G. P. VISHNEVSKAYA, P. G. TISHKOV

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Abstract

Full Text

G. P. VISHNEVSKAYA, P. G. TISHKOV

PARAMAGNETIC RELAXATION IN SOLUTIONS OF VANADYL SALTS

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In papers ([1], [2]) results were reported from studies of the relaxation parameters of aqueous solutions of vanadyl salts as a function of the concentration of VO^{2+} ions and the temperature of the samples studied. In the present work, using the method proposed in ([3]), the spin-lattice and spin-spin relaxation times ρ_L and ρ_S were determined for aqueous vanadyl solutions with different acid contents, as well as with additions of glycerin to the sample; measurements were also carried out in powders of $\mathrm{VOCl_2 \cdot 5H_2O}$ and $\mathrm{VOSO_4 \cdot 3H_2O}$.

1. Hausser and Laukien ([4]) noted that, as the acidity of dilute solutions of vanadyl salts is increased, the proton transverse relaxation time T_2 is shortened manyfold. This phenomenon was studied in detail by A. I. Rivkind ([5]). In particular, it was established that the observed effect is inherent only in vanadyl salts and that, in concentrated solutions, an increase in acidity does not affect the proton relaxation time, but causes narrowing of the EPR line ([6]). It was of interest to test the action of acidity directly on the times of spin-lattice and spin-spin electron relaxation.

Fig. 1. Dependence of the spin-lattice relaxation time on the acid concentration in the solution: **1** $-C_{\mathrm{VO}^{2+}} = 3$ mol/l; **2** $-C_{\mathrm{VO}^{2+}} = 4$ mol/l.

For the measurements, solutions of vanadyl chloride were chosen with VO^{2+} ion concentrations of 0.5 mol/l, 2 mol/l, 3 mol/l, 4 mol/l, and 6 mol/l. The 3 M and 4 M vanadyl solutions were studied in greatest detail. Their acidity was varied over wide limits. Fig. 1 gives the dependence of the spin-lattice relaxation time ρ_L for two concentrations of $\mathrm{VOCl_2}$ ($C_1 = 3$ mol/l and $C_2 = 4$ mol/l) when the HCl content in the solution is increased to 6.5 N and 4 N, respectively. It turned out that, at HCl concentrations below ~ 1 N, within the experimental error ρ_L does not depend on acidity. With a further increase in acid concentration, ρ_L falls rather sharply, reaching a value of $\sim 3 \cdot 10^{-8}$ sec. for both solutions at $H_0 = 3600$ oersted (this value of the spin-lattice relaxation time corresponds to a VO^{2+} concentration in solution with $N_{HCl} = 0.1 \sim 4.5 \div 5$ mol/l (^{2})). In a highly concentrated vanadyl solution ($C = 6$ mol/l), shortening of ρ_L begins upon addition of an even smaller amount of acid. Thus, when the acidity of the solution reaches slightly more than 0.1 N, ρ_L begins to shorten from a value of $2.3 \cdot 10^{-8}$ sec. to a value of $1.8 \cdot 10^{-8}$ sec. at an HCl normality equal to 1. In a two-molar solution of vanadyl chloride, it was possible to bring the HCl concentration up to 8.3 N. This caused a shortening of ρ_L at $H_0 = 3600$ oersted by approximately a factor of 2.5. Measurements were also made at a VO^{2+} concentration of 0.5 mol/l. At this dilution, exchange in the solution is already completely absent, but, by increasing the acidity to eleven-normal, we were able to produce a small ($\sim 300\%$) shortening of the spin-lattice relaxation time.

Especially characteristic is the temperature dependence of ρ_L, which we studied for a concentration of VO^{2+} ions of 3 mol/l. The temperature measurements were carried out in the interval from 278° to 368° K. It turned out that if, in a trimolar vanadyl solution containing 0.1 N HCl to prevent hydrolysis, ρ_L depends rather strongly on temperature (^{2}), then in the same vanadyl solution but with an HCl content of 6.5 N, the spin-lattice relaxation time, within the experimental error, does not depend on temperature, which corresponds to the behavior of systems with strong exchange (^{7}).

