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The Solvent Effect on Spin Exchange in Long-Chain Nitroxide Biradicals

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Abstract. Intramolecular electron spin exchange, as a function of temperature and the solvent viscosity, polarity and relaxation properties of the solvent molecules, has been studied by X-band electron paramagnetic resonance (EPR) spectroscopy in two long-chain flexible nitroxide biradicals existing in fluid solutions in three spectroscopically different spatial conformations. Certain thermodynamic parameters of the conformational rearrangements were calculated from the EPR spectra. Spin exchange in two biradicals dissolved in five different alcohols was compared with that in a nonpolar solvent (toluene), polar protic (water) and aprotic (acetonitrile), and with thermodynamic characteristics of the solvents. Distinct correlations were found between macroscopic (solvent viscosity, polarity) and microscopic (solvent longitudinal relaxation time) characteristics of solvents, and thermodynamic parameters of the intramolecular conformational transitions.

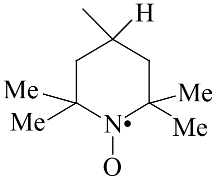
1 Introduction

In a previous paper [1], the effect of solvating paramagnetic $>$N–O$^{\cdot}$ fragments and functional groups in the bridge of two rigid nitroxide biradicals, existing only in one certain conformation, has been investigated. However, rigid biradicals represent a specific and rather small type of biradicals, which, in general, may be more or less flexible and exist in liquid solutions in several conformations with transitions among them [2–5]. Flexible nitroxide biradicals can be subdivided into two groups: the short ones and the long-chain flexible nitroxide biradicals (LCFNBs) with at least ten intermediate chemical bonds between nitroxide rings.

As it was shown in ref. 6, the electron paramagnetic resonance (EPR) behavior of the long-chain biradicals in liquid solutions with low viscosity can be described in terms of the three-conformation model with transitions among them. Such spin-labelled “oligomers” were described in terms of short polymeric systems providing a reasonable agreement with theory [7]. Different LCFNBs have been investigated in various solvents [6–11], but systematic attempts to analyze the influence of the solvent nature on conformational transitions in LCFNBs have not been done up to now, although this effect on intramolecular spin exchange in biradical systems is still one of the most unclear and interesting issues in physical chemistry of nitroxide biradicals. Therefore, in this paper we describe the effect of solvents with different viscosities and polarities on the intramolecular spin exchange in LCFNBs.

2 Experimental

Biradicals $S[(CH_2)_4COOR_6]_2$ (**I**) and $(CH_2)_5[CONHR_6]_2$ (**II**), used in this work, were synthesized as described in refs. 12–14 and their colors and melting points were in good correlation with the published ones. The paramagnetic fragment R_6 is



Toluene, acetonitrile, methanol, ethanol, 1-butanol, 1-octanol, cyclohexanol and water were selected as solvents because of their different viscosities and polarities. All organic solvents were specially purified according to literature procedures [15] and water was twice distilled. Solutions were prepared, bubbled with nitrogen for 20–25 min, whereafter 0.5 ml was taken to a thin capillary under nitrogen, degassed by freeze–pump–thaw cycles to remove molecular oxygen, and finally sealed off under vacuum. In the cases of 1-octanol and cyclohexanol, solutions were heated slightly while bubbling. Radical concentrations were kept sufficiently low ($\leq 5 \cdot 10^{-4}$ M) to eliminate intermolecular exchange broadening [16].

EPR spectra were recorded on a Varian E-101 X-band spectrometer equipped with a JEOL JNM-VT-30 temperature control system (accuracy, ±1 K) at a temperature range of 293–383 K. The hyperfine splitting (hfs) constant a, the amplitudes and widths of lines 1 and 2 (Fig. 1) were experimentally measured.

