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NUCLEAR MAGNETIC RESONANCE IN CONCENTRATED AQUEOUS SOLUTIONS OF VO^{++}

N. S. KUCHERYAVENKO

Kazan' State Pedagogic Institute

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Highly concentrated aqueous solutions of $VOCl_2$ and $VOSO_4$ have been investigated by the spin-echo method. The dependence on the concentration of the relaxation times $T_{\|}$ and $T_{\perp}$ agrees with existing theory when exchange interaction is taken into account.

INTRODUCTION

We have carried out an investigation of the longitudinal and transverse nuclear magnetic relaxation times $T_{\|}$ and $T_{\perp}$ in highly concentrated aqueous solutions of VO^{++}. A theory of nuclear resonance taking into account the exchange interaction between paramagnetic atoms at high concentrations N_S has been proposed by Valiev and Timerov[1,2]. They have shown that the exchange interaction, which gives rise to a variation of the internal fields in paramagnetic particles at the sites occupied by the nuclei under investigation simultaneously with the variations due to precession, electron-spin relaxation and thermal motion, leads to an additional averaging of the internal fields and, consequently, decreases the effectiveness of subsequently added paramagnetic atoms from the point of view of decreasing the relaxation times $T_{\|}$ and $T_{\perp}$. For the case of thermal motion they have obtained

$$\frac{1}{T_{\|}} = \frac{2}{15}\frac{\hbar^2\gamma_I^2\gamma_S^2 S(S+1)}{b^6}\frac{mN_S}{N_I}\left[\frac{3K_{01}^{-1}}{K_{01}^{-2}+\omega_I^2} + \frac{6K_{11}^{-1}}{K_{11}^{-2}+(\omega_I+\omega_S)^2} + \frac{K_{11}^{-1}}{K_{11}^{-2}+(\omega_I-\omega_S)^2}\right] + \frac{2}{3}S(S+1)\left(\frac{A}{\hbar}\right)^2\frac{mN_S}{N_I}\frac{K_{12}^{-1}}{K_{12}^{-2}+(\omega_I-\omega_S)^2}; \tag{1}$$

$$\frac{1}{T_{\perp}} = \frac{1}{15}\frac{\hbar^2\gamma_I^2\gamma_S^2 S(S+1)}{b^6}\frac{mN_S}{N_I}\left[4K_{01} + \frac{6K_{11}^{-1}}{K_{11}^{-2}+\omega_S^2} + \frac{3K_{01}^{-1}}{K_{01}^{-2}+\omega_I^2} + \frac{6K_{11}^{-1}}{K_{11}^{-2}+(\omega_S+\omega_I)^2} + \frac{K_{11}^{-1}}{K_{11}^{-2}+(\omega_I-\omega_S)^2}\right] + \frac{1}{3}S(S+1)\left(\frac{A}{\hbar}\right)^2\frac{mN_S}{N_I}\left\{K_{02} + \frac{K_{12}^{-1}}{K_{12}^{-2}+(\omega_I-\omega_S)^2}\right\}; \tag{2}$$

$$K_{01}^{-1} = \tau_1^{-1} + T_1^{-1} + \tau_e\omega_e^2, \quad K_{11}^{-1} = \tau_1^{-1} + T_2^{-1} + \tau_e\omega_e^2,$$
$$K_{02}^{-1} = \tau_2^{-1} + T_1^{-1} + \tau_e\omega_e^2, \quad K_{12}^{-1} = \tau_2^{-1} + T_2^{-1} + \tau_e\omega_e^2. \tag{3}$$