The experimental data also make it possible to calculate the spin-spin relaxation times ρ_S (^{8}) for solutions of different acidity. It was found that in a 3 M vanadyl solution, ρ_S increases somewhat as the acidity of the solution is raised (from $1.2 \cdot 10^{-9}$ sec at $C_{HCl} = 0.1$ N to $3.3 \cdot 10^{-9}$ sec at $C_{HCl} = 6.5$ N). The spin-spin relaxation time behaves in a completely analogous way when the concentration of VO^{2+} ions is changed from 3 mol/l to 6.5 mol/l (^{2}).

Thus, our experimental data directly indicate that a solution with a high acid content, in relation to a slightly acidified equimolar vanadyl solution, behaves like a more concentrated one; i.e., an increase in the acidity of the solution strengthens exchange interactions between the electron spins of VO^{2+}. Our relaxation data are in good agreement with the ESR-spectral experiment (^{6}) and confirm A. I. Rivkind' s suggestion that in an acidic medium the process of formation of hydrogen complexes of vanadyl,

$$VO^{2+} + H^+ \rightleftarrows [VO \cdot H]^{3+},$$

becomes significant. In such a complex, owing to the polarizing action of the proton, the multiple covalent bond of vanadium with its oxygen is diminished. It is quite natural that weakening of the $V = O$ bond inside the complex will increase the probability of the occurrence of exchange between vanadyl ions when two or more particles approach one another.

When strong exchange is present in solution ($C_{VO^{2+}} > 4$ mol/l), the introduction of a comparatively small amount of acid is already sufficient to strengthen the covalent bond between particles. At lower vanadyl concentrations, when exchange is weak (2 mol/l) or absent altogether (0.5 mol/l), and, consequently, the presence in solution of associates formed by VO^{2+} ions (^{6}) is already unlikely, slight exchange arises only at high acidity of the solution. Indeed, in this case a high acid content is necessary for the formation of as large as possible a number of hydrogen complexes $[VO \cdot H]^{3+}$, since at low concentrations exchange interactions can apparently be established only as a result of collisions (analogously to the Teich–Tatl mechanism (^{9})) of such complexes with weakened multiple bonds.

It cannot be left unmentioned, however, that with the indicated interpretation one question remains open: why does the change in the $V = O$ bond in the process of proton attachment not cause a lengthening of the spin-lattice relaxation time in dilute vanadyl solutions? Apparently, to clarify this question, additional theoretical calculations and optical measurements are necessary.

2. The spin-lattice relaxation times ρ_L were also determined for aqueous-glycerol solutions of vanadyl. For the measurements, $VOCl_2$ solutions with concentrations of 3 and 4 mol/l were chosen. The solution with the maximum glycerol content was prepared by diluting a 6.5 M aqueous solution of $VOCl_2$ with distilled glycerol of analytical grade to VO^{2+} concentrations of 3 mol/l and 4 mol/l, respectively. Solutions with glycerol contents of 75, 50, and 25% of the maximum, as well as aqueous solutions, were also prepared. It turned out that when the glycerol concentration is changed from zero (aqueous solution) to the maximum possible, the spin-lattice relaxation times gradually increase; thus, for a concentration of VO^{2+} ions of 3 mol/l at $H_0 = 3600$ oersted, $\rho_L = 5.4 \cdot 10^{-8}$ sec for the aqueous solution and $\rho_L = 10.2 \cdot 10^{-8}$ sec at the maximum possible glycerol concentration.

The measurements were also carried out in aqueous and glycerol solutions of vanadyl sulfate ($VOSO_4 \cdot 3H_2O$) with a concentration of about 1.5 mol/l. The relaxation times in the glycerol solution differed very little from the corresponding times in the aqueous solution.

For solutions with the maximum glycerol content, the measurements were carried out in the temperature interval from 295° to 368° K. Table 1 gives data on the relaxation times as a function of temperature for purely aqueous solutions and for solutions with the maximum glycerol content at $C_{VO^{2+}} = 3$ mol/l and $C_{VO^{2+}} = 4$ mol/l.

Table 1

Value of $\rho_L \cdot 10^{8}$ (sec.) for aqueous and aqueous-glycerol solutions at various temperatures. $H_0 = 3600$ oersted.

