Dynamic Polarization, Molecular Motion and Solvent Effects in Several Organic Solutions as Studied by Proton-Electron Double Resonance

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Dynamic proton polarization in several free radical solutions has been studied systematically with different radicals at five widely separated magnetic field strengths and at various temperatures. Normally, in organic solutions the dynamic enhancements of the solvent proton resonances decay with increasing field and decreasing temperature. Scalar proton-electron coupling has only been observed in exceptional cases. The spectral intensity functions describing the experimental behaviour are derived from the dipolar interaction whose time dependence is in the first place due to translational diffusion of individual molecules. In addition, a certain solvation effect has to be taken into account. Strong solvation occurs in solutions of hydroxyl containing solvents with nitroxide radicals. In this case, the dynamic proton polarization appears to be quite different. As an example, solutions of tetramethyl piperidineoxyl in acetic acid have been examined in more detail. The results are explained in terms of hydrogen bridged solvates. The important motional mechanism that modulates the proton-electron interaction switches from "translation" to "rotation", and electron spin density is temporarily transferred to the solvent molecule.

Studies of dynamic nuclear polarization (DNP) by the proton-electron Overhauser effect have already demonstrated the possibility of obtaining detailed information on the motion of the molecules involved. In organic liquids containing free radicals the solvent proton magnetic resonance is inverted and may be increased up to a factor of about 330, if the radical electron spin resonance is saturated. By measuring the DNP-enhancement factor and its dependence upon the frequency and the temperature the interactions between unpaired electrons and protons may be investigated. Furthermore from the time dependence of these interactions the intensity function of the spectrum of molecular motion can be derived. The results obtained so far have been explained by several workers in terms of dipolar interactions between the protons and electrons, where in a satisfactory approximation, quantitative agreement exists with a two-spin model of translationally diffusing molecules [1–6].

In the meantime DNP studies with nuclei other than protons (^{19}F, ^{13}C, ^{31}P, ^{7}Li) have shown that intermolecular scalar contact interactions between radical electrons and nuclei may also play an important role. Moreover in some cases an admixture of rotational motion has been found [7]. Finally drastic departures from the usual DNP behaviour have been reported, in a preliminary note, for a case, where an association exists between the solvent and free radical molecules [8]. All this has led us to reinspect the proton-electron Overhauser effect using improved techniques with a number of widely spread frequencies.

In this paper we mainly report proton DNP measurements on two selected liquids with a variety of free radicals in solution, and studies on an associated system. Comparable results have been obtained with other organic solutions. In some following papers similar studies with carbon-13, fluorine-19 and phosphorus-31 will be communicated.

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[1] K. D. KRAMER and W. MÜLLER-WARMUTH, Z. Naturforsch. **19 a**, 375 [1964].

[2] K. D. KRAMER, W. MÜLLER-WARMUTH, and J. SCHINDLER, J. Chem. Phys. **43**, 31 [1965].

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[7] G. J. KRÜGER, W. MÜLLER-WARMUTH, and R. VAN STEENWINKEL, Z. Naturforsch. **21 a**, 1224 [1966].

[8] W. MÜLLER-WARMUTH and EROL ÖZTEKIN, Mol. Phys. **17**, 105 [1969].

All the results will be discussed in terms of the polarization coupling parameter ϱ, which itself depends upon the nature of the nuclear-electron interaction and on the motional properties of the spin carrying molecules. In particular, ϱ can be expressed by a combination of various dipolar and scalar spectral intensity functions $J(\omega\,\tau_i)$ for the fluctuations of the liquid lattice parameters [1, 9]. The time-dependence of the dipolar interaction is due to fluctuations of the vector $\boldsymbol{r}_{ik}$ connecting the i-th nuclear spin and the k-th electronic spin. A distinction is made between "translational motions", where also the absolute value $|\boldsymbol{r}_{ik}|$ fluctuates with time, and "rotational motions", where only the spatial orientation varies. The corresponding reduced intensity functions $f(\omega\,\tau_i) = J(\omega\,\tau_i)/J(0)$ are $f_\mathrm{t}(\omega\,\tau_\mathrm{t})$ and $f_\mathrm{r}(\omega\,\tau_\mathrm{r})$ with the correlation times τ_t and τ_r, respectively [***]. The relative importance of rotational and translational motion is given by

$$R = J_\mathrm{r}(0)/J_\mathrm{t}(0) = 3\,d^3\,\tau_\mathrm{r}\,X/4\,\pi\,N_\mathrm{S}\,b^6\,\tau_\mathrm{t}$$

(b = constant distance between I and S in a solvate complex, d = distance of minimum approach of the interacting spins during the translational diffusion, N_S = electron spin concentration, X = mole fraction of associates).