Here τ_1 is the correlation time for the dipole-dipole interaction due to the rotational diffusion of the complex ion[3]:

$$\tau_1 = 4\pi a^3\eta/3kT, \tag{4}$$

where a is the radius of the complex ion $[VO^{++}(H_2O)_5]$; τ_2 is the proton lifetime in the first coordination sphere of the paramagnetic atom; τ_e is the correlation time for the exchange interaction due to the translational diffusion of the complex ions with respect to one another:

$$\tau_e = \pi a x^2\eta/2kT, \qquad x \approx a; \tag{5}$$

T_1, T_2 are the relaxation times of the S_z and S_x, S_y components of the spin of the paramagnetic atom[4]; ω_e is the frequency characterizing the exchange interaction between the paramagnetic atoms; γ_I, γ_S, ω_I, ω_S, N_I, N_S are the gyromagnetic ratios, the Larmor frequencies and the numbers of particles per unit volume of protons and of paramagnetic atoms respectively; S is the spin of the paramagnetic atom; m is the coordination number of the paramagnetic atom; b is the distance between the paramagnetic atom and the proton in the complex ion (in the first coordination sphere); A is the hyperfine interaction constant.

The criterion for the applicability of formulas (1), (2) is the condition $\tau_e\omega_e < 1$. For viscous liquids in which $\tau_e\omega_e > 1$, formulas (1), (2) are inapplicable, since in this case the frequency of the exchange interaction no longer varies as a result of translational diffusion. The relaxation times $T_{\|}$ and $T_{\perp}$ for the proton spin will be given by formulas (9)[2] and (28)[1]:

$$\frac{1}{T_{\|}} = 2\sqrt{\frac{\pi}{2}}\frac{1}{\omega_e}\sum_{\gamma=\pm1}\sum_{\beta=0,\,\pm1}\sigma_{\gamma\beta}^{(z)2}\,\mathrm{Re}\,L(z_{\gamma\beta\alpha}); \tag{6}$$

$$\frac{1}{T_{\perp}} = \sqrt{\frac{\pi}{2}}\frac{1}{\omega_e}\sum_{\gamma=0}^{1}\sum_{\beta=-1}^{1}\sigma_{\gamma\beta}^2\,\mathrm{Re}\,L(z_{\gamma\beta\alpha}); \tag{7}$$

$$L(z) = e^{-z^2}\left(1 + 2i\pi^{-1/2}\int_0^z e^{x^2}dx\right); \qquad (8)$$

$$z_{\gamma\beta\alpha} = \omega_e^{-1}(\gamma\omega_I + \beta\omega_S + i\,(T_\beta^{-1} + \tau_\alpha^{-1}))/\sqrt{2}. \qquad (9)$$

The values of $\sigma_{\gamma\beta}^{(z)2}$ are given in [2], and of $\sigma_{\gamma\beta}^{2}$ are given in [1]. The function (8) is the tabulated probability integral [5].

We see from formulas (1)—(9) that the relaxation times $T_{\parallel}$ and $T_{\perp}$ of the longitudinal and the transverse (with respect to the external fields) components of the nuclear magnetization M will be determined by the rates of thermal motion, of electronic relaxation or of the electron exchange motion depending on which process is characterized by the greatest rate.

EXPERIMENTAL RESULTS

We have carried out measurements of the relaxation times $T_{\parallel}$ and $T_{\perp}$ for protons in aqueous solutions of $VOCl_2$ in the temperature range 295—373°K. The concentration of the paramagnetic atoms N_S was varied from 0.05 to 6.72 mole/liter. Measurements in aqueous solutions of $VOSO_4$ were carried out at room temperature and at concentrations N_S from 0.04 to 2.87 mole/liter. All samples contained 0.1 mole/liter of $HClO_4$. The relaxation times $T_{\parallel}$ and $T_{\perp}$ were determined by the spin-echo method using the apparatus developed in our laboratory at a frequency of $\nu = 16.365$ Mc. The duration of the rf pulses t_p did not exceed 2 and 4 μsec respectively for the 90° and the 180° pulses. The relaxation time $T_{\perp}$ was measured by a sequence of 90°—180° pulses, while $T_{\parallel}$ was measured by an inverse sequence of pulses using the free induction signal following the 90° pulse. The accuracy in the determination of the values of $T_{\parallel}$ and $T_{\perp}$ was not worse than 5%. The temperature was kept constant within ±1°. The viscosity was measured by an Ostwald viscosimeter.