For rather long-chain flexible molecules, the influence of the solvent can be discussed as the "cage effect" [4, 6]. Temperature changes of the quintet spectra for both biradicals are typical for the case, where the biradicals exist in three conformations: an "elongated" conformation A with $J_A = 0$ (and lifetime τ), and two conformations B and C (with total lifetime τ_C), in which the radical fragments are close to each other inside the solvent cage, but with $J_B = 0$, and $|J_C| \gg a$ [6]. The EPR spectra may then be viewed as a superposition of two spectra, one of which corresponds to the conformation A and the other to conformations B and C. The observed line narrowing is caused by fast transitions between conformations B and C. Additional exchange effects caused by the conformation A may be neglected as transitions from the outside (A) to the inside

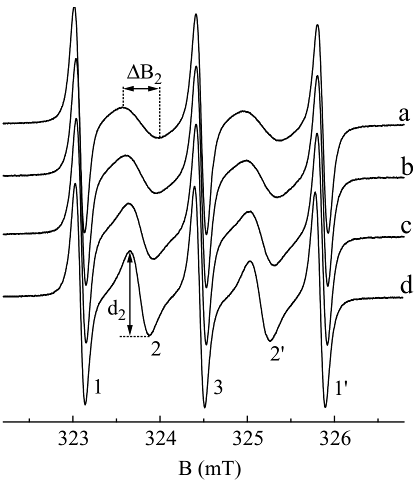


Fig. 1. EPR spectra of biradical **I** in toluene at 22 (a), 31 (b), 51 (c) and 71 °C (d).

of the cage (B and C) are slow, i.e., $\{a \cdot \max(\tau, \tau_C)\} > 1$ [4, 6]. This model allows one to obtain the thermodynamic parameters for the intramolecular transitions in the long-chain biradical. The ratio τ_C/τ can be calculated from the experimental EPR spectra by comparison with the integral intensities I_2 and I_1 of the lines 2, 2′ and 1, 1′ respectively, according to ref. 6:

$$I_1 / I_2 \approx d_2(\Delta B_2)^2 / d_1(\Delta B_1)^2 , \tag{1}$$

where d_1 and d_2 are the amplitudes and ΔB_1 and ΔB_2 the widths of lines 1 and 2 (averaged over the lines 1 and 1′ or 2 and 2′). It has been obtained that [6]

$$\tau_C / \tau = 3(I_2 / I_1)/[2 - (I_2 / I_1)] . \tag{2}$$

The analysis of the lines 2 and 2′ narrowing with temperature allows one to make conclusions about the motion of the radical fragments inside the cage. In the case of the fast modulation of the exchange interaction, the exchange broadening $1/T_2$ of these lines is described by [4, 6]

$$1/T_2 = a^2\tau_{\text{eff}} / 4 , \tag{3}$$

where τ_{eff} is a complex combination of the modulation parameters and its value is close to the longest of characteristic times of the intramolecular motions. For the Lorentzian lines [2]

$$a\tau_{\text{eff}} = 2\sqrt{3}\,|\gamma_e|(\Delta B_2 - \Delta B_1)/a , \tag{4}$$

where a is taken in frequency units and γ_e is the magnetogyric ratio of the free electron.

By assuming the Arrhenius dependence between τ_C/τ, τ_{eff} and temperature T as

$$\tau_C / \tau = \exp(\Delta S / R - \Delta H / RT), \tag{5}$$

$$\tau_{\mathrm{eff}} = \tau_0 \exp(\varepsilon / RT), \tag{6}$$

one can calculate the enthalpy ΔH and entropy ΔS values of the cage, as well as the parameters ε and τ_0, which characterize movements inside the cage. Here τ_0 is the characteristic time of the motions realizing the transition between the effective conformation with $J_B = 0$ and $|J_C| \gg a$ in the absence of the activation energy barrier ε between them.

3 Results and Discussion

Some typical EPR spectra of biradical **I** in toluene at different temperatures are given in Fig. 1. For biradical **II**, similar spectra have been recorded. It was seen for both biradicals that the temperature behavior of the spectra is analogous in all the solvents, but the interval of these changes sufficiently depends on the solvent's nature.