The possible scalar interaction can be written $A\,\boldsymbol{I}_i\,\boldsymbol{S}_k$, where $\boldsymbol{I}_i$ and $\boldsymbol{S}_k$ are the spin operators for the nucleus and the electron, respectively. The fluctuation due to molecular motion is involved in the time dependence or the local dependence of A. The corresponding reduced intensity function is called $f_\mathrm{sk}(\omega\,\tau_\mathrm{sk})$ with a scalar correlation time τ_sk. The relative importance of scalar and dipolar interaction is expressed by $K = 2\,J^\mathrm{sk}(0)/15\,J_1{}^\mathrm{D}(0)$. Taking all this into account, ϱ may most generally be written

$$\varrho = \frac{[f_\mathrm{t}(\omega_\mathrm{S}\,\tau_\mathrm{t}) + R\,f_\mathrm{r}(\omega_\mathrm{S}\,\tau_\mathrm{r}) - K\,f_\mathrm{sk}(\omega_\mathrm{S}\,\tau_\mathrm{sk})]\;0.5}{0.7\,f_\mathrm{t}(\omega_\mathrm{S}\,\tau_\mathrm{t}) + 0.3\,f_\mathrm{t}(\omega_\mathrm{I}\,\tau_\mathrm{t}) + R[0.7\,f_\mathrm{r}(\omega_\mathrm{S}\,\tau_\mathrm{r}) + 0.3\,f_\mathrm{r}(\omega_\mathrm{I}\,\tau_\mathrm{r})] + 0.5\,K\,f_\mathrm{sk}(\omega_\mathrm{S}\,\tau_\mathrm{sk})}\,. \tag{1}$$

The reduced intensity functions occur either at the ESR frequency $\omega_\mathrm{S} = \gamma_\mathrm{S}\,H_0$, or at the NMR frequency $\omega_\mathrm{I} = \gamma_\mathrm{I}\,H_0$ (γ_S and γ_I are the gyromagnetic ratios of the unpaired electron and nuclear spins, respectively, H_0 static magnetic field). The particular spectral dependence of f_t, f_r and f_sk will be discussed in a later chapter.

1. Experimental Details and Procedure

Five different double resonance spectrometers operating at 15, 176, 1070, 3420 and 13 200 gauss were used. The proton (and electron) magnetic resonance frequencies were 65 kHz (42.6 MHz), 750 kHz (493 MHz), 4.35 MHz (3.0 GHz), 14.6 MHz (9.58 MHz) and 56.3 MHz (37.04 GHz), respectively. At 14.6 and 56.3 MHz high resolution NMR technique was applied. The DNP enhancement factors were measured in the usual way by comparing the NMR signals in the presence and in the absence of the ESR saturating power under otherwise identical conditions. With P being the proton polarization and P_0 its thermal equilibrium value, the ratio

$$P/P_0 = 1 - \varrho\,f\,s(|\gamma_\mathrm{S}|/\gamma_\mathrm{I}) \tag{2}$$

was determined. The leakage factor f was derived from the measured relaxation times T_1 of the solution and T_{10} of the pure organic liquid. The free radical concentrations were in a range of around 10^{-2} molar, so that f took typical values of the order of 0.9. All samples were carefully degassed and sealed.

As a consequence of electron spin exchange the ESR lines of most radicals were relatively narrow, and there was no difficulty in saturating them. By plotting the reciprocal enhancement factors against reciprocal microwave power linear dependences were obtained that could easily be extrapolated to infinite power [$s = 1$ in Eq. (2)]. Actual saturations between 70 and 95% were achieved. An exception was the nitroxide radical TMPO. Because of the spin 1 of the ^{14}N nucleus, in a sufficiently strong magnetic field the hyperfine structure consists of three well resolved lines (Fig. 1 a). These can be

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[9] F. NOACK, G. J. KRÜGER, W. MÜLLER-WARMUTH, and R. VAN STEENWINKEL, Z. Naturforsch. **22 a**, 2102 [1967].