$VOCl_2$. Figure 1 gives the experimental dependence of the values of $T_{\parallel}$, $T_{\perp}$, $T_{\parallel}N_S$, $T_{\perp}N_S$, and $T_{\parallel}/T_{\perp}$ on the concentration of paramagnetic atoms at a temperature of 295°K. A characteristic feature is that the values of $\ln T_{\parallel}$ and $\ln T_{\parallel}N_S$ decrease with increasing concentration up to $N_S = 6$ mole/liter, and then increase again, while $\ln T_{\perp}$ and $\ln T_{\perp}N_S$ decrease linearly up to $N_S = 1.43$ mole/liter; at the same time the ratio $T_{\parallel}/T_{\perp}$ remains constant and has the value 2.19. Starting at a concentration $N_S = 1.43$ mole/liter the value of $\ln T_{\perp}$ approaches $\ln T_{\parallel}$, $\ln T_{\perp}N_S$ begins to increase, while the ratio $T_{\parallel}/T_{\perp}$ decreases, reaching the limiting value of 1.11 at a concentration of $N_S = 4.3$ mole/liter, and then remains constant.

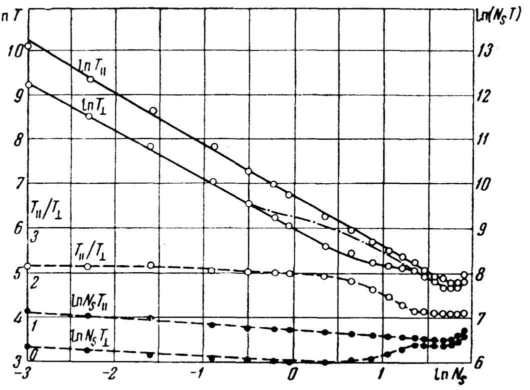

FIG. 1. The dependence of $T_{\parallel}$, $T_{\perp}$, $N_S T_{\parallel}$, $N_S T_{\perp}$, and $T_{\parallel}/T_{\perp}$ on the concentration of paramagnetic atoms N_S at a temperature of 295°K for $VOCl_2$ (both here and in subsequent figures T is expressed in μsec, and N_S in mole/liter). The points denote experimental values. The solid line for $T_{\parallel}$ is calculated in accordance with formulas (1), (6), and for $T_{\perp}$ in accordance with formulas (2), (7) in which A changes with concentration. The dash-dotted line is calculated for $T_{\perp}$ by means of formulas (2), (7), with constant A (in the region of low and high concentrations of N_S it coincides with the solid line).

The temperature dependence of $T_{\parallel}$ and $T_{\perp}$ at a concentration of $N_S = 0.1$ mole/liter is given in Fig. 2. Here, as the temperature increases from 24 to 100°C, the value of $\ln T_{\parallel}$ increases, while $\ln T_{\perp}$ decreases linearly. Figure 3 gives the temperature dependence of $T_{\parallel}$ and $T_{\perp}$ for a concentration of $N_S = 2.15$ mole/liter. As in the case of

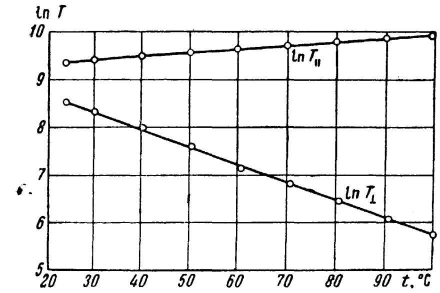

FIG. 2. The temperature dependence of $T_{\parallel}$ and $T_{\perp}$ for a paramagnetic atom concentration of $N_S = 0.1$ mole/liter ($VOCl_2$). The points denote experimental values, the solid lines calculated values.

