acta physica slovaca vol. 56 No. 2, 141 – 144 April 2006

NUCLEAR SPIN-LATTICE RELAXATIONS IN ETHANOL WITH DISSOLVED TEMPO RADICALS [1]

H. Štěpánková[2,*], J. Englich*, J. Štěpánek*, J. Kohout*, M. Pfeffer*, J. Černá*, V. Chlan*, V. Procházka*, E. Bunyatova†

**Faculty of Mathematics and Physics, Charles University Prague, V Holešovičkách 2,*
18000 Prague 8, Czech Republic
†Joint Institute for Nuclear Research Dubna, Russia

Received 6 December 2005, in final form 3 January 2006, accepted 4 January 2006

Alcohols with nuclear spins highly polarized due to the polarization transfer from stable nitroxyl radicals are suitable materials for polarized nucleon targets. In this work the ethanol-TEMPO system was studied by ^{1}H and ^{13}C high resolution NMR in a liquid phase. The concentration and temperature dependences of spin-lattice relaxation rates, linewidths and chemical shifts were measured. The highest impact of doping was seen for protons of OH group as a result of hydrogen bonds to the oxygen of TEMPO. For the other nuclei the relaxation enhancement corresponds to the diffusion-controlled regime above 210 K.

PACS: 76.60.Es, 82.56.Na, 82.30.Rs

1 Introduction

Interactions between electron and nuclear spins are known to give rise to effective relaxation mechanisms for an excited nuclear spin system. On the other hand, these interactions can be employed in processes of dynamical nuclear polarization to achieve a high polarization of the nuclear spin systems which exceeds many times the equilibrium values in accessible static magnetic fields. Materials with highly polarized nuclear spins are needful for spin-dependent scattering experiments in nuclear and particle physics [1, 2]. Stable free nitroxyl radicals added to the alcohols are one of the real systems in which the polarization transfer from electron spins to hydrogen nuclei (^{1}H and ^{2}D) of alcohol molecules in solid samples is well enabled [3, 4]. Our aim is to characterize in details interactions between the electron spin of TEMPO radical and ethanol nuclear spins.

TEMPO (2,2,6,6 tetramethylpiperidin-1-oxyl, Fig.1) or its derivates are used widely as spin labels for electron spin resonance experiments and can also be employed as paramagnetic probes in experiments based on nuclear magnetic resonance (NMR) [5]. NMR spectra and spin relaxations in alcohols have been studied for a rather long period to get information on molecular

---

[1] Presented at 15-th Conference of Czech and Slovak Physicist, Košice, Slovakia, September 5–8, 2005

[2] E-mail address: helena.stepankova@mff.cuni.cz

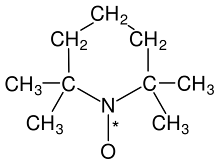

Fig. 1. The radical TEMPO molecule.

dynamic, hydrogen exchange, and particularly to understand forming and properties of intermolecular hydrogen bonds in polar solvents (e.g. [6–9]). This work presents results of the first phase of our investigation devoted to the effect of TEMPO on NMR characteristics of liquid ethanol within a wide temperature range.

2 Experimental

TEMPO of 98 % purity was purchased from Aldrich; ethanol absolute for analysis, purity > 99.9 %, from Merck. A series of six ethanol samples was prepared with the TEMPO content from zero to 1.5 weight %. The samples in standard 5 mm NMR tubes were degassed and then sealed under argon atmosphere. ^1H and ^{13}C NMR spectra were measured using the NMR pulse spectrometer Bruker AVANCE 500 in a temperature range of 150 - 300 K. Relaxation times T_1 were determined by the inversion recovery.

3 Results and conclusions

Ethanol molecule includes three groups of equivalent protons and two carbons atoms. Its ^1H and ^{13}C NMR spectra consist then of 3 and 2 lines, respectively. The effect of TEMPO on chemical shifts and linewidths was detectable starting from the concentration of 0.05 wt%. While only a weak modulation of the chemical shift was obtained, the increase of the linewidth with the TEMPO concentration was significant (especially at low temperatures). The broadening of the $^1H(OH)$ line was several times larger than that of the other lines indicating clearly that particularly at low temperatures the ethanol molecules interact with TEMPO by means of hydrogen bonds between the OH donor group of ethanol and the nitroxyl acceptor group of TEMPO.