[***] In literature τ_t values which differ by a factor 2, 3 or 6 are unfortunately used. The correct definition of the translational correlation time is now available [10] and will be adopted throughout. All the translational correlation times given in previous papers of our group and also the values of R and K defined below have therefore to be multiplied by some numerical factor.

[10] F. NOACK and G. HELD, Z. Phys. **210**, 60 [1968]. — G. J. KRÜGER, Z. Naturforsch. **24 a**, 560 [1969].

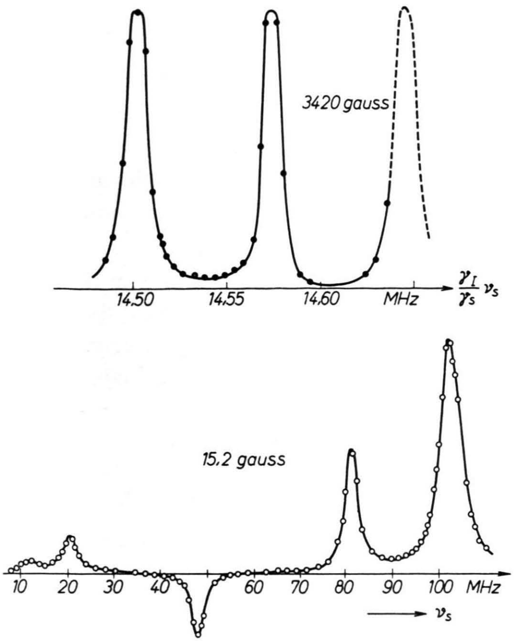

Fig. 1. ESR spectrum of the nitroxide radical tetramethyl-2,2,6,6 piperidineoxyl-1 in acetic acid as measured by proton-electron double resonance at weak microwave power, a) at 3420 gauss, b) at 15.2 gauss. In the weak field spectrum one line is inverted because it corresponds to a hyperfine transition, where in contrast to the others, the magnetic quantum number of the upper level is smaller.

separately saturated and the enhancement measured for one line is one third of the total enhancement. In a weak field, however, the spectrum is more complex (Fig. 1 b). In this case the saturation parameter s in Eq. (2) is given by [11]

$$s=\sum_i s_i=\sum_i \frac{\sigma_i\, g(\omega-\omega_i)}{1+\sigma_i\, g(\omega-\omega_i)}\, h(\omega_i)\,, \tag{3}$$

where $g(\omega-\omega_i)$ is the line shape function of the hyperfine line i, and $h(\omega_i)$ a weighting factor, which depends upon the electronic relaxation mechanism [12]. σ_i is proportional to the microwave power. Experimentally each line of Fig. 1 b was saturated separately ($\sigma_i \gg 1$) leading after Eqs. (2) and (3) to extrapolated enhancements

$$\left(\frac{P}{P_0}\right)_i = 1-\varrho\, f\,\frac{|\gamma_S|}{\gamma_I}\, h(\omega_i)\,.$$

Because of $\Sigma\, h(\omega_i)=1$, the proton-electron coupling parameter ϱ could thus be obtained by summing up all the $(P/P_0)_i$'s.

Measurements were carried out over the total liquid range of the various solutions. Temperature control and temperature measurement of the samples was achieved by familiar techniques.

2. Results and Discussion

(a) Dimethoxyethane Solutions

The nuclear-electron Overhauser effect has been studied in solutions with four different free radical anions. With the exception of (coronene)$^-$, comparable enhancement factors of the DME protons have been observed in all these solutions. The points of Fig. 2 show ϱ as a function of reciprocal temperature as measured in the different magnetic fields.

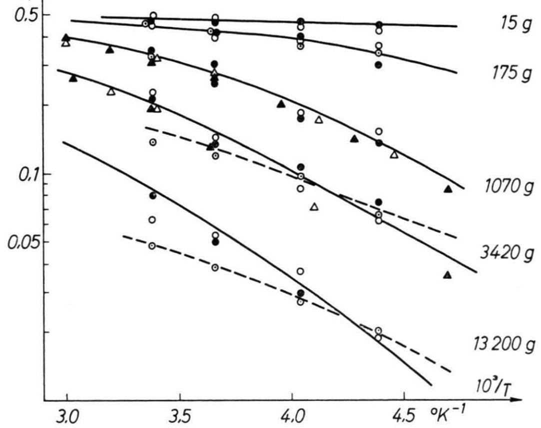

Fig. 2. Experimental results of the dynamic proton polarization (ϱ versus reciprocal temperature) in solutions of dimethoxyethane (DME) containing galvinoxyl (▲) and the free radical anions diphenyl$^-$ (△), acenaphthene$^-$ (⊙), pyrene$^-$ (○) and chrysene$^-$ (●). The solid lines correspond to the interpretation given in the text.