Temperature dependences of the ratio τ_C/τ (in the Arrhenius axes) for biradical **I** dissolved in methanol, ethanol, 1-butanol, 1-octanol and toluene, calculated from the EPR spectra by Eq. (2), showed that in protic solvents τ_C/τ decreases slightly with temperature, while in aprotic solvent (toluene) τ_C/τ increases (Fig. 2). Temperature changes of these parameters are very small since for the long-chain biradicals entrance into the cage is mainly connected with the steric, i.e., en-

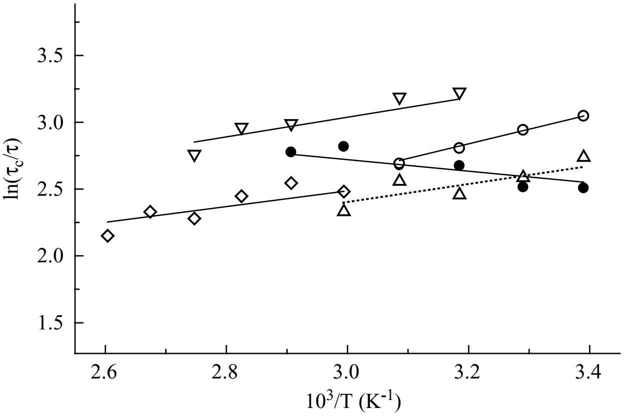


Fig. 2. τ_C/τ as a function of temperature for biradical **I** dissolved in methanol (○), ethanol (△), 1-butanol (▽), 1-octanol (◇) and toluene (●).

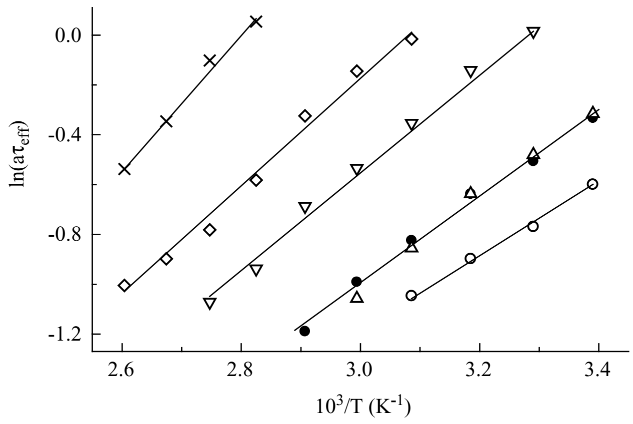


Fig. 3. $a\tau_{\mathrm{eff}}$ as a function of temperature for biradical **I** dissolved in methanol (○), ethanol (△), 1-butanol (▽), 1-octanol (◇), cyclohexanol (×), toluene (●) and acetonitrile (▲).

tropy and not energy factors. Estimated parameters ΔH and ΔS in toluene were equal to 3.6 $\mathrm{kJ \cdot mol^{-1}}$ and 16.7 $\mathrm{J \cdot mol^{-1}K^{-1}}$, respectively, which is in good agreement with those published in ref. 6. It is interesting that in protic solvents (alcohols), enthalpies ΔH have negative values in contrast to aprotic ones, such as benzene, toluene, CCl_4, etc. [6, 8]. This fact will be investigated in detail later. Surprisingly, we could not find a direct correlation between τ_C/τ, ΔH and ΔS parameters and the viscosity of the solvents used.

Figures 3 and 4 show linear temperature dependences of $a\tau_{\mathrm{eff}}$ values in all solvents used for both biradicals. The appropriate thermodynamic parameters ε and τ_0 were calculated for biradicals **I** and **II** by Eq. (6) and are listed in Table

