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PROTON RESONANCE IN NONAQUEOUS SOLUTIONS OF PARAMAGNETIC SALTS

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1. In works (^{1,2}) it was shown that the presence of a sufficiently stable short-range order in the environment of paramagnetic particles (solvation of ions), and the presence of rapid hydrogen exchange between protons of solvent molecules (water), affect the nature of the phenomenon of proton resonance in paramagnetic solutions. It was found that in aqueous solutions the hydrate shells do not shield the paramagnetic ions from the solvent protons: owing to rapid hydrogen exchange, all protons, in a time $\ll T_1$ (T_1 is the longitudinal magnetic relaxation time of the protons, equal to $10^{-2} \div 10^{-4}$ sec.), have time to penetrate through the solvating layers of water molecules and to remain at distances of closest approach to the paramagnetic ions. In other words, hydrogen exchange makes the hydrate atmosphere around the ions so "transparent" to the solvent protons that it is effectively permeated by them during the relaxation cycle T_1. Therefore, in aqueous solutions the presence of short-range order leads only to the fact that, within a certain distance from the paramagnetic ion, the predominant process in rate is not the thermal motion of water molecules, but changes in the orientation of the electron spin relative to the externally applied static magnetic field H_0, occurring with the characteristic time $\rho/2\pi$ (ρ is the time of electronic paramagnetic relaxation). This time, $\rho/2\pi$, is of the order of 10^{-8} sec. or less (depending on the type of ions) and is always shorter than the characteristic time of hydrogen exchange. Specific manifestations of the established molecular mechanism in proton-resonance experiments were considered in works (^{1,2}).

2. In connection with the above, it was of interest to investigate proton resonance in paramagnetic solutions in which rapid hydrogen exchange is either absent or, if it occurs, only a small fraction of the solvent protons participates in it. It was assumed that in such solutions the presence around paramagnetic particles of an "impermeable" solvation atmosphere (in the sense indicated in item 1) should lead to a sharp lengthening of the relaxation time T_1 owing to a strong increase in the distances of proton–ion approaches. This indeed was observed experimentally.

As objects of investigation, solutions of crystalline hydrates of paramagnetic salts of elements of the iron group in absolute (anhydrous) acetone and alcohol were chosen*. In acetone solutions all protons, being in the C—H bonds of acetone molecules, are incapable of rapid hydrogen exchange; in alcoholic solutions only the hydroxyl protons of the alcohol molecules, i.e. 1/6 of all solvent protons, undergo rapid hydrogen exchange.

For carrying out the measurements, the apparatus and technique used

* Results on acetone solutions of salts of divalent manganese and copper were mentioned in (^{1}). However, the attempt made then to explain the anomalously long relaxation times T_1 of these solutions is not justified by the totality of the experimental data of the present work.

varied in studies (^{1,2}).* All experiments were carried out at room temperature and in a constant magnetic field $H_0 \sim 2300$ oersted.

3. Table 1 presents the main results of measurements in acetone solutions.

The table gives the mean values of the products T_1N in the concentration intervals studied (N is the concentration of the solutions), and $T_1/T_{1\text{water}}$ is the ratio of the relaxation time in acetone solutions to the relaxation time in equimolar solutions of the same salt. From the data of Table 1 it is seen that, in acetone, dissolved paramagnetic salts have a comparatively weak effect on proton relaxation, and T_1 is considerably greater than $T_{1\text{water}}$. The effect of salts of trivalent ions is especially small (for solutions of $\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Cr(NO}_3)_3 \cdot 9\text{H}_2\text{O}$).

The dependence of the proton relaxation time T_1 on the electric charge of the paramagnetic particles is a qualitatively new effect, not characteristic of aqueous solutions of paramagnetic salts. The picture becomes clearer if, instead of T_1, one turns to another relaxation parameter—the effective magnetic moment μ_{eff} (^{4}) (see Table 1). The values of μ_{eff} were calculated by formula (4)