Likewise, previous measurements [2] on the same solvent, which were carried out with two further free radicals in solution (galvinoxyl, diphenyl$^-$), but at three magnetic fields only, are indicated in the figure. In all cases of Fig. 2, in the low-field/high-temperature limit ("extreme narrowing") ϱ tends towards 0.5. At 16 G only a few of the coinciding measured points are indicated.

The results of the solutions containing (coronene)$^-$ are presented in Fig. 3 as a function of the ESR frequency. Because saturation has proved very difficult, investigations on the temperature-dependence have not been made in this particular case. For purposes of comparison, the room temperature results of solutions containing (pyrene)$^-$ and (chrysene)$^-$ are also given in the presentation of Fig. 3.

The variety of data of Fig. 2 offers an opportunity for testing the theory more carefuly than hitherto and for obtaining more detailed information on the random motion in the solution. The limit of

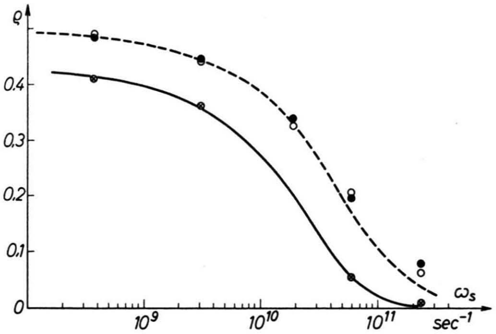

Fig. 3. Coupling parameter ϱ for solutions of coronene⁻ (⊗), pyrene⁻ (○) and chrysene⁻ (●) in dimethoxyethane at 23 °C as a function of the ESR frequency. The lines are explained in the text.

$\varrho = 0.5$ proves that the proton-electron interaction is in fact purely dipolar within the experimental accuracy, where of course an extremely small scalar contribution with K in Eq. (1) smaller than 0.04 (this means a contribution of less than 2% to the nuclear relaxation) would escape observation. If the very high field results are first neglected, the measurements might well be described by the translational model of molecular motions, as done in the past by many authors [1–7]. K and R in Eq. (1) are zero in this case, and f_t is the well known spectral intensity function for isotropic translational diffusion [13, 10]. Such an interpretation is proposed in Fig. 4. ϱ is plotted against $\omega_S \tau_t$. In order to figure the frequency- and temperature-dependence of the experimental data in one graph, an Arrhenius law

$$\tau_t = \tau_{t0} \exp\{E_t/R\,T\}\,, \tag{4}$$

with an activation energy $E_t = 3.0$ kcal/mole is assumed for the correlation time.

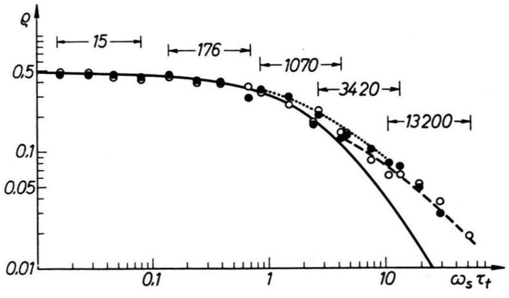

Fig. 4. Coupling parameter ϱ for the case, where the time dependence of the dipolar interaction is only caused by translational diffusion (solid line). ○ and ● are the experimental data for DME solutions containing pyrene⁻ and chrysene⁻, resp. The magnetic field ranges at which the measurements at various temperatures have been carried out, are indicated in the graph. Corrections as explained in the text are the dotted lines, viz. ······ at +23 °C and – – – at −45°.