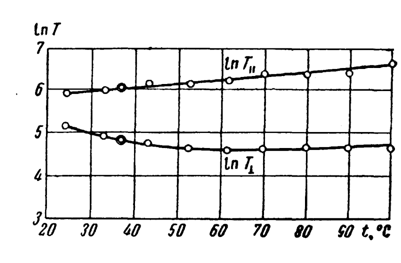

FIG. 3. The temperature dependence of $T_{\parallel}$ and $T_{\perp}$ for a paramagnetic atom concentration of $N_S = 2.15$ mole/liter ($VOCl_2$). ◎ are control points.

the concentration of 0.1 mole/liter, $\ln T_{\parallel}$ increases linearly, while $\ln T_{\perp}$ decreases as the temperature is increased up to 60°C, and then varies slowly showing a small increase. In order to exclude accidental irreversible processes as a result of heating, the samples were cooled down to room temperature after the high temperature measurements were made and the measurements were repeated. The agreement of the results obtained is satisfactory, and confirms the assumption that the measured temperature dependence of the relaxation time $T_{\parallel}$ and $T_{\perp}$ is reproducible.

$VOSO_4$. The experimental dependence of the values of $T_{\parallel}$, $T_{\perp}$, $N_S T_{\parallel}$, and $N_S T_{\perp}$ on the concentration of paramagnetic atoms at room temperature is shown in Fig. 4. Here $\ln T_{\parallel}$, $\ln T_{\perp}$, $\ln N_S T_{\parallel}$ and $\ln N_S T_{\perp}$ decrease linearly as the concentration is increased while the ratio $T_{\parallel}/T_{\perp}$ stays constant.

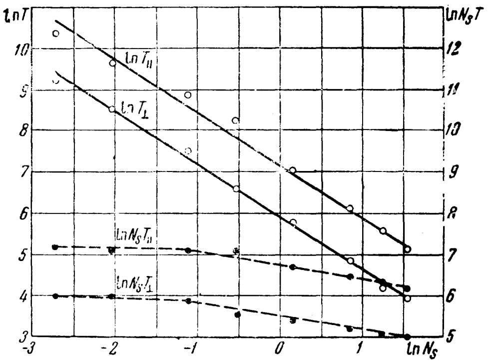

FIG. 4. Dependence of $T_{\parallel}$, $T_{\perp}$, $N_S T_{\parallel}$, $N_S T_{\perp}$ on the concentration of paramagnetic atoms (for $VOSO_4$).

DISCUSSION OF RESULTS

Formulas (1)—(9) contain a series of parameters, and this expresses the complex character of the phenomenon being studied. We give first of all the values of the parameters which can be determined most simply. The spin of the vanadyl ion is $S = 1/2$; the coordination number is $m = 5$; we shall take the distance between the center of the VO^{++} ion and the proton belonging to the molecule of water contained within the first coordination sphere to be equal to 2.7 Å. Further,

$$\gamma_I = 2.67 \cdot 10^4 \text{ rad sec}^{-1} \text{ Oe}^{-1}$$

$$\gamma_S = 1.76 \cdot 10^7 \text{ rad sec}^{-1} \text{ Oe}^{-1}$$

For the intensity of the external magnetic field H = 3843 Oe used in our work the values of the Larmor frequencies are equal to $\omega_I = 102.77 \times 10^6 \text{ sec}^{-1}$, $\omega_S = 6.769 \times 10^{10} \text{ sec}^{-1}$.

It is considerably more difficult to determine the values of the parameters appearing in $K_{\beta\alpha}^{-1}$. We shall evaluate here the characteristic times τ_1 and τ_e by means of formulas (4) and (5) taking the radius of the complex ion $[VO^{++}(H_2O)_5]$ to be equal to 3.36 Å. In (4) and (5) η is the viscosity of the liquid in the given particular state (concentration, temperature). Measurements of the viscosity of solutions studied by us were carried out specifically to determine τ_1 and τ_e. We have determined the dependence on the concentration of the electron relaxation times T_2 and T_1 from the results of measurements of line widths of electron resonance[6] and of the spin-lattice relaxation time[7] in solutions of VO^{++}. The dependence on the concentration of η, τ_1, τ_e, T_1, and T_2 is given in Table I.