The longitudinal relaxation rates $R_1 = 1/T_1$ increased with TEMPO concentration linearly at all temperatures (see Fig. 2). For a particular sample, a strong temperature dependence was found (Fig. 3). R_1 of the OH proton, for which the effect of TEMPO was the strongest, was maximal at $\sim$ 200 K. On the contrary, relaxation rates of the other ^1H and ^{13}C signals predominantly increased monotonously with decreased temperature.

The enhancement of relaxation rates R_1 is caused by fluctuating interactions between the electron spin of the unpaired electron of TEMPO radical and the nuclear spin. These fluctuations may origin in spontaneous transitions of the electron spin, in a rotational motion of the ethanol-TEMPO complex, or in a chaotic diffusion motion of ethanol molecules in respect to TEMPO [10]. In all cases, the relationship between R_1 and TEMPO concentration should be linear, i.e. the first derivative (slope) k_1 of R_1 with respect to TEMPO concentration should be constant for a given temperature. The slopes k_1 are therefore the basic measures of the relaxation behaviour (Fig. 4, symbols).

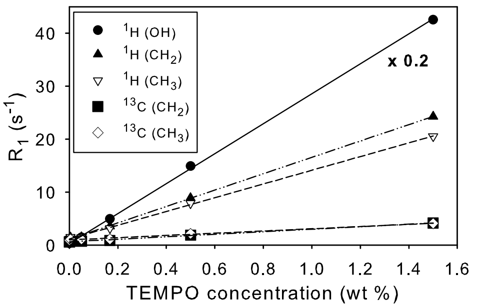

Fig. 2. Dependence of the relaxation rates R_1 in ethanol on the TEMPO concentration at 210 K. Data for ^{1}H(OH) are multiplied by 0.2; lines for ^{13}C(CH$_2$) and ^{13}C(CH$_3$) nearly coincide.

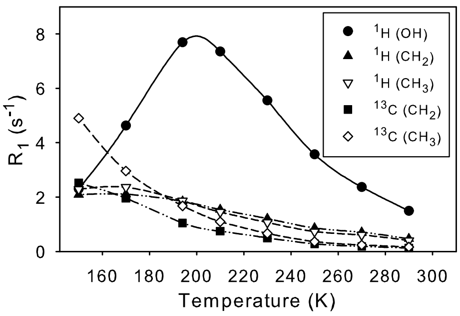

Fig. 3. Dependence of R_1 in ethanol on temperature for 0.05 wt% of TEMPO.

Published estimations of the correlation times in alcohol - TEMPO derivative systems [5, 11] reveal that at room temperature the system should be in a diffusion-controlled regime [10]. It is characterized by translation-diffusion coefficients D_i and the distance of the closest approach d of ethanol molecule to TEMPO. The diffusion correlation time τ_D can be evaluated as

$$\tau_D = \frac{d^2}{D_{ethanol} + D_{TEMPO}} \quad ; \quad D_i = \frac{k_B T}{6\pi a_i \eta}, \tag{1}$$

where a_i represents a size of the i-molecule (its dynamic radius), η stands for a viscosity of the liquid and k_B is Boltzmann constant. These formulae imply that τ_D is proportional to η/T. This allows us to model the temperature dependence of the relaxation enhancement by using the tabulated ethanol viscosity [12], according to equation describing the diffusion-controlled regime [10] (in SI units):

$$k_1 = \frac{100\, \mu_0^2\, \hbar^2 N_A\, \gamma_S^2\, \gamma_I^2}{27\, \pi\, d\, (D_{ethanol} + D_{TEMPO})}\, (7J(\omega_S) + 3J(\omega_I)), \tag{2}$$

where ω_S and ω_I are electron and nuclear Larmor frequencies, γ_S and γ_I are corresponding gyromagnetic ratios, N_A is Avogadro constant, μ_0 is permeability of vacuum. A spectral function $J(\omega)$ is given [10] by

$$J(\omega) = \frac{1 + 5z/8 + z^2/8}{1 + z + z^2/2 + z^3/6 + 4z^4/81 + z^5/81 + z^6/648} \quad ; \quad z = (2\omega\tau_D)^{1/2}. \tag{3}$$

We made a fit of k_1 (eq. (2)) for protons except the ^{1}H(OH) and for carbon nuclei, using common $\zeta = (a_{ethanol} . a_{TEMPO})/(a_{ethanol} + a_{TEMPO})$ and d as free parameters. The predicted temperature dependences fitted well to the experimental results for ^{13}C relaxations and quite reasonably also to the relaxations of ^{1}H(CH$_2$) and ^{1}H(CH$_3$) for temperatures above ~210K. The optimized values of the free parameters, d=0.40 nm and ζ=0.12 nm, correspond nicely to the geometry of interacting molecules. This confirms that the diffusion-controlled regime is dominant for the relaxation enhancement of ^{13}C and ^{1}H in ethanol except the OH group.

