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Abstract

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PARAMAGNETIC RELAXATION IN CONCENTRATED AQUEOUS SOLUTIONS OF $(VO)^{2+}$

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In works ([1,2]), carried out by the EPR method, significant exchange interactions between VO^{2+} ions in concentrated solutions of salts of this ion were established. The authors of work ([2]) showed that the line width in a 6-molar solution of $VOCl_2$ depends only very weakly on temperature. This agrees with Timerev' s theory of paramagnetic relaxation ([3]) in liquid systems with strong exchange, which is a further development of works ([4,5]). For a quantitative test of this theory, measurement of the paramagnetic relaxation times ρ_S and ρ_L is of great interest. Since in electrolyte solutions the saturation method ([6]) encounters almost insurmountable difficulties, we undertook a study of the relaxation characteristics by the method of paramagnetic absorption in parallel fields ([7,8]).

In Timerev' s work ([3]), formulas were obtained for the longitudinal and transverse relaxation times T_1 and T_2 in solutions both for very strong exchange interaction and for the case when the energy of the exchange interaction itself is modulated by thermal motion with a certain characteristic time τ_1. When the condition of strong exchange, $\omega_e^2\tau_c^2 \gg 1$ (where ω_e is the exchange-interaction frequency, and τ_c is the characteristic correlation time of thermal Brownian motion), is fulfilled, the longitudinal time can be expressed as

$$1/T_1 = \sqrt{\frac{\pi}{2}}\frac{\sigma^2}{\omega_e}\left[\frac{2}{5}e^{\omega_0^2/2\omega_e^2} + \frac{8}{5}e^{2\omega_0^2/\omega_e^2}\right]. \tag{1}$$

With simultaneous allowance for exchange and motion,

$$1/T_1 = \sigma^2 K\left[\frac{2}{5}\frac{1}{1+\omega_0^2k^2} + \frac{8}{5}\frac{1}{1+4\omega_0^2k^2}\right]. \tag{2}$$

Here $K = \dfrac{\tau_c}{1+\tau_c\tau_1\omega_c^2}$; $\sigma^2 = g^4\beta^4\hbar^{-2}S(S+1)\sum\langle r_{ke}^{-6}\rangle$; $\omega_0 = g\beta H_0\hbar^{-1}$; $\tau_1 \leqslant \tau_c$.

For the measurements, aqueous solutions of vanadyl chloride $VOCl_2$ and vanadyl sulfate $VOSO_4$ were chosen in the concentration range from 2 mol/l to 6.5 mol/l. To prevent hydrolysis, all samples contained 0.1 mole of hydrochloric acid per liter. Vanadyl sulfate dissolves in water much less readily than the chloride (the limiting solubility for the sulfate is approximately 3-3.5 mol/l). Therefore data for the sulfate are absent at higher concentrations. The relaxation times

calculated for $VOSO_4$ solutions of concentrations 3 mol/l and 2 mol/l do not differ greatly from ρ_L and ρ_S for the same concentrations. However, this difference lies outside the experimental errors and corresponds to expectation: by the NMR method ([9]) and EPR method ([10]) it was shown that exchange in $VOSO_4$ solutions is weaker than in $VOCl_2$ solutions.

Measurements of paramagnetic absorption were carried out by the Q-meter method ([7]). Absorption curves were recorded as a function of the strength of the constant field H at four frequencies: 12, 22, 34, and 44 MHz. The spin-lattice relaxation times were determined from measurements of χ'' at two frequencies, assuming the validity of the Casimir–du Pré equation with a correction for spin-spin absorption according to Shaposhnikov ([7,8]).

Table 1 gives data on the spin-lattice relaxation times ρ_L as a function of the strength of the constant field H_0 in the range of concentrations studied. From the data of Table 1 it is seen that ρ_L increases strongly upon dilution. Thus, for $H_0 = 3600$ Oe, the spin-lattice re-

relaxation upon dilution from 2 mol/l to 6.5 mol/l changed by approximately a factor of 6. (The value of the constant-field strength $H_0 = 3600$ Oe was not chosen at random, but because it approximately corresponds to the resonance field at which the measurements by the EPR method were made ([2]).)

It should be noted that upon dilution from 6.5 mol/l to $\sim$ 4–5 mol/l the growth of ρ_L is much slower than upon further decrease in concentration. Such a dependence of the spin-lattice relaxation time on the concentration of vanadyl ions in solution corresponds to the presence of strong exchange interactions in the concentration region from 6.5 to approximately 4 mol/l and to their sharp weakening upon further dilution.

Table 1

$\rho_L \cdot 10^8$ (sec.)

C, mol/l	H_0						
C, mol/l	1200	2000	2800	3600	4400	5200	5600
2	3.3	4.5	7.3	12			
3	2.2	3.2	4.6	5.4	7.8	10.4	11.8
4	1.6	2.2	3.0	3.8	4.8	5.8	6.5
4.5	1.3	1.9	2.5	3.2	3.9	4.7	5.1
5	1.5	1.9	2.2	2.8	3.3	3.6	3.9
5.5	1.3	1.8	2.1	2.5	2.8	3.1	3.9
6	1.2	1.7	2.0	2.3	2.6	2.9	3.2
6.5	1.5	1.7	2.0	2.1	2.2	2.6	2.7

From the data of Table 1 one can also see the dependence of ρ_L on the strength of

the constant field H_0. For high concentrations it is very weak. At $C = 3$ mol/l and $C = 2$ mol/l the dependence $\rho_L(H_0)$ already becomes rather significant. This agrees with expectation. From formula (1) it is evident that, under strong exchange, when the frequency of exchange interaction is $\omega_e \simeq 10^{11}$ sec.$^{-1}$ ([2]), the field dependence for $\omega_0 \ll \omega_e$ cannot be significant. The increase in the dependence $\rho_L(H_0)$ at lower concentrations confirms the weakening of exchange interactions upon dilution, as discussed above.