A. The domain of low concentrations of paramagnetic atoms N_S: $\omega_e = 0$. For low concentrations (up to 1 mole/liter) there is as yet no exchange and we can set $\omega_e = 0$ in (3). Then τ_2 and $A/\hbar$ remain unknown in (1) and (2). In order to determine them we have one equation. Indeed, Eqs. (1) and (2) can be divided into contributions of the dipole-dipole and the contact hyperfine interactions (hfi) to the nuclear relaxation times $T_{\parallel}$, $T_{\perp}$:

$$1/T_{\parallel} = (1/T_{\parallel})_{\text{dip}} + (1/T_{\parallel})_{\text{hfi}}, \qquad (10)$$

$$1/T_{\perp} = (1/T_{\perp})_{\text{dip}} + (1/T_{\perp})_{\text{hfi}}. \qquad (11)$$

In these equations the dipole parts do not depend on τ_2 and $A/\hbar$ and, since $K_{01}^2 \omega_I^2 \ll 1$, it can be shown that

$$(T_{\parallel}/T_{\perp})_{\text{dip}} = 1.11. \qquad (12)$$

By combining relations (10)—(12) and neglecting the value of $(1/T_{\parallel})_{\text{hfi}}$ (since $K_{12}^2 \omega_S^2 \gg 1$) we obtain

$$\left(\frac{1}{T_{\perp}}\right)_{\text{hfi}} = \frac{1}{T_{\perp}} - \frac{1.11}{T_{\parallel}} = \frac{1}{3} S(S+1) \left(\frac{A}{\hbar}\right)^2 \frac{mN_S}{N_I} K_{02}. \qquad (13)$$

In this equation $A/\hbar$ and τ_2 are unknown. We have assumed that the parameter τ_2 (the lifetime of the proton (or of the water molecule) in the first coordination sphere of the VO^{++} ion) varies in accordance with the formula[8]

$$\tau_2 = \tau_2^0 \exp(V_2/RT) \qquad (14)$$

and we have estimated it from the temperature dependence of the quantities $T_{\parallel}^{-1}$ and $T_{\perp}^{-1}$ for a solution of concentration $N_S = 0.1$ mole/liter (Fig. 2). With increasing temperature the value of $T_{\perp}^{-1}$ and the contribution of the dipole part to $T_{\perp}^{-1}$ decrease, since the correlation time for the dipole-dipole interaction which determines the value of $K_{\beta,1}^{-1}$ de-

Table I

N_s, mole/liter	N_I mole/liter	η, cP	$10^{11}\tau_1$, sec	$10^{11}\tau_e$, sec	$10^8 T_1$, sec	$10^9 T_2$, sec	$10^6 A/h$, sec^{-1}	$10^{-10}\omega_e$, sec^{-1}
0.05	55,5	1	3,8	1,42	1	3	0.31	
0.1	55	1.05	4.02	1.5	1	3	0,31	
0.2	54.8	1.08	4.12	1,54	1	3	0.31	
0.4	54.2	1,13	4,31	1.61	1	3	0,31	
0.6	53,7	1.26	4.81	1.8	1	3	0.31	
0.8	53.2	1.43	5.43	2.03	1	3	0.33	
0.95	52.7	1.55	5.9	2,13	1	2	0.336	
1.43	51.8	2.05	7.77	2.91	1	1	0.57	1,03
1.91	50.4	2.71	10.3	3.86	0,98	0.5	2.34	1,25
2,39	49.4	3.53	13.4	5	0,95	0.3	2.6	1,35
2,87	48	4.9	18.6	6.9	0,92	0.2	7	1,85
3,35	46.6	6,6	25,1	9,4	0.9	0.25		1,92
3.83	46	9.01	34,1	12.8	0,85	0.28		2,037
4.3	44,6	11.8	45.6	17	0.78	0.38		2.16
4,79	43,3	17.35	66	25	0,65	0.48		2.28
5.27	42.4	20	91	34	0.5	0.55		2.38
5.74	40.9	36	137	51	0.3	0.8		2.5
6.24	39.9	56,5	215	80	0.15	0,95		5
6,72	38	93,5	355	133	0.11	1,1		8