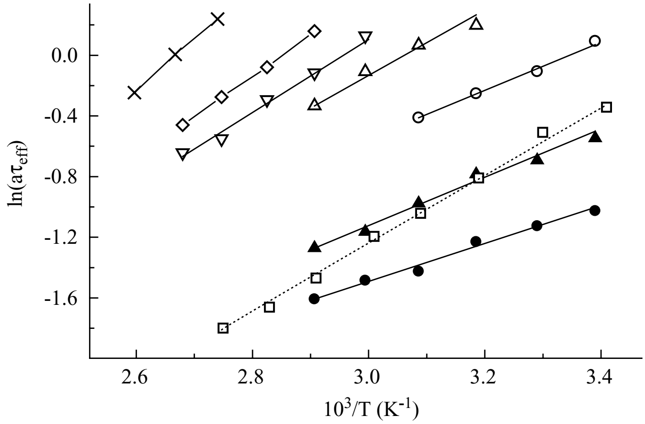


Fig. 4. $a\tau_{\mathrm{eff}}$ as a function of temperature for biradical **II** dissolved in water (□), methanol (○), ethanol (△), 1-butanol (▽), 1-octanol (◇), cyclohexanol (×), toluene (●) and acetonitrile (▲).

Table 1. Thermodynamic parameters ε and τ_0 for biradicals **I** and **II**.

Solvent	Temperature range (K)	Biradical **I**		Biradical **II**	
		ε^a (kJ/mol)	$-\log \tau_0{}^b$	ε^a (kJ/mol)	$-\log \tau_0{}^b$
Water	293–364	–	–	18.9 ± 0.4	12.0
Methanol	295–325	12.7 ± 0.2	11.0	13.8 ± 0.3	10.8
Ethanol	295–344	14.7 ± 0.4	11.2	18.2 ± 0.3	11.4
1-Butanol	304–364	16.6 ± 0.3	11.3	20.3 ± 0.4	11.6
1-Octanol	324–384	18.4 ± 0.5	11.4	23.0 ± 0.3	11.9
Cyclohexanol	354–385	23.0 ± 0.5	11.8	28.6 ± 0.5	12.4
Toluene	295–344	14.5 ± 0.3	11.2	10.6 ± 0.3	10.8
Acetonitrile	295–344	10.59 ± 0.3	10.8	13.4 ± 0.3	11.1

[a] Error is ±10%.
[b] Error is ±0.3.

1. In both cases, noticeable differences in the temperature–$a\tau_{\text{eff}}$ behavior, depending on the alcohol molecule size, were observed, and a plot for **II** in water was in the same order (Figs. 3 and 4). ε values increased systematically: twofold from methanol to cyclohexanol (Table 1). The aprotic solvents (toluene, acetonitrile) did not reveal such a regularity. Parameters τ_0 for both biradicals practically did not depend on the solvent nature, and their values were about 10^{-11} s, characteristic for the rotational movement around conventional σ-bonds.

The results obtained allowed us to compare values of ε characterizing movements of the nitroxide rings inside the cage of solvent molecules with param-

Table 2. Physical properties of the solvents used.[a]

Solvent	τ_D (ps)	ε_S	ε_μ	$E_\eta{}^b$ (kJ/mol)	π^*	α
Methanol	51.5	32.5[c]	4.9[c]	11.3	0.6	0.98
Ethanol	163	24.3[c]	3.8[c]	15.0	0.54	0.86
Butanol	520	16.0[d]	1.9[d]	19.8	0.47	0.84
Octanol	1360	10.3	2.0[e]	24.9	0.40	0.77
Cyclohexanol	2290	15.0[f]	2.4[f]	41.7	0.45	0.66
Acetonitrile	3.5	35.8[g]	1.4[g]	7.5	0.66	0.19
Toluene	7.4	2.4	2.2[e]	9.1	0.51	0
Water	8.4	78[h]	6.3[h]	15.3	1.1	1.17

[a] All data were taken from ref. 17 unless noticed otherwise.
[b] Reference 23.
[c] Reference 18.
[d] Reference 19.
[e] Calculated from equation $\varepsilon_\infty = n_D{}^2$.
[f] Reference 20.
[g] Reference 21.
[h] Reference 22.

