywords: EPR in solutions; line widths

1. INTRODUCTION

Many studies on nitroxide free radicals in the recent years at 0.3 T field region were concentrated on the simulation of spectra and by this way the determination of temperature and solvent dependence of hyperfine coupling constants and correlation times [1–5]. In these studies TEMPO, TEMPOL and TEMPAMINE were the most often used free radicals. However, the studies on the determination of hyperfine coupling constants were limited to only a few solutions [6–12]. As

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[*] Corresponding author.

known the hyperfine coupling constants change with the changes in viscosity, temperature and solvent polarity. Although there are some studies to describe the change with solvent polarity by a certain relation [8, 11], the confirmation of this relation necessitates further studies, using different solvents and temperatures.

Under the nitrogen hyperfine envelop, proton hyperfine lines were hidden and their intrinsic line widths include dynamic information on the spin probes in solutions. These intrinsic line widths can be calculated from the simulation of the nitroxide spectra.

In this study, the solutions of TEMPO, TEMPOL and TEMPAMINE were prepared in ethyl alcohol and THF in a range of 0.1–10 mM. The spectra of the samples were recorded and simulation of spectra were performed by the use of a FORTRAN program which utilize the high field approximation. The hyperfine coupling constants and line widths were determined. The intrinsic line widths of protons were used in the formula given by Kivelson [13] and the rotational correlation times were calculated. The results obtained were compared with the results in the literature.

2. EXPERIMENTAL

The solutions of the nitroxide free radicals TEMPO, TEMPOL in ethyl alcohol and tetrahydrofurane (THF), and TEMPAMINE in THF were prepared at 0.1, 1, 10 mM concentration. All the samples were degassed by freeze-pump-thaw technique. The spectra of the samples were recorded at room temperature using a Varian E-9, X-band spectrometer. In order to avoid from saturation effects and modulation broadening all spectra were recorded at 2.5 mW. Modulation amplitude was 1 μT, time constants were changed between 0.3–1 s and scan ranges were 1, 2, and 10 mT. The nitroxide spin probes were obtained from Aldrich Chemical Co.

3. RESULTS AND DISCUSSION

Since the aim of the study was to calculate the proton hyperfine coupling constants in solvents having various viscosity and polarity, it was first necessary to determine the equivalent groups of protons for each sample and than to arrange the program to give the nitrogen envelope. For the samples studied the equivalent groups of protons were determined by NMR, ENDOR and for some solvents also by EPR [11]. Accordingly for TEMPO there are three equivalent groups having 12, 4 and 2 protons respectively. For TEMPOL there are five different groups of protons and the proton numbers in the groups are 6, 6, 2, 2, and 1. TEMPAMINE free radical has the same equivalent groups like TEMPOL but there is an additional splitting sourced from the second nitrogen in its structure (Fig. 1). In solutions of nitroxides the Hamiltonian did not include anisotropic contributions and since the spectra were recorded at 0.3 T, high field approximation was used.

Therefore in simulation of spectra at first the resonance field values were determined and the intensity of each transition was calculated from Binomial coefficients. For each resonance line, Lorentzian line shape was used and by summing up the derivatives of Lorentzian lines the theoretical spectra were obtained. Within a nitrogen manifold, the same line width was used for each hyperfine line. The above calculations were performed by a on purpose written subroutine FUNK [14]. This subroutine and SIMPLEX [15] routine for iteration were joined under a main program and were used in the simulation of experimental spectra. The simulation was performed for each sample at each nitrogen line ($m_\mathrm{I} = 1, 0, -1$). The hyperfine coupling constants were determined from the low concentration spectrum of each sample. Then for higher concentrations the line widths were obtained using these coupling constants. The goodness of fit was determined from

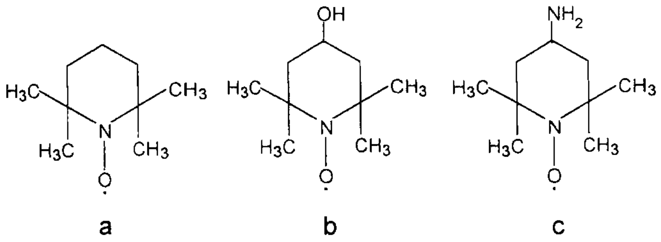

FIGURE 1 Spin probes used in this study. a) TEMPO, b) TEMPOL and c) TEMPAMINE.

$$\sigma = [F/(\ell - k)]^{1/2}$$

where F is the sum of the squares of the intensity differences between experimental and calculated spectra, ℓ is the number of experimental data points and k is the number of the parameters. The goodness of fit was also controlled by eye. The results obtained were given in Table I. TEMPOL/ethyl alcohol sample was studied before [10] and the results obtained in our calculations were very close to the values found in the earlier study.