Table II

T, °C	η, cP	$10^{11}\tau_1$, sec	$10^9 T_2$, sec	$10^8 T_1$, sec	$10^8 K_{02}$, sec	T, °C	η, cP	$10^{11}\tau_1$, sec	$10^9 T_2$, sec	$10^8 T_1$, sec	$10^8 K_{02}$, sec
24	1.05	4.01	3	1	1	70	0,466	1.77	3,85	11.7	11,7
30	0.916	3.49	3.1	1.84	1.84	80	0.405	1.55	4.03	17.3	17.3
40	0.75	2.85	3.3	3.18	3,18	90	0,36	1.38	4.21	25.7	25.7
50	0.628	2,39	3.48	5,04	5.04	100	0,324	1,24	4,4	36.4	36,4
60	0,54	2.05	3,66	8,01	8.01						

creases (T_1^{-1}, $T_2^{-1} \ll \tau_1^{-1}$, and τ_1^{-1} increases, while T_1^{-1} and T_2^{-1} decreases with increasing temperature (cf. Table II)).

Thus, the linear increase of $\ln T_\perp^{-1}$ observed as the solution is heated to a temperature of 100°C is explained by the contribution to $T_\perp^{-1}$ made by the hyperfine interaction (13) in which A does not depend on the temperature, while $K_{02}^{-1} = \tau_2^{-1} + T_1^{-1}$ decreases, this being due to an increase in the electron spin-lattice relaxation time T_1 as the temperature increases. Since in accordance with (14) τ_2^{-1} increases with increasing temperature, at the same time remaining smaller than T_1^{-1}, we can assume that at room temperature $\tau_2^{-1} \ll T_1^{-1}$, while $K_{02}^{-1} = T_1^{-1} = 10^8$ sec^{-1}. On substituting into (13) the value $K_{02}^{-1} = 10^8$ sec^{-1} and the experimentally found values $T_{\parallel} = 25.5$ μsec and $T_\perp = 11.6$ μsec for a solution of concentration $N_S = 0.05$ mole/liter, we obtain $A/h = 0.314 \times 10^6$ sec^{-1}.

By utilizing the obtained values of A/h and the temperature dependence of $T_\perp^{-1}$ (cf. Fig. 2) we can obtain the dependence of the electron spin-lattice relaxation time T_1 on the temperature and estimate the upper limit for τ_2^{-1}. (The experimentally obtained temperature dependence of T_1 is given in Table II.) We have determined the variation of T_2 with increasing temperature from the results of measurements of the dependence of the line width on the temperature[9]. At a temperature of 100°C we obtain the value $K_{02}^{-1} = 2.75 \times 10^6$ sec^{-1}, which gives for the upper limit $\tau_2^{-1} \leq 2.75 \times 10^6$ sec^{-1}. This agrees in order of magnitude with the values $\tau_2 = 10^{-4}$—10^{-8} sec obtained earlier for protons[8] and for O^{17} of water molecules[10] in solutions of certain elements of the first transition group.

Thus, for solutions of low concentration of paramagnetic atoms N_S, where there is no exchange, all parameters are determined. With the aid of these parameters we can explain the experimental values of $T_{\parallel}$ and $T_\perp$ for low concentrations of $VOCl_2$ up to $N_S = 1.43$ mole/liter, and for $VOSO_4$ up to maximum possible concentrations $N_S = 2.87$ mole/liter.