To clarify the temperature dependence of the spin-lattice relaxation time, measurements were carried out on $VOCl_2$ solutions of concentrations 6.5, 6, 4, and 3 mol/l in the temperature range from 278° to 368° K. It turned out that ρ_L at 6.5 and 6 mol/l is independent of temperature within the experimental error. This fact is in complete agreement with formula (1); it is also indirectly confirmed by measurements of EPR line widths at different temperatures ([2]).

Using our spin-lattice relaxation times for $C = 6.5$ mol/l, we estimated the frequency of exchange interaction by means of formula (1). It proved to be equal to $3 \cdot 10^{11}$ sec.$^{-1}$.

If for the correlation time of thermal motion one adopts, as is usually done, the expression

$$\tau_c \leq \frac{4}{3}\frac{\pi a^3 \eta}{kT},$$

where $a = 2.8 \cdot 10^{-8}$ cm ([11]), and η are the values of the viscosity coefficient measured by us over the temperature interval, then we obtain that the condition of strong exchange $\omega_e^2 \tau_c^2 \gg 1$ is fulfilled throughout the entire temperature region at $\omega_e = 3 \cdot 10^{11}$ sec.$^{-1}$.

At a vanadyl-ion concentration of 4 mol/l, a very weak dependence of ρ_L on temperature begins to be observed; at $C = 3$ mol/l the temperature dependence becomes much stronger. Figure 1 gives a plot of the dependence $\rho_L(T^\circ \text{ K})$ at field strength $H_0 = 3600$ Oe for the concentrations studied. From the figure it is evident that ρ_L for $C = 3$ mol/l at first decreases; then, beginning at $T \sim 343^\circ$ K, the decrease slows down, and upon further heating ρ_L depends only slightly on temperature. Such behavior of the spin-lattice relaxation time with temperature could be explained in the following way. As noted above, in the case when exchange is no longer strong enough to completely "erase" the thermal motion, the energy of exchange interaction itself is modulated by thermal motion with a time $\tau_1 \leq \tau_c$. The temperature dependence enters into T_1 (see formula 2) through

$$K = \frac{\tau_c}{1 + \tau_c \tau_1 \omega_e^2},$$

but at sufficiently strong

···in exchange one may put $\tau_c\tau_1\omega_e^2 \gg 1$*, so that $K = 1/\tau_1\omega_e^2$. For $H_0 = 3600$ Oe, $T = 293^\circ$ K, $\omega_e \sim 10^{11}$ s^{-1}, we have $\omega_0^2K^2 \simeq 4\cdot10^{-3}$, i.e., the condition $\omega_0^2K^2 \ll 1$ is satisfied; therefore $T_1 = 1/2\sigma^2K$. Thus, an increase in temperature should lead to a shortening of the spin-lattice relaxation time, which is also observed experimentally. But with increasing temperature the relative effectiveness of exchange decreases and thermal motion begins to play an ever greater role. At $T > 333^\circ$ K the condition $\tau_c\tau_1\omega_e^2 \gg 1$ is violated, and as heating is continued $\tau_1\tau_c\omega_e^2$ approaches 1, but does not become smaller than it in the temperature range studied by us up to 368° K (see Fig. 1). Thus, the dependence of ρ_L on temperature for the three-molar solution is also explained by Timerov' s theory ([3]).

Fig. 1

The situation is more complicated with the dependence of ρ_L on the field. At $C = 3$ mol/l this dependence is already quite significant. Meanwhile, it follows from ([3]) that if $T_1 = 1/2\sigma^2K$, the field strength should not affect the value of ρ_L. The matter is evidently that, for this concentration, the relaxation time is determined not only by exchange but also by mechanisms associated with thermal motion ([12], [13]), and these mechanisms should lead to a dependence of ρ_L on the field.

Let us now turn to the results obtained for the spin-spin relaxation time ρ_S. The method for determining this time is set forth in ([8]). Previously, in ([14]), ρ_S was found for aqueous solutions of $VOSO_4$ in the concentration range from 0.5 to 3 mol/l. It turned out that at low concentrations, when there is no exchange, the spin-spin relaxation time is determined by dipole-dipole interactions and is described by the Bloembergen formula ([15]).

Measurements of concentrated vanadyl chloride solutions carried out in the present work showed that with increasing concentration, beginning at 3 mol/l, ρ_S increases slowly ($\rho_S = 1.2\cdot10^{-9}$ s at $C = 3$ mol/l and $\rho_S = 3.3\cdot10^{-9}$ s at $C = 6.5$ mol/l). This behavior of the dependence $\rho_S(C,$ mol/l) is in qualitative agreement with the theory of Kubo and Tomita ([4]) for the transverse relaxation time T_2 in systems with strong exchange.

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* For $C = 3$ mol/l in the temperature range (278-333° K) this condition is satisfied, since $\omega_e \sim f(C \text{ mol/l})$ and, upon dilution by about a factor of two, it still remains high.

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