$$1/T_1 = C\mu_{\text{eff}}^2 N,$$

where C is a coefficient that includes the temperature dependence. The values of μ_{eff} in Table 1 were obtained from the above formula with the coefficient C chosen conditionally so that, for acetone solutions of $\text{Mn(NO}_2)_2 \cdot 6\text{H}_2\text{O}$, the equality $\mu_{\text{eff1}} = \mu_{\text{st}} = 5.9\,\mu_B$ would hold (μ_{st} is the static magnetic moment from susceptibility measurements of aqueous solutions).** In this case, for solutions of copper salts one also obtains values $\mu_{\text{eff1}} \simeq \mu_{\text{st}}$, but for solutions of salts of trivalent ions (Fe, Cr), μ_{eff1} proves to be strongly underestimated relative to the corresponding static values (see Table 1). On the other hand, if one assumes that, for acetone solutions of $\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (see μ_{eff2} in Table 1), the effective and static moments are equal, then for solutions of the second trivalent ion—chromium—one obtains $\mu_{\text{eff2}} \simeq \mu_{\text{st}}$, but for solutions of salts of divalent ions—manganese and copper—$\mu_{\text{eff2}} \gg \mu_{\text{st}}$.*** The acetone solutions of cobalt and nickel salts fall outside the regularity considered; for them it was found that $\mu_{\text{eff1}} \ll \mu_{\text{st}}$, $\mu_{\text{eff2}} \ll \mu_{\text{st}}$. An analogous situation was also noted in the investigation of aqueous solutions of these salts ($^{4-6}$). The principal reason probably lies in the exceptionally rapid relaxation of the electron spins of Co^{2+} and Ni^{2+} ($\rho \lesssim 10^{-11}$ sec.).****

The regular dependence of the relaxation time T_1 on the charge of the paramagnetic particles for acetone solutions of chromium, manganese, iron, and copper is not accidental. Like the large T_1 values obtained for all acetone solutions ($T_1/T_{1\text{water}} \gg 1$), it indicates the presence of solvation shells that are impermeable (at least for a time $\lesssim T_1$) to the protons of the solvent. The higher the charge of the paramagnetic ions, the greater the thickness of the solvating layers and, consequently, the larger the distances of proton-ion approaches must be. As a result, the magnetic dipole interaction between these particles is correspondingly weakened, which increases the relaxation time T_1.

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* A detailed description of the experimental technique is contained in ([3]).

** Within the accuracy meaningful for comparing μ_{eff} and μ_{st}, we considered it permissible to use μ_{st} from measurements in aqueous solutions.

*** It is necessary to emphasize that, owing to the arbitrary assignment of the coefficient C, all the values of μ_{eff1} and μ_{eff2} in Table 1 are purely conventional in character and are intended only for a comparative characterization of the intensity of the influence of paramagnetic salts on proton relaxation in one and the same solvent—acetone.

**** For aqueous solutions this was established unambiguously ([1]).

Finally, let us dwell on one more feature of relaxation in acetone solutions. Using antipyrine complexes of trivalent iron as an example, the effect of chemical complex formation was studied. It was found that, in contrast to aqueous solutions, where shielding of Fe^{3+} ions by antipyrine molecules causes a sixfold increase in the time T_1 (3), in acetone solutions of $Fe(NO_3)_3 \cdot 9H_2O$ the formation of complexes with antipyrine has almost no effect on proton relaxation. The explanation follows unambiguously from what was said above: the bulk of the protons, being unable to penetrate through the solvating layers of acetone molecules, "does not know" about changes occurring in the immediate environment of the paramagnetic particles.

Fig. 1. Ratio of the relaxation time in an alcoholic solution T_1 to the relaxation time in an equimolar aqueous solution $T_{1\,\text{water}}$ as a function of the concentration of the solutions N:
1 –solution of $Fe(NO_3)_3 \cdot 9H_2O$; 2 –$Mn(NO_3)_2 \cdot 6H_2O$; 3 –$CuCl_2 \cdot 2H_2O$; 4 – $CuCl_2$. To prevent hydrolysis, the alcoholic solutions of $Fe(NO_3)_3 \cdot 9H_2O$ were acidified with concentrated nitric acid.

Assuming proportionality of the time T_1 to the cube of the effective distance of proton-ion approaches (1), we find that the solvate atmosphere in acetone solutions, in its shielding action, is approximately equivalent to a stationary shell of two or three layers of solvent molecules.

