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Abstract

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HYDROGEN BONDING IN RADICALS

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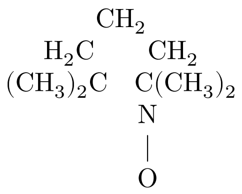
In the study of organic free radicals in the liquid phase, it has been noted in a number of cases that the hyperfine splitting in electron paramagnetic resonance (EPR) spectra depends significantly on the nature of the medium in which the radicals are found. This effect, naturally, is due only to the properties of the medium and is considered in a number of works (1-4) as a solvation effect. However, the nature of solvation and the structure of solvates have not been investigated; the very concept of solvation is too general and lacks concrete meaning.

In order to clarify the nature of this effect, the EPR spectra of the radical 2,2,6,6-tetramethylpentamethylene nitroxide



were studied in various solvents. The results are given in Table 1, where a_N is the splitting between the components of the nitrogen triplet in the EPR spectrum. (All measurements here and below were carried out on evacuated samples.)

Table 1

Splittings between the triplet components in various solvents

Solvent	$a_N \pm 0.2$, oersted
Acetone	15.6
Carbon tetrachloride	15.6
Benzene	15.6
Tetrahydrofuran	15.7
Water	17.1
Nitrobenzene	15.7
Methyl alcohol	16.3
Acetic acid	16.6
Chloroform	15.6

Analysis of the values of a_N shows that all the solvents listed in Table 1 can be divided into two groups. In the first group—water, methanol, acetic acid—the splittings on nitrogen change, whereas in all the other solvents, regardless of their dielectric properties, these splittings are constant. It should be noted that the solvents of the first group, unlike the others, are capable of forming hydrogen bonds with the oxygen atom in the radical.

In order to determine changes in a_N with sufficient accuracy, the following method was used: two ampoules containing radical solutions of the same concentration in different solvents were placed simultaneously in the resonator of the EPR spectrometer, and their EPR spectra were recorded simultaneously. Figure 1 gives two examples of such a recording. The first spectrum (a) is the superposition of spectra from radicals in acetone and carbon tetrachloride. It is seen that the positions of the components of both spectra coincide exactly. The second spectrum (b) is the superposition of spectra from radicals in acetone and water. Here the positions coincide only for one component of the spectrum, located in the lower fields. Its intensity is also close to twice the intensity of the individual components. The components located in higher fields are shifted in field; moreover, the central components are shifted by the amount $\Delta a = a_2 - a_1$, where a_2 and a_1 are the splittings in water and acetone, respectively, while the outer components (in larger fields) are shifted relative to one another by $2\Delta a$. By measuring in this way the shifts of the components in various solvents, one can calculate a_N and the g-factors of radicals in these solvents. It should be noted that such shifts are observed

only in solvents of the first group, which are capable of forming hydrogen bonds, and they were measured relative to solvents of the second group. The analysis of shifts, if they were small, was carried out with the aid of an EPR spectra atlas (^{5}). The shift of the g-factors was determined relative to the g-factor in carbon tetrachloride. The results are given in Table 2.

The data given in Tables 1 and 2 indicate that a new type of hydrogen bond is formed between radicals and solvent molecules with the participation of an unpaired electron. The formation of such a bond causes an increase in the hyperfine splitting constant on nitrogen and a decrease in the g-factor, which may be connected either with a decrease in the absolute value of the spin-orbit coupling constant or with an increase in the distance between orbital levels.

It may be assumed that solvation of the free radical R_0 through hydrogen bonds with the solvent S proceeds reversibly according to the scheme

$$R_0 + S \overset{K}{\rightleftarrows} R_S \tag{1}$$

with equilibrium constant K. It is of interest to study the dynamics and character of such an equilibrium.

Fig. 1. Superposition of EPR spectra of radicals in different solvents: a — acetone-water; b —acetone-carbon tetrachloride

Figure 1: Fig. 1. Superposition of EPR spectra of radicals in different solvents: a —acetone-water; b —acetone-carbon tetrachloride

Fig. 1. Superposition of EPR spectra of radicals in different solvents: **a** — acetone-water; **b** —acetone-carbon tetrachloride.