It is easily realized that there are systematic departures from this description at high frequencies and low temperatures. As long as only measurements in not too strong magnetic fields were considered, these departures did not carry weight and were compensated for by choosing a smaller activation energy. The many new data, including those on further organic solutions show, however, that the enhancements in very high fields are in general higher than those extrapolated from measurements in weaker fields. The molecular motions in these solutions are evidently a little more complex than has been assumed so far. We believe that the reason for this is a second mechanism of motion, which could be a rotational contribution to the proton relaxation and polarization. Such an assumption is particularly justified, since the temperature-dependence of the solvent proton relaxation rates sometimes shows two maxima, if an appropriate frequency and temperature range is accessible [14]. A rotational contribution would mean that some solvation takes place, a certain number of radical molecules being for a time more closely associated with solvent molecules. The solvated complex then tumbles as an unit in the liquid, and the correlation time in the corresponding intensity function is either given by the residence time or by the rotational correlation time.

An attempt at such an explanation is shown by the solid and dotted lines in Fig. 2. These are the result of an application of Eq. (1) with R now being unequal to zero. For τ_t and f_t the same dependence as before had to be chosen. f_r is equal to $1/(1+\omega^2 \tau_r{}^2)$ and τ_r has turned out to be smaller than τ_t having also a smaller activation energy. Since the rotational contribution is only a correction in Eq. (1), being only important at big $\omega_S \tau_t$-values, the determination of τ_r is much less accurate than that of τ_t. The R values used are listed together with the other model parameters in Table 1 of the next paragraph. Therein, R' is equal to R/β with $\beta = \tau_r/\tau_t$. In DME/(acenaphthene)⁻ the sol-

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[11] J. Haupt and W. Müller-Warmuth, Z. Naturforsch. **17 a,** 1011 [1962].

[12] W. Müller-Warmuth, Z. Naturforsch. **15 a,** 927 [1960].

[13] H. Torrey, Phys. Rev. **92,** 962 [1953]. — H. Pfeifer, Ann. Phys. Leipzig **8,** 1 [1961].

[14] G. J. Krüger, private communication.

Table 1. List of the free radical solutions studied, with the model parameters for a best fit of the experimental data.

Solution	τ_t (23 °C) in 10^{-11} s	E_t in kcal/mole	R'	Other Parameters
DME/(acenaphthene)$^-$			0.2−1	$K=0$
DME/(pyrene)$^-$ DME/(chrysene)$^-$	4.7	3.0	0.8	$\beta=0.04, \dots, 0.09$ $\left(\frac{10^3}{T}=4.4, \dots, 3.0\right)$
DME/(coronene)$^-$				$K=0.08$
Toluene/TBP	4.8	3.1	1	$K=0$ $\beta=0.03-0.2$
Toluene/ADBP			0.5	$K=0$ $\beta=0.02-0.1$
Toluene/GV	6.2		0.5−0.8	$\left(\frac{10^3}{T}=4.7, \dots, 3.0\right)$
Acetic acid/BPA	17	3.5	0.15	$K=0$
Acetic acid/TMPO			Fig. 8	$E_r \approx 1.5$ kcal/mole; K see Fig. 8

vation and R', for a reliable fit, have been assumed to depend a little upon temperature.

In contrast to the other solutions, (coronene)$^-$ radical ions evidently possess a slight scalar contribution of the coupling to the solvent protons. This is in agreement with earlier observations on other (coronene)$^-$ solutions[15], and with high resolution NMR studies done elsewhere[16]. K turns out to be about 0.08 (solid line in Fig. 3), this means in the extreme narrowing case a contribution of approximately 4% to the proton relaxation. (Coronene)$^-$ is favourable for contact coupling with solvent nuclei since the unpaired electron occupies a π-orbital which is greatly delocalized, and the contact area during molecular collisions is large. On the other hand it is difficult to understand why no scalar interaction at all has been found with pyrene- and chrysene-negative ions (dotted line, interpretation of Fig. 2).

(b) Toluene Solutions

Earlier studies were concerned with solutions containing the BPA (bis-diphenylene phenyl allyl) radical[7]. Further measurements have now been made with galvinoxyl (GV, Fig. 5), with tri-t-butyl-phenoxyl (TBP) and amino-di-t-butyl-phenoxyl (ADBP, Fig. 6). The results are in many ways comparable with those discussed in the last paragraph. Again ϱ approaches the limit 0.5 in low field, and there are departures from an interpretation by a purely translational diffusion model in high fields. The differences between the radicals are even more important.