4. From the point of view set forth above, the results of measurements in alcoholic solutions also become understandable. Here, too, for solutions of salts of trivalent iron the ratio $T_1/T_{1\,\mathrm{water}}$ is much greater than for solutions of salts of divalent manganese (Fig. 1, 1 and 2), despite the approximate equality of the static moments. Just as in acetone solutions, the ratio $T_1/T_{1\,\mathrm{water}}$ is especially large for solutions of salts of trivalent chromium (for alcoholic solutions of $CrCl_3 \cdot 6H_2O$, $T_1/T_{1\,\mathrm{water}} \simeq 14.2$). There is also an anomalously low effectiveness of cobalt and nickel salts, etc.

An important distinctive property of alcoholic solutions is that for them the ratio $T_1/T_{1\,\mathrm{water}}$ decreases intensively with decreasing con-

Table 1

Relaxation parameters of protons in acetone solutions of paramagnetic salts ($H_0 \sim 2300$ oersted; $T \sim 290$°K)

Salt	Concentration interval, mol/l	$T_1 N \cdot 10^2$, sec · mol/l	$T_1/T_{1\,\mathrm{water}}$	μ_{eff1}, in units of μ_B	μ_{eff2}, in units of μ_B	μ_{st}, in units of μ_B (from measurements in aqueous solutions)
$Cr(NO_3)_3 \cdot 9H_2O$	0.05–0.1	0.87 ± 0.02	45	2.66	3.79	3.8
$Mn(NO_3)_2 \cdot 6H_2O$	0.02–0.05	0.177 ± 0.002	12.3	5.9**	8.4	5.9
$Fe(NO_3)_3 \cdot 9H_2O$	0.01–0.05*	0.36 ± 0.00	25	4.14	5.9**	5.9
$Co(NO_3)_2 \cdot 6H_2O$	0.15–0.5	5.8 ± 0.5	7.68	1.03	1.47	5.0
$Ni(NO_3)_2 \cdot 6H_2O$	0.12–0.5	4.62 ± 0.25	15.6	1.15	1.65	3.1
$Cu(NO_3)_2 \cdot 3H_2O$	0.15–0.5*	1.43 ± 0.09	12.5	2.07	2.96	2.0
$CuCl_2 \cdot 2H_2O$	0.025–0.1	1.46 ± 0.07	12.8	2.05	2.92	2.0

* Salts whose solutions, in order to avoid hydrolysis, were acidified with concentrated nitric acid.
** Conventional.

concentration N (Fig. 1, 1, 2, and 3). Apparently, when salt crystal hydrates are dissolved in absolute alcohol, a considerable amount of crystallization water is retained in the inner coordination spheres of the paramagnetic particles, promoting the formation of more dissociated and, consequently, better-solvated ionic forms. As N decreases, the total content of water introduced into the solution falls; as a result, an ever larger fraction of it is absorbed by the alcohol. The latter leads to a decrease in the degree of dissociation and to a corresponding decrease in the time T_1. It is characteristic that, for alcoholic solutions of crystal hydrates of trivalent chromium salts, which coordinate water strongly (7), $T_1/T_{1\ \mathrm{water}} \simeq$ const up to very high dilutions.

In addition to solutions of crystal hydrates, alcoholic solutions of anhydrous copper chloride were investigated (Fig. 1, 4). As could be expected, the ratio $T_1/T_{1\ \mathrm{water}}$ for these solutions does not depend on the concentration N and has the value toward which $T_1/T_{1\ \mathrm{water}}$ tends, with decreasing concentration, for alcoholic solutions of $\mathrm{CuCl} \cdot 2\mathrm{H_2O}$.

Although in an alcohol molecule only one (hydroxyl) proton participates in rapid hydrogen exchange, the ratios $T_1/T_{1\ \mathrm{water}}$ for alcoholic solutions are, as a rule, several times lower than for acetone solutions. It may be assumed that the indirect magnetic interaction of the hydroxyl proton with the other protons of the molecule (8) causes a substantial reduction of their spin temperature T_s.

The results of this work show that, in the phenomenon of proton resonance in paramagnetic solutions, in the absence of rapid hydrogen exchange among all or most of the protons, the effects associated with the presence of ordering in the immediate environment of the paramagnetic particles manifest themselves very strongly, determining both the character of the behavior and the very order of magnitude of the measured relaxation parameters.

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