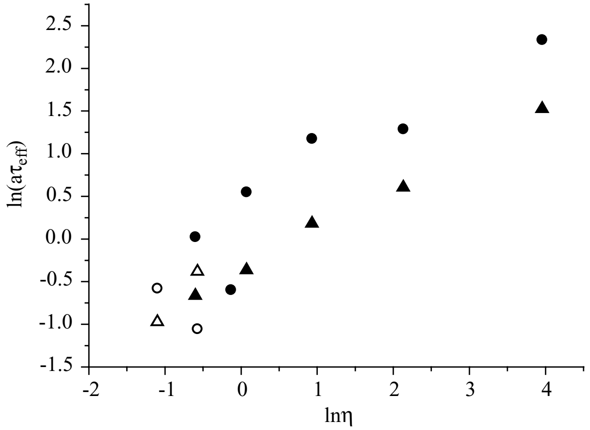


Fig. 5. ln($a\tau_{\text{eff}}$) as a function of lnη at 25 °C for **I** (▲, △) and **II** (●, ○) in protic (▲, ●) and aprotic (△, ○) solvents.

eters characterizing various properties of the solvent: viscosity, polarity and the longitudinal relaxation time, τ_L. Values of the different solvent parameters are collected in Table 2.

A correlation between ε and solvent viscosity η has already been reported for short-chain flexible nitroxide biradicals [24], taking a linear dependence of lnη vs. T^{-1} with a characteristic activation energy value E_η. It was interesting to compare the behavior of a bulk macroscopic characteristic of the solvent (η) with that of a similar parameter on the microscopic level (τ_{eff} or experimentally measured $a\tau_{\text{eff}}$). Viscosity parameters η for all solvents were taken from refs. 25 and 26. Indeed, we have observed the appropriate experimental dependences in

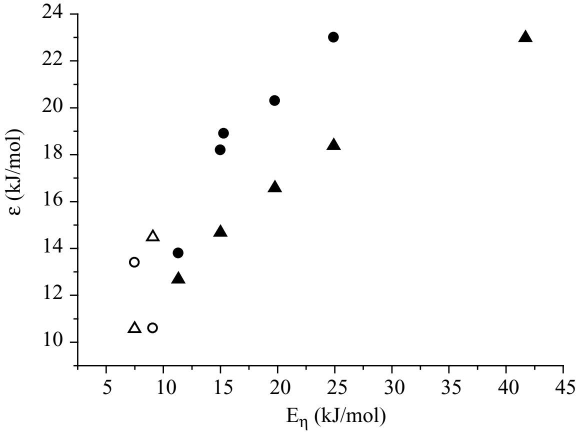


Fig. 6. ε as a function of E_η for **I** (▲, △) and **II** (●, ○) in protic (▲, ●) and aprotic (△, ○) solvents.

all protic and aprotic solvents used both for **I** and **II** (Fig. 5). Correlation between ε and E_η revealed a nonlinear dependence for **I** and **II**, although ε increased with increasing of E_η (Fig. 6). The only exception was the toluene solution of **I**, which one can possibly explain by some specific interaction peculiarities of **I** and toluene molecules. It follows from our data that the molecular motions (i.e., conformational rearrangements) inside the cage depend on the bulk characteristics of the cage, which is formed of the solvent molecules.

We should also stress that plots in ethanol and toluene for **I** (Fig. 3), and in water, acetonitrile and toluene for **II** (Fig. 4) are similar, i.e., changes in $a\tau_{\mathrm{eff}}$ depend not on the polarity of the solvent molecule (the dielectric constants are different for these solvents), but rather on structural aspects of the cage formation.

When investigating the influence of solvent polarity on a chemical reaction the most widely used parameters are Dimroth and Reichardt's $E_T(30)$ [27] and Kamlet and Taft's π^* [17], which are both used to determine so-called linear solvent energy relationships. The Kamlet–Taft parameter, π^*, has the advantage that it does not include the hydrogen bonding abilities of the solvent, which according to Kamlet and Taft is instead accounted for by the parameter α. These parameters, as listed in Table 2, are known for a large number of solvents and have been related to each other, empirically, by Marcus [17]:

$$E_T(30) = 15.2\alpha + 11.6\pi^* + 31.2\,. \tag{7}$$

When comparing the experimentally determined ε for **I** and **II** with the polarity parameter π^*, a good correlation is found in both cases, with the only exception being the aqueous measurements of **II** (Fig. 7). When plotting the same values versus the parameter α (Fig. 8) one notices that proticity is an important