If the frequency of formation and rupture of the hydrogen bond is less than the difference in splittings for the free and solvated radicals, then components belonging to both types of radicals should be observed in the EPR spectrum.

Table 2

Values of a_N and g-factors of radicals in various solvents

Solvent	a_N, Oe	g-factor
CCl_4	15.6	2.0065
Methyl alcohol	16.3	2.0060
Acetic acid	16.6	2.0058
Water	17.1	2.0054
D_2O	16.9	2.0056

Table 3

Values of $\bar{a}$ and ρ in mixtures of water with acetone of different composition $(T = 19^\circ)$

(H_2O), molecules/cm^3	$\bar{a}$, Oe	ρ
0	15.6	−1.00
$2.0 \cdot 10^{21}$	16.0	−0.47
$8.6 \cdot 10^{21}$	16.2	−0.20
$9.5 \cdot 10^{21}$	16.3	−0.07
$11.1 \cdot 10^{21}$	16.5	0.20
$13.4 \cdot 10^{21}$	16.6	0.33
$16.6 \cdot 10^{21}$	16.8	0.60
$33.3 \cdot 10^{21}$	17.1	1.00

However, if this frequency is much greater than the difference in splittings, then a certain averaged splitting value $\bar{a}$ will be observed, which lies between the values of a_N for the free and solvated radicals. In the general case, for any periodic perturbation leading to a change in a_N, the expression for $\bar{a}$ has the form (^{2}):

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

$$\bar{a} = \frac{1}{2}(a_1 + a_2) + \frac{1}{2}\rho(a_2 - a_1), \tag{2}$$

where a_1 and a_2 are the splittings for the free and solvated radicals,

$$\rho = \frac{K\alpha - 1}{K\alpha + 1}. \tag{3}$$

Here K is the equilibrium constant (1), and a is the concentration of that component of the solvent in the mixture which causes solvation.

Equilibrium (1) was studied in mixtures of acetone with water. As before, two ampoules were placed simultaneously in the resonator: one with a solution of radicals in acetone, the other with a solution in acetone-water mixtures of different composition. Fig. 2 shows several double lines, representing the superposition of the extreme components at large fields from both solutions. It is seen that in mixtures of water with acetone only one averaged value $\bar{a}$ is observed, which increases with increasing concentration of water in the mixture. From (2), with $a_1 = 15.6$ oersted,

Fig. 2. Superposition of the extreme components of the EPR spectra of radicals from solutions in acetone and in acetone-water mixtures at the following water-to-acetone ratios: *a*—0.06; —0.40; —0.50; —0.67; —1.00; *e*—100% water

Fig. 3. Dependence of ρ on the concentration of water in aqueous-acetone mixtures

$a_2 = 17.1$ oersted, the value of ρ can be calculated from the found $\bar{a}$. The values of $\bar{a}$ and ρ at different water concentrations in the mixture are given in Table 3.

Fig. 3 shows the dependence of ρ on the concentration of water in the mixture. From equation (3), $\rho = 0$ when $K = 1/\alpha$. Then from Fig. 3 it is easy to find that $K = 10^{-22}\,\text{cm}^3$.

By measuring $\bar{a}$ in mixtures of water with acetone at various temperatures, one can find the temperature dependence of the equilibrium constant and the energy of the hydrogen bond of the radical with water molecules. These measurements were carried out in the temperature interval from -12 to 80°. It was found that the energy of the hydrogen bond is 2.4 kcal/mol, and the equilibrium constant has the form:

$$K = 2 \cdot 10^{-24} \exp(2400/RT)\ \text{cm}^3.$$

The results obtained and the conclusions concerning the formation of hydrogen bonds in radicals appear to be significant from the standpoint of reactivity. Polar factors, as is known, play the principal role in the reactivity of radicals. A hydrogen bond, representing an interaction of the donor-acceptor type, produces the greatest polar effects, especially if this bond is formed in the activated complex of the reaction. Thus, this fact can substantially change the reactivity of radicals. The results presented may be of interest from the standpoint of the theory of the hydrogen bond.

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Note: Figure translations are in progress. See original paper for figures.