NUCLEAR RELAXATION IN SOLUTIONS OF VANADYL SALTS. FORMATION OF HYDROGEN COMPLEXES $\mathrm{VO}\cdot\mathrm{H}^{

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NUCLEAR RELAXATION IN SOLUTIONS OF VANADYL SALTS. FORMATION OF HYDROGEN COMPLEXES $VO \cdot H^{3+}$

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In our work (^{1}), for aqueous solutions of $VOSO_4$ we obtained a value of the ratio of the "longitudinal" (T_1) to the "transverse" (T_2) relaxation time of the protons of the solvent (water) equal to ~ 16.5. However, later other authors (^{2}) found, for aqueous solutions of this same salt, T_1/T_2 equal to only 2.2. Comparison of the results led to the supposition that the cause of the discrepancy might be the different acidity of the solutions studied (^{2})*. Subsequent measurements (^{3}) confirmed the existence of a strong influence of acidity on proton relaxation in solutions of vanadyl salts. In detail, however, this somewhat unexpected effect has not been studied by anyone, and its nature has remained unexplained.

The aim of the present work was a further, more complete investigation of the influence of acidity on nuclear relaxation in solutions of vanadyl salts. The measurements were carried out by the nuclear spin-echo method, at an oscillating magnetic-field frequency of 18.1 MHz and at room temperature. The values of the relaxation times T_2 were obtained by means of a 90—180° sequence of radio-frequency pulses (^{4}); the opposite, 180—90° pulse sequence was used to determine the relaxation times T_1 (the "null" method (^{5})). The principal measurement results are presented in Fig. 1, which shows the dependence on acidity of the proton relaxation times T_1, T_2 and of their ratio T_1/T_2 for 0.02 M solutions of $VOSO_4$. The acidity of the solutions was varied over wide limits by addition of up to 10 N HNO_3 (Fig. 1A), up to 5.5 N $HClO_4$ (Fig. 1), up to 35.2 N H_2SO_4 (Fig. 1), and 0.7 mole of $H_2C_2O_4$ (Fig. 1). Without yet considering the region of high H_2SO_4 concentrations, one may conclude that, from the qualitative point of view, the action of all the acids used is approximately the same: with a comparatively small change in the time T_1, the time T_2 is sharply shortened, as a result of which the ratio T_1/T_2 increases strongly, reaching, for example, for a solution in 10 N HNO_3 the unusually high value $T_1/T_2 = 81.5$, whereas without addition of acid this ratio is only ~ 2.5 (Fig. 1). It is true that, in contrast to the other acids, oxalic acid causes not a shortening but a lengthening of T_1 (Fig. 1), but this is unambiguously explained by the additional process occurring in this case—the formation of vanadyl complexes with $C_2O_4^{2-}$ ions ($^{6-8}$).

Fig. 1. Change in relaxation parameters of protons of 0.02 M aqueous solutions of VOSO4 as a result of acid addition: A—nitric and 0.7 mol oxalic; —hydrochloric; —sulfuric. 1—T1; 2—T2; 3—T1/T2; a—T1, —T2, —T1/T2 for a solution containing oxalic acid, T1, T2 (msec.)

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The sharp increase in the ratio T_1/T_2 indicates that, with increasing acid content, the time of the electronic paramagnetic relaxation of VO^{2+} ions is lengthened. The connection between the relaxation of electron and nuclear spins in paramagnetic solutions, as a result of which, for sufficiently long electronic paramagnetic relaxation times τ_s ($\gtrsim 10^{-8} \div 10^{-9}$ sec), the ratio of nuclear relaxation times (T_1/T_2) proves to be much greater than unity, was established in work (^{1}). At present, the existence of such a connection is generally recognized (see, for example, (^{9})).

The tetravalent vanadium ion is in the ^2D ground state. In a cubic electric field the lower orbital level is a triplet. As shown by Van Vleck' s calculations (^{10}), carried out for salts of trivalent titanium, whose ions have the same system of energy levels as V^{4+}, the time of electron paramagnetic relaxation τ_s in the case under consideration is proportional to the sixth power of the splitting of the orbital triplet ($\tau_s \sim \Delta^6$).* But a cubic field cannot remove the orbital degeneracy of the lower level; fields of lower symmetry are required for this. In the VO^{2+} ion, a field of low (axial) symmetry is created by the bonding electrons with the oxygen atoms. Therefore the electron paramagnetic relaxation time of vanadium, τ_s, should be a sensitive indicator of changes in the character of the $V = O$ bond. There is every reason to suppose that the increase in the ratio T_1/T_2 and in τ_s discussed here is the result precisely of such changes. Apparently, with increasing proton concentration, the process of formation of hydrogen complexes of vanadyl becomes significant:

Fig. 1. Change in the relaxation parameters of protons of $0.02\,M$ aqueous $VOSO_4$ solutions as a result of the introduction of acids: **A**—nitric and 0.7 mol oxalic; —hydrochloric; —sulfuric. 1—T_1; 2—T_2; 3—T_1/T_2; a—T_1, —T_2, —T_1/T_2 for a solution containing oxalic acid, T_1, T_2 (msec.).

$$VO^{2+} + H^+ \rightleftarrows VO \cdot H^{3+}. \tag{1}$$

Capture of a proton by the oxygen of vanadyl should lead to partial dissociation of the $V = O$ bond and, probably, as often occurs when bond order is lowered (^{12}), to an increase in the degree of its covalency. As a result, the bonding

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* To prevent hydrolysis we worked with acidic solutions.

electrons, being shifted toward the vanadium atom, will cause an increase in the splitting of the lower triplet (Δ), and consequently an increase in τ_s and in the ratio T_1/T_2.