We propose a similar description to the preceding case. By chance, in the investigated temperature range τ_t and E_t have turned out to be nearly the same as for DME. At low temperatures, however, Eq. (4) does not hold at all, which was concluded from measurements of the self diffusion constant of toluene[†, 17]. Moreover, the diffusion data and new relaxation studies, as well as the present study, have shown that the assignment of the two maxima of the relaxation rate to translation and rotation is just the inverse of the suggestion of Ref. [7]. This changes little for the translational model parameters. The rotational contribution would, however, also in the case of the BPA radical turn out to be similar to those discussed here. A final fit of the data (solid and dotted lines in Figs. 5 and 6) is possible by taking account of the rotational term in Eq. (1). The inserted parameters are listed in Table 1.

(c) Acetic Acid Solutions

Finally, some associated liquids, such as ethanol and acetic acid solutions have been studied. Impor-

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[15] J. HAUPT, Dissertation (unveröffentlicht), Universität Mainz 1963.

[16] J. VAN VOORST and E. DE BOER, private communications.

[†] There is practically no difference between the diffusion constant of toluene in a solution like ours and that in the pure liquid[14].

[17] G. J. KRÜGER and R. WEISS, Z. Naturforsch., in press.

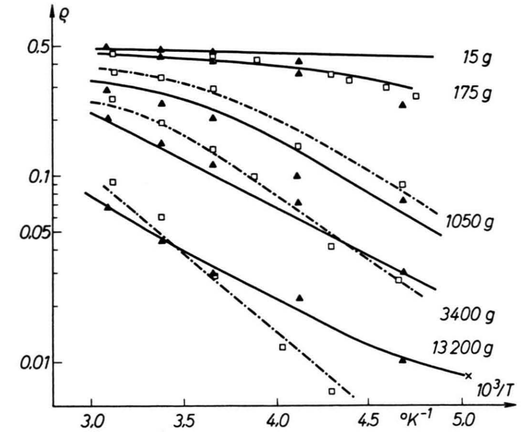

Fig. 5. Experimental results of the dynamic proton polarization in solutions of galvinoxyl in toluene (▲). For comparison the results of earlier measurements with BPA (☐) are indicated. The solid and dotted lines correspond to the interpretation given in the text.

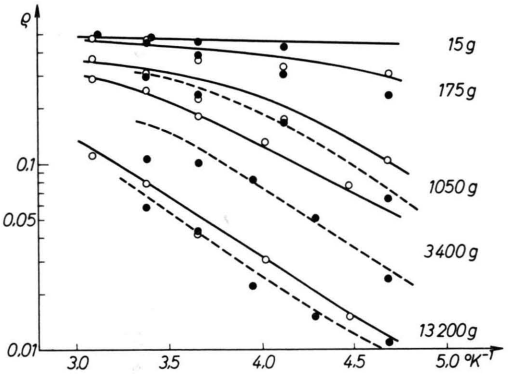

Fig. 6. As Fig. 5 for toluene solutions containing tri-t-butyl-phenoxyl (○) and amino-di-t-butyl-phenoxyl (●).

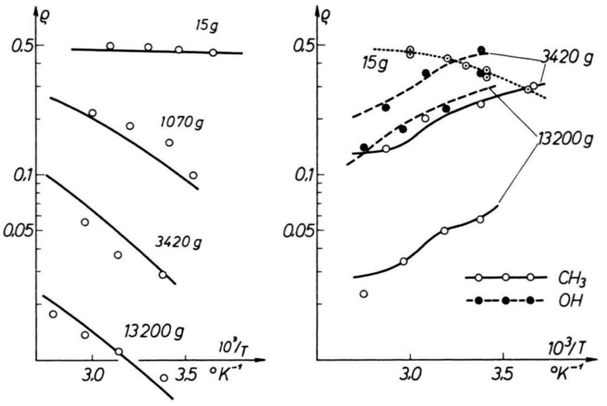

Fig. 7. Experimental results of the dynamic proton polarization in acetic acid solutions. Left: bis-diphenylene phenyl allyl (BPA); right: tetramethyl piperidineoxyl (TMPO). The solid and dotted lines correspond to the interpretation given in the text.

tant changes occured with nitroxide radicals[18] in solution. ESR studies on the hyperfine coupling within the radical[19] and NMR studies on the solvent proton chemical shift[20] had already yielded abnormal dependences upon the specific type of solvent. Since the ESR saturation of a nitroxide radical is worse in ethanol, in the present paper we shall discuss the measurements made in acetic acid solutions. The left hand side of Fig. 7 shows the results of solutions containing bis-diphenylene phenyl allyl (BPA). Corresponding data obtained in solutions with the nitroxide free radical tetramethyl-piperidineoxyl (TMPO) are given at the right of the same figure.