In a previous study a linear relationship between nitrogen coupling constant a_N and proton coupling constant a_H has been suggested [8] and in another study the need of further studies was mentioned [11]. A consideration of Figure 2 indicates no simple linear relation between a_N and a_H for TEMPOL. Similar plots were drawn for the other samples and a linear dependence between a_N and a_H could not be found.

The recorded spectra of the samples indicated a good resolution of proton hyperfine structure for TEMPOL/ethyl alcohol sample at 0.1 and 1 mM, for TEMPAMINE/THF at 0.1 mM concentrations (Figs. 3 a, b, c). For TEMPO/ethyl alcohol and TEMPOL/THF samples at 0.1 mM concentration the observed proton hyperfine structure was not as clear as the above mentioned samples and for TEMPO/THF sample the proton hyperfine structure could not be observed (Figs. 4 a, b, c). In Figure 5a the separate simulation of each nitrogen manifold was given for TEMPOL/THF at 1 mM concentration. The joint simulation of the nitrogen spectrum of same probe at 10 mM concentration was given in Figure 5b. The reason of the joint and separate simulations of

TABLE I Hyperfine coupling constants and the goodness of fits for nitroxide spin probes in ethyl alcohol and THF

Probes	*Solvents*	*Hyperfine coupling constants* $(T)\times10^4 \pm 0.1\ \mu T$							σ
		a_N	a_{CH_3} (eq)	a_{CH_3} (ax)	a_{CH_2} (eq)	a_{CH_2} (ax)	a_H (4)	a_N (4)	
TEMPO	Ethyl alcohol	16.32	0.210	0.210	0.377	0.377	0.153		0.044
	THF	15.57	0.264	0.264	0.396	0.396	0.171		0.018
TEMPOL	Ethyl alcohol	16.12	0.432	0.020	0.479	0.320	0.070		0.043
	THF	15.51	0.404	0.072	0.518	0.334	0.097		0.028
TEMPAMINE	THF	15.58	0.456	0.037	0.402	0.311	0.050	0.087	0.034

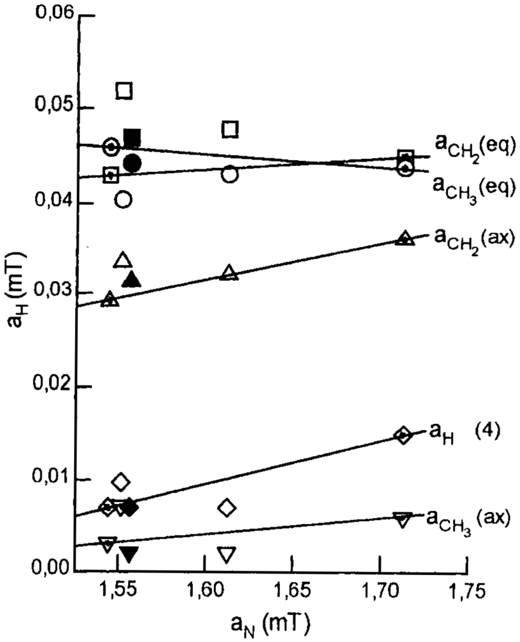

FIGURE 2 Hyperfine coupling constants versus ring nitrogen hyperfine coupling constants for TEMPOL. Open symbols for ethyl alcohol and THF, dotted symbols for water and CCl_4 [8] and solid symbols for pyridine [10].

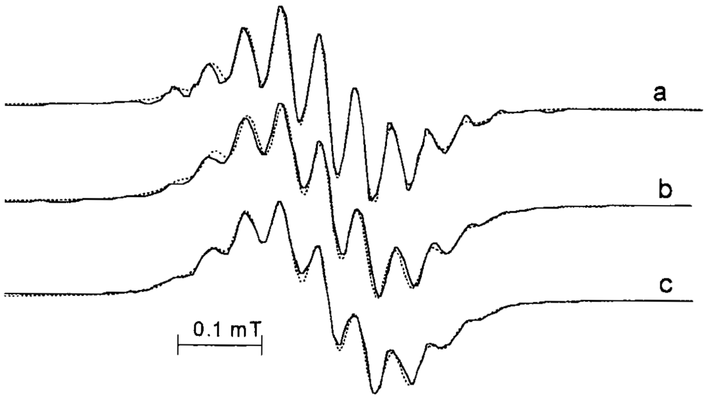

FIGURE 3 $m_N = 1$ hyperfine lines of computed (dotted lines) and the experimental (full lines) EPR spectra of a) TEMPOL in ethyl alcohol at 0.1 mM, b) TEMPOL in ethyl alcohol at 1 mM and c) TEMPAMINE in THF at 0.1 mM concentration.