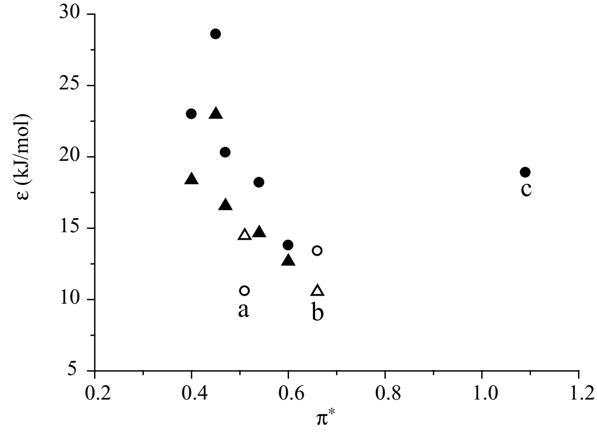


Fig. 7. ε as a function of Kamlet–Taft parameter π^* (at 25 °C) for **I** (▲, △) and **II** (●, ○) in protic (▲, ●) and aprotic (△, ○) solvents. a, toluene; b, acetonitrile; c, water.

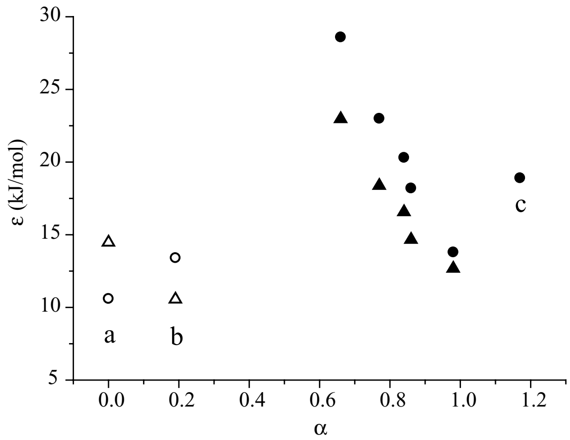


Fig. 8. ε as a function of Kamlet–Taft parameter α (at 25 °C) for **I** (▲, △) and **II** (●, ○) in protic (▲, ●) and aprotic (△, ○) solvents. a, toluene; b, acetonitrile; c, water.

factor in the spin exchange, as the points corresponding to the aprotic solvents fall clearly out off the linearity, which may be seen for the protic ones. This suggests that the breakage and formation of hydrogen bonds are likely to be involved during the conformational changes of the biradicals. Such bonds may be formed with the solvent both by the nitroxide groups and by the functional groups present in the bridges of both biradicals.

The solvent effect may also be studied by using the longitudinal relaxation time, τ_L, which is known to play an important role in the intermolecular electron transfer [28]. For a given solvent, it may be calculated as $\tau_L = (\varepsilon_\infty/\varepsilon_S) \cdot \tau_D$, using its Debye relaxation time, τ_D, together with the static and infinite frequency permittivities, ε_S and ε_∞. Values of τ_D and ε_S are usually available with good accuracy, but ε_∞ is determined by large extrapolations and, if at all, is known with less accuracy. Therefore, it is common practice to use the approximation $\varepsilon_\infty \approx n_D^2$, where n_D is the refractive index of the solvent.