The experiments with BPA can be interpreted in more or less the same manner as the measurements discussed in the last paragraphs. Both the absolute value and the activation energy of the translational correlation time (Table 1) are only somewhat higher, which is certainly a consequence of the molecular association. As before, the solid lines in Fig. 7, correspond to the theoretical interpretation.

In TMPO solutions, however, the proton polarization decreases with the temperature instead of increasing. Only in a very weak magnetic field does ϱ increase, and there more rapidly than usual. Furthermore, the hydroxyl resonance is much more strongly enhanced than the methyl resonance. In all the other cases studied there was no important difference in the enhancement of non-equivalent solvant nuclei. Finally a "paramagnetic shift" of the solvent NMR has been observed which is removed by saturating the ESR of the radical. In order to check, that all these abnormalities are really a property of the solution and not of the radical, TMPO has also been studied in toluene, where no peculiarities were observed.

The particular effects occur only in solutions of nitroxide radicals in hydroxyl containing solvents. We explain them by the formation of hydrogen

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[18] R. Brière, H. Lemaire, and A. Rassat, Bull. Soc. Chim. France 1965, p. 3273.

[19] A. L. Buchachenko and O. P. Suchanova, Zh. Strukt. Khim. **6**, 32 [1965].

[20] N. A. Sysoeva, A. U. Stepanyants, and A. L. Buchachenko, Zh. Strukt. Khim. **9**, 311 [1968].

bridges between the $=$NO... of the radical and the $-$OH... of the solvent. A certain amount of spin density may temporarily be transferred from the radical into a molecular orbital of the solvent via the hydrogen bridge. Furthermore, during the association the mechanism responsable for the time dependence of the dipolar interaction would no longer be principally the translational diffusion of individual molecules, but a rotational tumbling of associates.

Quantitatively this would mean that the rotational contribution in Eq. (1) becomes more and more important with decreasing temperature. The process of H-bridge formation is described by

$$\mathrm{A} + \mathrm{B} \rightleftarrows \mathrm{A} \cdot \mathrm{B} \tag{5}$$

with the association constant

$$K_\mathrm{X} = \frac{X}{X_\mathrm{A} \cdot X_\mathrm{B}} \tag{6}$$

(X_A = mole fraction of solvent molecules A, X_B = mole fraction of free radical molecules B). At lower temperature the equilibrium tends towards the right hand side of Eq. (5), and K_X increases. The experimental data can be fitted by an exponential dependence of R in Eq. (1) upon reciprocal temperature. Since R is proportional to X, and because of Eq. (6), it is concluded, that the number of solvent molecules associated to the radical is still much less than the total number of solvent molecules. The best fitting R values for the methyl- and hydroxyl proton resonances are given in Fig. 8. With the aforementioned condition the temperature-dependence of R is equal to that of the association constant. The slope therefore yields approximately the formation enthalpy of the solvated complex, which turns out to be around 10 kcal/mole. τ_r is about one order of magnitude smaller than τ_t and varies much less with the temperature. No final explanation has been found, why in this description $\tau_\mathrm{r}(\mathrm{OH})$ is about twice as short as $\tau_\mathrm{r}(\mathrm{CH_3})$.

In the numerical evaluation it has been assumed that the scalar contribution to ϱ only plays a role in the 15 gauss field, because the correlation time τ_sk is of the order of τ_t or a little longer and the function f_sk at 3400 and 13 200 g has thus decayed to zero. Since K as well as R is proportional to X, the mole fraction of associates, its temperature dependence derived from the weak field data looks similar (Fig. 8). The translational contribution to ϱ, finally, has been taken from the measurements in the BPA-solution.