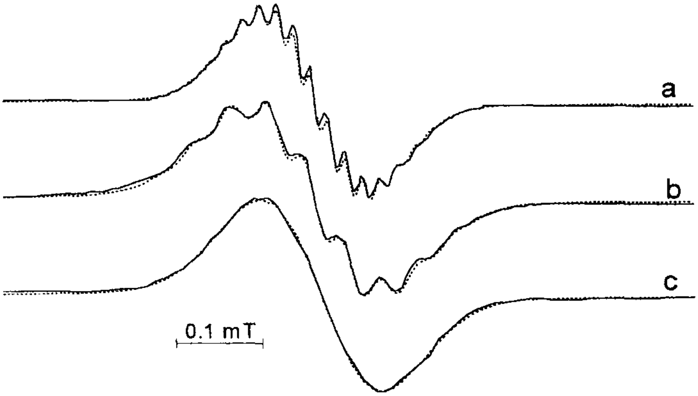

FIGURE 4 $m_N = 1$ hyperfine lines of computed (dotted lines) and the experimental (full lines) EPR spectra of 0.1 mM solution of a) TEMPO in ethyl alcohol, b) TEMPOL in THF and c) TEMPO in THF.

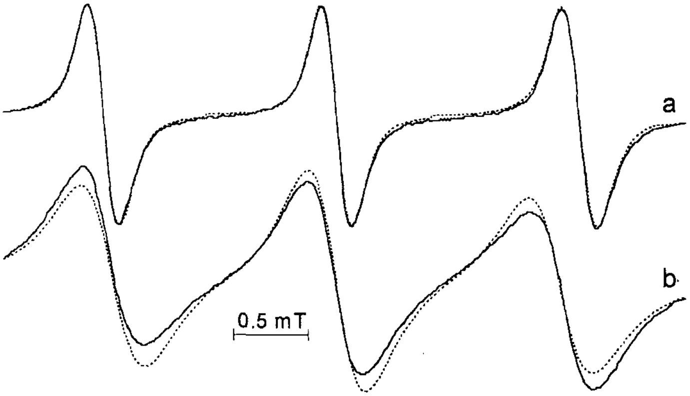

FIGURE 5 The computed (dotted lines) and the experimental (full lines) EPR spectra for TEMPOL in THF. a) The separate simulation of each nitrogen manifold at 1 mM concentration. b) The joint simulation of nitrogen spectrum at 10 mM concentration.

the $m_I = 1, 0, -1$ lines was the Heisenberg spin exchange, which causes the broadening and overlapping of the nitrogen lines with increasing concentration [16]. Therefore the separate simulation of each resonance line is correct only if the nitrogen lines are not overlapping. The increase in the nitrogen line widths depending on the concentration was given in Figures 6a and b. An inspection of this figure

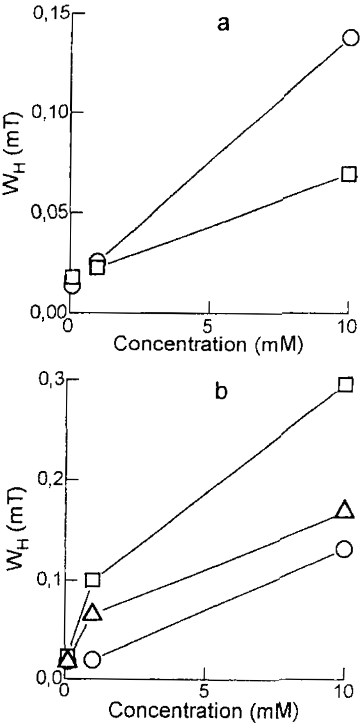

FIGURE 6 Variation of intrinsic line widths as a function of concentrations for TEMPO (○), TEMPOL (□) and TEMPAMINE (△) in a) ethyl alcohol and b) THF.

indicates that for TEMPO the change in the line width with increasing concentration was similar for both solutions. But for TEMPOL, this change was at about 0.05 mT for ethyl alcohol and 0.3 mT for THF. This might be sourced from the higher rates of the spin exchange with increasing concentration.