C, mol/l	295° K	314° K	333° K	353° K	368° K
3 aqueous	5.3	4.6	4.3	4.05	4
3 aqueous-glycerol	10.2	8.9	7.6	6.3	5.4
4 aqueous	3.6	3.5	3.4	3.3	3.3
4 aqueous-glycerol	5.6	4.8	4.1	4	

It turned out that ρ_L in aqueous-glycerol solutions changes with temperature more strongly than in purely aqueous ones. Thus, at $C = 4$ mol/l in an aqueous solution, the spin-lattice relaxation times, as a result of fairly considerable exchange, practically do not depend on temperature; upon the addition of glycerol, however, the times lengthen and a noticeable dependence $\rho_L(T)$ appears. Probably, when glycerol is added to the solution, mixed solvation shells are formed, containing both glycerol and water (10). An increase in the size of the paramagnetic complex leads to a weakening of exchange interactions and, accordingly, to an increase in ρ_L. In addition, for intermediate concentrations, where exchange is not sufficiently strong, ρ_L, through the correlation time of thermal motion τ_c, will also depend on the viscosity of the solution and will increase with increasing τ_c. The more rapid change of ρ_L with temperature for aqueous-glycerol solutions is due, as it seems to us, to the fact that the viscosity of glycerol relative to the viscosity of water changes more strongly with temperature. Attention should also be drawn to the fact that, when the viscosity changes by more than a factor of 60 (thus, for $C = 3$ mol/l, $\eta_{\text{aq. sol.}} = 11$ centipoise and $\eta_{\text{aqueous-glyc.}} = 670$ centipoise), the relaxation times both for one-and-a-half-molar and for three-molar solutions changed only very insignificantly (by no more than a factor of 2). Apparently, it should be assumed that the correlation time of thermal motion τ_c, in the case of vanadyl as well, is connected not with the macroscopic viscosity of the solution as a whole, but is determined by intermolecular forces at the boundary between the paramagnetic complex and the solvent, as was shown for solutions of Mn^{2+} (10) and Cr^{3+} (11).

In work (1) it was noted that the spin-lattice relaxation times ρ_L for solid vanadyl sulfate $VOSO_4 \cdot 3H_2O$ and its concentrated solutions approximately coincide. Two possible reasons for such equality were indicated: an accidental coincidence of the spin-lattice relaxation times as a result of stronger exchange in the solid phase, and a second reason connected with the molecular nature of the VO^{2+} ion itself; namely, the suggestion was made that one of the sources of orbital-lattice interactions could be the intrinsic vibrations of the molecular ion itself.

In the present work we carried out a more detailed study not only of solid vanadyl sulfate, but also of $VOCl_2 \cdot 5H_2O$ powder. Solid vanadyl chloride was prepared by drying a 6.5-aqueous solution in a desiccator over sulfuric acid.

Temperature measurements in $VOSO_4 \cdot 3H_2O$ powder showed that the spin-lattice relaxation time ρ_L in the temperature range from 293 to 268° K, within the experimental error, does not depend on temperature, whereas in a solution with the greatest possible concentration ($\sim$ 3 mol/l) a noticeable dependence $\rho_L(T)$ is observed. The independence of ρ_L from temperature in $VOSO_4 \cdot 3H_2O$ powder indicates stronger exchange in the solid phase. Passing

In measurements on powdered $VOCl_2 \cdot 5H_2O$, we observed that the paramagnetic absorption is independent of the strength of the constant static field H_0 in parallel fields, whereas in perpendicular fields an absorption curve is recorded that has a Lorentzian form with a line width at a frequency of 44 MHz of $\Delta H \simeq 80$ Oe. This fact is usual for systems with very strong exchange, when ρ_L and ρ_S become equal (12). Estimating the relaxation time from the width for $VOCl_2 \cdot 5H_2O$ gives $\rho_L = \rho_S = 4.4 \cdot 10^{-9}$ sec. For solid vanadyl sulfate the exchange, though strong (ρ_L no longer depends on temperature), is nevertheless weaker than in the chloride (the spin-lattice relaxation time for vanadyl sulfate at $H = 0$ is $\rho_0 = 1.9 \cdot 10^{-8}$ sec., and the spin-spin relaxation time is $\rho_S = 3 \cdot 10^{-9}$ sec.). Thus, on the basis of all that has been said above, we come to the conclusion that the equality of the spin-lattice relaxation times for the solid and liquid phases in vanadyl sulfate is accidental and is due to the stronger exchange in solid vanadyl sulfate.

In conclusion, we take this opportunity to express our sincere gratitude to B. M. Kozyrev for guidance and constant assistance in the work.

Physico-Technical Institute
of the Kazan Branch of the Academy of Sciences of the USSR

Kazan Chemical-Technological
Institute

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