The foregoing is well confirmed by the measurement results. We shall proceed from the T_1/T_2 curves as directly characterizing the course of the protolytic process of equation (1). Assuming additivity of the reciprocal relaxation times of protons produced by the paramagnetic ions VO^{2+} and $VO \cdot H^{3+}$, from the measured T_1/T_2 data it is not difficult to estimate the instability constants (K) of the $VO \cdot H^{3+}$ complexes:

$$K = \frac{[VO^{2+}][H^+]}{[VO \cdot H^{3+}]}. \tag{2}$$

The method of calculation has been discussed for a large number of examples in works ([7,8]). It turned out that the instability constants of the hydrogen complexes $VO \cdot H^{3+}$

* Although the theory ([10]) pertains directly to solid layers, here, as in ([11]), it is used for a qualitative interpretation of the results of measurements in solutions.

depend strongly on the acid chosen as the source of protons. The following series of approximate values was obtained:

$$\begin{array}{ccccccc} H_2C_2O_4 & > & H_2SO_4 & > & HNO_3 & > & HClO_4. \\ \sim 0.4 & & \sim 3 & & \sim 4 & & \sim 8 \end{array} \tag{3}$$

The numbers under the acid formulas are the estimated approximate values of the instability constants of the complexes $VO \cdot H^{3+}$. The most stable hydrogen complexes are formed upon addition of oxalic acid to aqueous vanadyl solutions ($K \sim 0.4$), and the least stable upon addition of perchloric acid ($K \sim 8$); i.e., the basic properties (affinity for the proton) of VO^{2+} ions decrease as the strength of the added acids increases. The reason is obvious. In the process of formation of $VO \cdot H^{3+}$ complexes, solvation of VO^{2+} ions by acid anions must play an important role, lowering the effective positive charge of the vanadyl ions and thereby facilitating proton addition. This influence of solvation will be stronger the higher its stability. The above series of approximate values of instability constants (equation 3) precisely reflects this circumstance: oxalic acid is the most effective, since its anions form stable chelates with VO^{2+} ions, whereas the anions of the most weakly acting perchloric acid, at the concentrations used (Fig. 1), are unlikely to have any appreciable probability of entering the coordination sphere of vanadium.

G. B. Bokii et al. ([13]), using X-ray structural analysis and taking ruthenium complexes as an example, established that when a hydroxyl group is present in the structure of complexes, the multiple bond Me—addend tends to become a single bond. If this is also true for the multiple bond $V = O$, then, in accordance with what was stated above, in vanadyl solutions a sharp increase in the ratio T_1/T_2 (shortening of T_2) should be accompanied not only by formation of $VO \cdot H^{3+}$ complexes (equation (1)), but also by formation of hydroxo complexes. The latter indeed occurs experimentally: upon careful increase of the pH of a 0.02 M aqueous solution of $VOSO_4$ to $pH_{max} \sim 3.6$*, a two- to threefold shortening of the time T_2 is observed.

In work $^{(15)}$, for vanadyl solutions an acid-induced shift of the optical absorption bands toward shorter wavelengths by several hundred reciprocal centimeters was found. Naturally, no conclusions about changes in the first coordination sphere could be drawn on the basis of this fact alone. Probably, the indicated shift should be attributed, at least in part, to an increase in the splitting of the lower orbital triplet (Δ) as a result of formation of $VO \cdot H^{3+}$ complexes.

As shown in Fig. 1 and noted in the text, the full range of changes in the ratio T_1/T_2 is very large. Does this occur as a result of only a change in the electron paramagnetic relaxation time τ_s? According to the approximate theory $^{(9)}$, a contribution to the ratio T_1/T_2 can also be made by a change in the hyperfine coupling constant (A) in the scalar $\vec{A}\vec{I}\cdot\vec{S}$ interaction of the nuclear and electron spins. However, no reasons are apparent why the latter circumstance could become the principal one. Therefore, within the framework of this brief discussion, we have not taken it into account.

At high concentrations of sulfuric acid the curve of T_1 values passes through a minimum, and the ratio T_1/T_2 tends to unity (Fig. 1). This special course of the relaxation curves is due to the chemical combination of water with sulfuric acid. The minimum on the T_1 curve corresponds practically exactly to the stoichiometric ratio $H_2O : H_2SO_4 = 1 : 1$ (vertical I—I in Fig. 1), i.e., it corresponds to the formation of the monohydrate $H_2SO_4 \cdot H_2O$ $^{(16)}$.**

* Further increase of pH is impossible because of the appearance of turbidity (precipitate). At ~ pH 3.6, the concentration of hydroxo complexes is less than 10% of the total vanadyl concentration $^{(14)}$.

** The reason for the influence on relaxation of the chemical combination of solvent components (H_2O and H_2SO_4) requires additional clarification.

The observed affinity of VO^{2+} ions for the proton indicates that the V = O bond is polar to a considerable degree and that the valence capabilities of oxygen are not exhausted entirely by this bond. As is known, the functions of vanadyl in its double salts with mineral acids have not yet been established (^{17}). On the basis of the results of the present work, it is possible that these salts are built according to the type of oxonium compounds. For example, "acid vanadyl sulfate," $2VOSO_4 \cdot H_2SO_4$, very probably has the structure $(BH^+)_2SO_4^{2-}$, where $B = VOSO_4$.

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