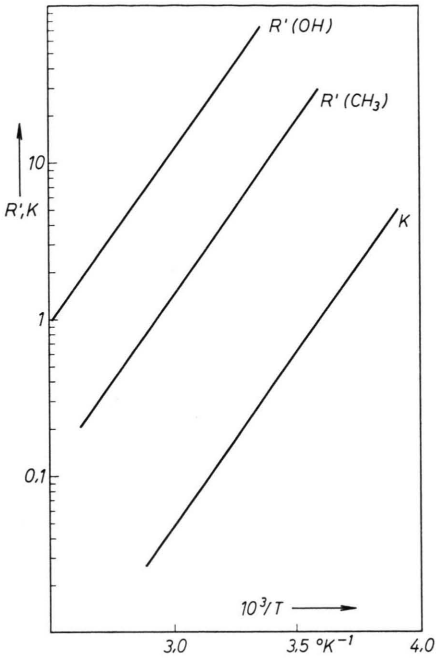

Fig. 8. Temperature-dependence of the parameters $R' = R/(\tau_\mathrm{r}/\tau_\mathrm{t})$ and K as derived from the experimental data and the model explained in the text.

Further parameters of the interpretation can be determined from the values of $R'_\mathrm{CH_3}$, R'_OH and K in Fig. 8. Because of $R'_\mathrm{CH}/R'_\mathrm{CH_3} = b^6_\mathrm{CH_3}/b^6_\mathrm{OH}$ it follows $b_\mathrm{CH_3} \approx 1.4\, b_\mathrm{OH}$ for the distances between proton and electron spins. Compatible values are $b_\mathrm{OH} = 1.6$ Å and $b_\mathrm{CH_3} = 2.3$ Å leading to the average structure of the solvated complex of Fig. 9. Applying the "sticking model" for the scalar interaction [21, 9], from the ratio K/R the hyperfine coupling constant may be estimated. This is $\mathrm{A_{CH_3}}$ and $\mathrm{A_{OH}}$, resp., when the two molecules in question are associated, and zero when they are not. In the weak magnetic field it is not possible to distinguish between OH- and $\mathrm{CH_3}$-protons. Therefore only an average coupling constant of about 1.0 MHz is evaluated which mainly takes account of the methyl protons.

3. Conclusions

The extensive new investigations of the proton-electron Overhauser effect in organic solutions have shown that the model of isotropic translational molecular motions for the dipolar interaction may only be used in a limited spectral range. At very low temperatures, there exist still random motions which are faster than expected from this model. The same effect occurs, if very high frequencies are applied in the experiment. Relative to these frequencies the motions are not as slow as extrapolated from studies in lower magnetic fields. This means that the total spectral intensity function of the relative molecular motion in the solution decays a little more slowly than in the translational diffusion model.

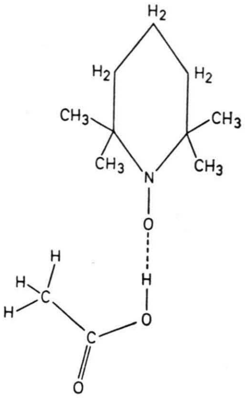

Fig. 9. Hydrogen-bonded complex as formed in solutions of tetramethyl piperidine-oxyl in acetic acid.

It is concluded, also from the occasional appearance of two maxima in the temperature-dependence of proton relaxation rates in free radical solutions, that a second mechanism of motion may play a role. Taking into account, in addition, a weak dependence upon the type of the free radical in solution, this mechanism could be a rotation of solvent-radical complexes. An appropriate model for mixed phases of motion describes the experimental data quite well. At low temperature, it leads to rotational correlation times, which are much smaller than the translational correlation times. From an estimate of the parameter R' used in the model (Table 1) and its definition, it turns out that in cases of maximum solvation each radical would have about one solvent partner. On the other hand, as previously reported, for most solutions scalar contact interactions between solvent protons and radical electrons have either not been observed at all, or are only of minor importance.

All this is quite different, if there exist particular associative forces between radical and solvent molecules such as hydrogen bridges. These do not occur in π-electron radicals, but in free radical molecules, where the unpaired electron spin density is mainly localized in a NO-group. In such a case, dynamic proton polarization studies offer a new and effective method of obtaining information on the formation of solvate cmplexes and on the different time constants involved. The unpaired electron delocalization in the complex may be studied, and the DNP temperature- and frequency-dependences are very different from the usual behaviour. Unfortunately the ESR-lines of nitroxide radicals are broad and sometimes difficult to saturate. It would otherwise be of great interest to investigate this kind of association in more systems, and particularly in those with a larger liquid range.

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[21] A. ABRAGAM, Nuclear Magnetism, Clarendon Press, Oxford 1961, p. 308.