Rotational correlation time is given by [1, 17].

$$\tau = \frac{4\pi r^3 \eta}{3kT}$$

Here η is the viscosity of the solvent, T is the temperature and r is the hydrodynamic radius of the molecule. Rotational correlation time can also be calculated from intrinsic line widths (in second) [8, 18].

$$\tau = \frac{7.77 \times 10^{-10}}{b^2}[W_{\mathrm{H}}(-1) - W_{\mathrm{H}}(0)]$$

Here $b = 2\pi(a_Z - a_N)$ in Tesla. a_N is the nitrogen hyperfine coupling constant, which was determined from simulation of the spectra and a_Z is the Z component of the hyperfine coupling tensor. $a_Z \approx 3.2$ mT for nitroxides [11]. In calculation of the correlation time for TEMPO/THF solution because of the unresolved hyperfine structure at the lowest concentration, the joint simulation values were used. The calculated correlation times were listed in Table II. At room temperature, viscosities of water and CCl_4 are close to each other. For THF, the room temperature viscosity is low and for ethyl alcohol it has higher value. As the results for TEMPO and TEMPOL in ethyl alcohol and THF solutions were compared, an increase in the correlation times with increasing viscosity was observed. For TEMPAMINE spin probe studied, a comparison of the correlation times in THF solution with the correlation times in CCl_4 and water at the same concentration and temperature indicated that, although the viscosity of THF low, the correlation time obtained was higher for this solution [8]. This might be as a result of the increase in the effective radius of the molecule in this solution. However for a complete search of correlation times, temperature dependent studies should also be done.

In conclusion, in this study, using an on purpose written FORTRAN program, simulation of spectra were performed, the hyperfine line widths of the samples were determined and correlation times were calculated. In further studies using the same program, temperature dependent measurements will be performed.

TABLE II Intrinsic line widths and correlation times for nitroxide spin probes in ethyl alcohol and THF

Probes	*Solvents*	*intrinsic line widths* $(T) \times 10^4 \pm 0.1\ \mu T$			*Correlation times* (*s*)
		$W_H(1)$	$W_H(0)$	$W_H(-1)$	$\tau \times 10^{11}$
TEMPO	Ethyl alcohol	0.134	0.144	0.160	1.28
	THF	0.180	0.181	0.191	0.73
TEMPOL	Ethyl alcohol	0.177	0.188	0.238	3.90
	THF	0.221	0.221	0.246	1.81
TEMPAMINE	THF	0.174	0.181	0.229	3.50

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References

[1] Jolicoeur, C. and Friedman, H. L. (1971). *Ber. Bunsenges. Phys. Chem.*, **15**, 248.

[2] Poggi, G. and Johnson, S. Jr. (1970). *J. Magn. Reson.*, **3**, 436.

[3] Lim, Y. Y., Smith, E. A. and Symons, R. C. (1976). *J. Chem. Soc. Fraday. Trans.*, **1**, **72**, 2876.

[4] More, K. M., Eaton, G. R. and Eaton, S. S. (1984). *J. Magn. Reson.*, **60**, 54.

[5] Sünnetçioğlu, M. M., Bingöl, G. and Sungur, R. (1991). *Z. Naturforsch*, **46a**, 976.

[6] Whisnant, C. C., Ferguson, S. and Chesnut, D. B. (1974). *J. Phys. Chem.*, **78**, **14**, 1410.

[7] Labsky, J. J., Pilar, J. and Lovy, J. (1980). *J. Magn. Reson.*, **37**, 515.

[8] Windle, J. J. (1981). *J. Magn. Reson.*, **45**, 432.

[9] Martini, G., Ottaviani, M. F. and Romanelli, M. (1983). *J. Colloid Interf. Sci.*, **94**(1), 105.

[10] Ottaviani, M. F. (1987). *J. Chem. Phys.*, **91**, 779.

[11] Bales, B. L. (1989). *Biological Magnetic Resonance, Spin Labeling Theory and Applications*, Ed. L. J. Berliner and J. Reuben (New York, Plenum Press), Chap. 2, 77–131.

[12] Sünnetçioğlu, M. M. and Bingöl, G. (1993). *Phys. Chem. Liq.*, **26**, 47.

[13] Kivelson, D. (1960). *J. Chem. Phys.*, **33**, 1094.

[14] Uçar, E. (1997). M. Sc. Thesis, Department of Physics, Graduate School of Natural Applied Sciences, Zonguldak, Turkey.

[15] Press, W. H., Tevkolsky, S. A., Vetterling, W. T. and Flannery, B. P. (1992). *Numerical Recipes in FORTRAN. The Art of Scientific Computing* (Cambridge University Press), Chap. 10, pp. 387.

[16] Eastman, M. P., Kooser, R. G., Das, M. R. and Freed, J. H. (1969). *J. Chem. Phys.*, **51**(6), 2690.

[17] Kivelson, D., Kivelson, M. G. and Oppenheim, I. (1970). *J. Chem. Phys.*, **52**(4), 1810.

[18] Smith, J. C. P. (1972). *Biological Applications of Electron Spin Resonance*, Eds. H. M. Swartz, J. R. Bolton, D. C. Borg (New York, Wiley), Chap. 11, pp. 483.