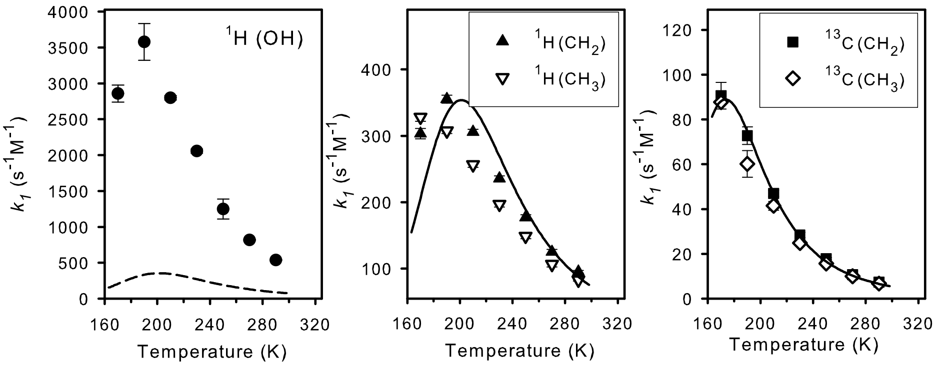

Fig. 4. Determined concentration slopes k_1 of the paramagnetic relaxation enhancement from experiment (symbols) and the values predicted assuming the diffusion controlled regime (lines).

On the other hand, the translation-diffusion mechanism represents only a minor part of the OH proton relaxation enhancement. It is obvious from Fig. 4 (on the left) where the enhancement calculated according to eq. (2) is indicated by the dashed line. The main relaxation enhancement concerns obviously a formation of a complex of ethanol molecule with the TEMPO via the hydrogen bridge. The OH proton in the complex is situated at the closest distance from the electron spin which makes a rotational mechanism more effective. Besides the dipolar mechanisms a Fermi contact interaction can take a role for the OH protons. The hydrogen bridge formation seems to influence also but weakly the other protons in ethanol.

Acknowledgement: This work is a part of the research plan MS0021620835 that is financed by the Ministry of Education of the Czech Republic. We gratefully acknowledge also the support of EU through FP6 ”HadronPhysics” (JRA8: Polarized Targets).

References

[1] D. G. Crabb, W. Meyer: *Annu. Rew. Nucl. Part Sci* **47** (1997) 67

[2] S. Goertz, W. Meyer, G. Reicherz: *Progress in Particle and Nuclear Physics* **49** (2002) 403

[3] E. I. Bunyatova: *Nucl. Instr. and Meth. in Phys. Res. A* **526** (2004) 22

[4] M. Plückthun, Ch. Bradtke, H. Dutz et al.: *Nucl. Instr. and Meth. in Phys. Res. A* **400** (1997) 133

[5] G. I. Lichtenshtein, I. Adin, A. Novoselsky et al.: *Biophys. J.* **77** (1999) 443

[6] Z. Luz, D. Gill, C. Meiboom: *J. Chem. Phys.* **30** (1959) 1540

[7] W. E. Blumberg: *Phys. Rev.* **119** (1960) 79

[8] H. G. Hertz: *Progress in NMR spectroscopy* **16** (1983) 115

[9] M. P. Jannelli, S. Magazu, P. Migliardo et al.: *J.Phys.:Condens. Matter* **8** (1996) 8157

[10] I. Bertini, C. Luchinat: *NMR of paramagnetic substances in Coordination Chemistry Reviews (ed. A.P.B.Lever), vol. 150, Elsevier, Amsterdam 1996*

[11] H.-W. Nientiedt, K. Bundfuss, W. Mller-Warmuth: *J. Magn. Resonance* **43** (1981) 154

[12] FYDAT Database *(http://home.tiscali.cz/cz050233)*