In accordance with formulas (1) and (2) as the concentration of paramagnetic atoms N_S increases the nuclear relaxation times $T_{\parallel}$ and $T_\perp$ become shorter. Moreover, we see from Table I that as the concentration of the paramagnetic atoms N_S increases, the viscosity of the solution η also increases and, as a consequence of this, so does the correlation time for the dipole-dipole interaction

τ_1. The electron spin-lattice relaxation time T_1 practically does not change, while the spin-spin relaxation time T_2 becomes somewhat shorter as a result of an increase in the dipole-dipole interaction between paramagnetic atoms; at the same time the inequality $T_1^{-1}, T_2^{-1} \ll \tau_1^{-1}$ is retained, and $K_{\beta,1}^{-1}$ is determined as before by the correlation time for the dipole-dipole interaction τ_1. This leads to an additional decrease in the nuclear relaxation times $T_{\parallel}$ and $T_{\perp}$ as a result of which $\ln N_S T_{\perp}$ and $\ln N_S T_{\parallel}$ decrease linearly as the concentration increases.

B. The domain of high concentrations of paramagnetic atoms N_S: $\omega_e \neq 0$, $\omega_e \tau_e > 1$. The exchange frequency ω_e remained an unknown parameter in formulas (1)—(9), and we determined it utilizing the experimental dependence of $T_{\parallel}$ on the concentration N_S. For the calculation of $T_{\parallel}$ either formula (1) (the region $\omega_e \tau_e < 1$, $N_S \leq 2.87$ mole/liter) or formula (6) (the region $\omega_e \tau_e > 1$, $N_S > 2.87$ mole/liter) was used. The values of ω_e so obtained are summarized in Table I. The calculated curve for $T_{\parallel}$ computed in accordance with formulas (1) and (6) is shown by the solid line in Fig. 1.

By utilizing the values of the parameters obtained from the interpretation of the behavior of $T_{\parallel}$ we have calculated the curve for $T_{\perp}$ in the region of high concentrations, and this is shown by the dash-dotted line in Fig. 1. As can be seen from the figure, $T_{\perp}$ does not agree with the experimental values in the intermediate region. Agreement of experimental and calculated values of $T_{\perp}$ is obtained if we assume that the constant A increases with increasing concentration starting with $N_S = 0.8$ mole/liter. (It is worth noting that this assumption does not destroy the agreement between the experimental and the calculated values of $T_{\parallel}$.) Without making this assumption it is also not possible to explain the temperature dependence of $T_{\parallel}$ and $T_{\perp}$ obtained by us for the concentration $N_S = 2.15$ mole/liter (Fig. 3). Here, as in the case of the solution of concentration $N_S = 0.1$ mole/liter, the value of $T_{\parallel}^{-1}$ is determined by the proton-ion dipole-dipole interaction, and $T_{\parallel}^{-1}$ decreases as the temperature increases. In the case of the hyperfine interaction we have for $T_{\perp}^{-1}$ the relation

$$K_{02}^{-1} = \tau_2^{-1} + T_1^{-1} + \tau_e \omega_e^2 = 10^7 + 10^8 + 8 \cdot 10^9 \ \text{sec}^{-1}$$

It will be determined by the exchange frequency which decreases the contribution of the hyperfine interaction by one or two orders of magnitude. As a result of this, if we take A to remain unchanged, then $T_{\perp}^{-1}$ must also be determined by the dipole-dipole interaction and $T_{\perp}^{-1}$ must decrease with increasing temperature. However, experiment yields an increase of $T_{\perp}^{-1}$ with increasing temperature up to 60°C, and this can be explained in terms of the hyperfine interaction which for somewhat larger values of A will under these conditions also give an appreciable contribution to $T_{\perp}^{-1}$. The value of K_{02}^{-1} depends on τ_2 which can vary with increasing concentration, and which can be dominant in the hyperfine interaction; however, the temperature dependence of τ_2 (14) is such that $T_{\perp}^{-1}$ must decrease if we assume that K_{02}^{-1} is determined by the characteristic time τ_2 contrary to the observed increase in $T_{\perp}^{-1}$. Therefore, the dependence of τ_2 on concentration is not apparent in our experiment.

At the present time it is hardly possible to indicate definitely the physical reason for the increase postulated by us in the hyperfine interaction constant A with increasing concentration of the solution. A possible cause of this effect could be the dependence of A on the electric field characteristic of systems which do not have an inversion center. Bloembergen[11] has shown that the value of A increases linearly as the electric field intensity increases. Since the internal fields in an electrolyte increase with increasing concentration, this must be accompanied by an increase in A. In order to elucidate this problem a special investigation will be required.

