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Abstract

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CHEMISTRY

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THE INFLUENCE OF ACIDITY ON THE EXCHANGE INTERACTION OF ELECTRON SPINS IN SOLUTIONS OF VANADYL SALTS

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In work (1), using the method of proton magnetic relaxation, it was shown that in aqueous solutions the oxygen of vanadyl ions is chemically active and is capable of attaching positively charged particles—protons. In this connection it was suggested that the high viscosity of concentrated $VOCl_2$ solutions (~ 140 centipoise at $N = 6$ mol/l) and the presence in them of fairly strong exchange interactions (2,3) are a consequence of association of vanadyl ions of the form:

$$| \cdot (\cdot V = O \cdot)^{2+} \cdots (\cdot V = O \cdot)^{2+} \qquad (1)$$

In search of confirmation of this hypothesis, we studied the effect on the e.p.r. spectra of aqueous VO^{2+} solutions of additions of strong mineral acids and diamagnetic mineral salts. In dilute (centimolar) solutions these additions cause no changes in the spectra. Even in the limiting case, when concentrated acids were used as solvents, the e.p.r. spectra of 0.02 mol/l $VOCl_2$ did not differ appreciably from the e.p.r. spectrum of an equimolar aqueous solution and, as usual (2,4), consisted of eight completely resolved components of hyperfine structure, in accordance with the value of the nuclear spin of V^{51}, $I = 7/2$. Vanadyl solutions behave quite differently at concentrations $N \sim 2$ mol/l and higher. Here the presence of acids sharply enhances the exchange interaction between the electron spins of VO^{2+}, as a result of which the e.p.r. lines narrow and the hyperfine structure is "erased" (if it is still preserved to some extent). As an example, Fig. 1 gives e.p.r. spectra of $2.3\,M$ $VOCl_2$ in water (Fig. 1a) and in $3.6\,N$ $HClO_4$ (Fig. 1b). The measurements were performed at the frequency of the oscillating magnetic field $\nu_0 = 9330$ MHz and at room temperature, on a standard radiospectroscope of the RE-1301 type, with double modulation, a synchronous detector, and automatic frequency tuning to the operating resonator. As is seen from Fig. 1, the width of the curve ΔH (the distance between the points of maximum slope), owing to the action of the acid, decreased almost twofold, from $\Delta H \simeq 850$ Oe for the purely aqueous solution (Fig. 1a), to $\Delta H \simeq 450$ Oe for the solution with $3.6\,N$ $HClO_4$ (Fig. 1b). Traces of hyperfine structure present in Fig. 1a are not observed in Fig. 1b.

In weakly concentrated VO^{2+} solutions, addition of acids produces a manyfold shortening of the proton relaxation time T_2 and, correspondingly, an increase in the ratio of relaxation times T_1/T_2 (^{5,1}). This is due to the formation of hydrogen complexes of vanadyl (^{1}):

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

(for simplicity we do not write the water molecule bound to the proton). It is not surprising, however, that in the e.p.r. spectra of dilute solutions the protolytic process (2) is not reflected. Indeed, if (presumably), as a result of attachment of a proton, the time of paramagnetic relaxation of VO^{2+} ions is somewhat lengthened (^{1}), this will not cause a narrowing of the hyperfine e.p.r. components, since the width of the components is structural rather than relaxation in nature (^{6}). On the other hand, pro-

process (2) should lead to an increase in the coefficient A of the scalar $\vec{A}\vec{I}\cdot\vec{S}$-coupling $^{(7,8)}$ between the electron spins and the spins of the protons of the solvent*. The latter circumstance strongly affects the relaxation of protons, but is unlikely to be of great importance for EPR spectra.

The situation is different in concentrated solutions. It is possible that in dimeric vanadyl ions (A_1A_2) the probability of transition of an unpaired electron from A_1 to the vanadium orbitals in A_2 is zero, since the formation of a covalent bond between A_1 and A_2 is prevented by the multiple covalent bond of the vanadium in A_2 with its oxygen. Consequently, exchange is absent. When acid is added to the solution, ions $[VO\cdot H]^{3+}$ are formed (process (2)), in which, owing to the polarizing action of the proton, the multiplicity of the $V=O$ bond is somewhat lower than in VO^{2+} ions, and exchange upon approach of two particles becomes possible. It will occur in associates

$$(V=O\cdot)^{2+}\cdots(\cdot V=O\cdot H)^{3+}.$$

In larger associates ($(VO^{2+})_n,\ n>2$) the necessary degree of polarization of the $V=O$ bond of one of the exchanging partners is probably provided by the presence in the chain of a third VO^{2+} ion, so that at very high vanadyl concentrations ($\gtrsim 4$ mol/l) strong exchange is observed even without the participation of acid $^{(3)}$.

Fig. 1. EPR spectra of a 2.3 M solution of $VOCl_2$: a –in water; b –in $3.6\,N$ $HClO_4$. $\nu_0 = 9330$ MHz; $T \sim 290$°K.

An effect analogous to the action of acids (Fig. 1) cannot be obtained by adding diamagnetic salts to vanadyl solutions.

Figure 1. EPR spectra of a 2.3 M solution of VOCl2: a —in water; b —in 3.6 N HClO4. $ $0 = 9330 MHz; T ~ 290°K

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At unchanged VO^{2+} concentration, the influence of acids on EPR spectra depends on the nature of the anion, increasing in the following order:

$$HNO_3 < HCl < HClO_4,$$

which coincides with the order of increasing acid strength. Both facts are in agreement with the proposed mechanism.

It is interesting to note that, in contrast to dilute solutions (1), in highly concentrated $VOCl_2$ solutions additions of acids do not exert a significant influence on the relaxation parameters of protons. This is understandable as well: exchange between the electron spins of VO^{2+} averages the scalar $\vec{A}\vec{I}\cdot\vec{S}$-coupling between the electron spins and the spins of the protons of the solvent. The action of acids on proton relaxation, however, occurs through the $\vec{A}\vec{I}\cdot\vec{S}$-coupling (1).

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* We shall discuss the experimental facts confirming this effect in the following communication.