In the first approximation, the Debye relaxation time is proportional to the molar volume, V_M, of the solvent and its viscosity, η [29]. The expression of τ_L then becomes

$$\tau_L = \frac{\varepsilon_\infty}{\varepsilon_S}\tau_D = \frac{3\varepsilon_\infty V_M \eta}{\varepsilon_S RT}. \qquad (8)$$

For some solvents, multiple relaxation pathways have been reported, each having an associated τ_L. Water and lower alcohols are good examples of such solvents, since two relaxation times are found there. The longer time is attributed to hydrogen bond kinetics, which is associated with the breakage of H-bonds in the immediate vicinity of the solute. The shorter time has been suggested to account for more localized fluctuations that happen during the continuous “re-

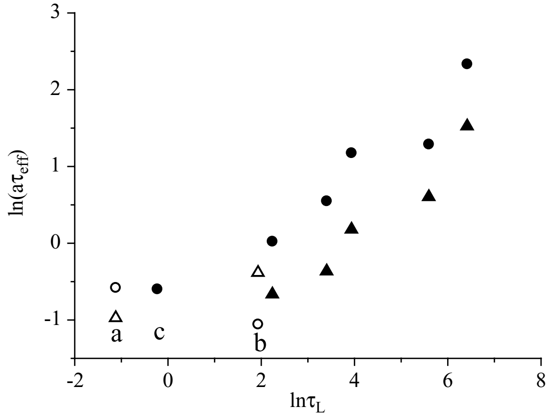


Fig. 9. $\ln(a\tau_{eff})$ as a function of $\ln\tau_L$ (at 25 °C) for **I** (▲, △) and **II** (●, ○) in protic (▲, ●) and aprotic (△, ○) solvents. a, toluene; b, acetonitrile; c, water.

alignment" of H-bonds that occurs in the bulk of the solution [30]. In investigations on intermolecular exchange, it is normally assumed that only the longest relaxation time will influence the reaction, since all shorter times are expected to be outside its time scale.

In Fig. 9 the influence of the longitudinal relaxation time on the experimental parameters is investigated. For a better comparison with Figs. 6–8 it would be desirable to obtain plots where ε is plotted against a temperature-independent energetic parameter, as it was done with, e.g., E_η, but since the longitudinal relaxation energy, H_L, which describes the temperature dependence of τ_L, is not known for several of the solvents used in our investigation, we have decided to use $\ln(a\tau_{eff})$ and $\ln\tau_L$ at 25 °C in the representations. Here, it is noted that for some of the solvents used in this investigation, the values plotted are obtained by extrapolation, since the spin exchange could not be registered at 25 °C. The indications obtained from Figs. 8 and 9 are confirmed, as the data owing to protic solvents show a linear behavior, whereas the experimental points for the aprotic solvents do not obey the same correlation. We should also mention that the correlation between $\ln(a\tau_{eff})$ and $\ln\tau_L$ (Fig. 9) is much more smooth in comparison with the other ones.

The differences which could be observed between **I** and **II** in Figs. 8 and 9 are likely to be attributed to the differences in the bridges of the biradicals as their nitroxide fragments are identical.

4 Conclusions

The energy parameter ε describing the temperature dependence of the chemical exchange between the two conformations in the solvent cage was found to depend strongly on the solvent used. This was found to happen not only on a macroscopic level, where the bulk properties of the solvent become important, but also on a microscopic level, where the specific solvent properties are relevant. Linear solvent energy relationships were investigated between ε and solvent properties using the viscosity energy, E_η, as well as the Kamlet–Taft solvent parameters π^* and α.

The macroscopic influence was seen in the form of clear linear trends in plots concerning viscosity and polarity, with some degree of deviance found in the former of the two for the solvents cyclohexanol and octanol. Possibly, this may, at least partially, be explained by the fact that E_η has been determined in literature using a comparatively narrow range of temperatures fit to a simple exponential model. Marcus [17] has shown that such simplicity may not always be assumed and that more complex models may be needed.

Specific interactions were deduced from the comparisons of ε with α, where a linear relationship was found when using the aprotic solvents. This means that the spin-exchange of the investigated biradicals, which undergo conformational changes inside the solvent cage, is assisted by hydrogen bonds between solvent and solute. This observation could be confirmed by comparison with the longitudinal relaxation time of the solvents, which is generally accepted to be attributed mainly to hydrogen bonding. Both correlations showed a clear difference between the two biradicals used, with the solvent effect being slightly more prominent for **II**, indicating that hydrogen bonds not only with the nitroxide groups but also with the heteroatoms of the bridge are important.

Acknowledgments

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