Starting with a concentration $N_S = 4.79$ mole/liter, the values of both $T_{\perp}$ and $T_{\parallel}$ are determined only by the dipole-dipole interaction, since the contribution made by the hyperfine interaction to $T_{\perp}$ decreases rapidly with increasing ω_e. The experimentally obtained ratio $T_{\parallel}/T_{\perp} = 1.11$ corresponds to the value expected under the condition that relaxation occurs through the dipole-dipole coupling. For concentrations higher than 5.74 mole/liter the exchange frequency increases very rapidly, and, therefore, a further increase in the concentration leads to a decrease in $T_{\parallel}^{-1}$ and $T_{\perp}^{-1}$. The beginning of the decrease in $T_{\parallel}^{-1}$ and $T_{\perp}^{-1}$ with increasing concentration corresponds to a sharp exchange narrowing of the electron paramagnetic resonance line, with the latter assuming the Lorentz shape[6].

We now proceed to discuss the frequency ω_e characterizing the exchange interaction between paramagnetic atoms. According to a theoretical evaluation[1,2] the value of ω_e^2 must increase proportionately to the concentration of paramagnetic atoms N_S. The experimental values of ω_e^2 obtained by us agree with this expectation up to a concentration $N_S = 5.74$ mole/liter. However, at high concentrations ω_e^2 increases nonlinearly.

It can be assumed that electrostatic repulsion plays quite an important role in the exchange interaction between paramagnetic complex ions. Indeed, the radius of the sphere associated with a single ion, $R = (3/4\pi N_S)^{1/3}$, becomes of the order of the radius of the complex ion a at a concentration $N_S \approx 6$ mole/liter. In this case the complex ions are in direct contact, and this leads to a nonlinear increase in ω_e^2. In order to understand the effect of electrostatic interaction and of the type of anion on the exchange interaction we have studied the dependence on the concentration of $T_{\parallel}$ and $T_{\perp}$ in the case of $VOSO_4$ (Fig. 4). A comparison of these results with the results for $VOCl_2$ (Fig. 1) shows that $\ln N_S T_{\perp}$ falls off linearly up to $N_S = 2.87$ mole/liter, while in the case of $VOCl_2$ the value of $\ln N_S T_{\perp}$ increases starting with a concentration $N_S = 1.43$ mole/liter, as a result of the effect of exchange on the hyperfine interaction. If we admit the possibility of the inclusion of the anion into the complex cation, then Cl^- decreases the charge of the complex ion, being more electronegative than SO_4^{--} (the density of the electron cloud of SO_4^{--} is not great, and the electrostatic interaction of Coulomb type with the cation is weaker). In this case the probability of close approach of cations is increased. On the other hand, the SO_4^{--} anion is considerably larger than Cl^- and, being hydrated, represents a large complex ion which prevents the close approach of cations.

The results of analyzing the experiment with the aid of the theory of [1,2] show that the concepts which serve as the foundation of that theory describe fairly well the processes occurring in paramagnetic media both for low and for high concentrations of paramagnetic atoms. At the same time the possibility is demonstrated of determining from nuclear magnetic resonance experiments the dependence on the concentration and on the temperature of the electron relaxation times T_1 and T_2, the exchange frequency and the correlation time for the exchange interaction, the hyperfine interaction parameter A and other parameters. It should also be noted that the exchange interaction between paramagnetic atoms begins to affect the values of $T_{\parallel}$ and $T_{\perp}$ already at a concentration $N_S = 1.43$ mole/liter (in the case of VO^{++}), while in an experiment on electron paramagnetic resonance in this concentration range the exchange interaction is not yet apparent[6].

In conclusion it should be noted that in highly concentrated solutions another aspect of the complexity of the phenomenon studied is that effects of "multinuclear complex compounds," of changes in the activity of the solution, of the solute, etc., can become apparent. All these problems require further detailed study.

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