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ELECTRON PARAMAGNETIC RESONANCE IN CONCENTRATED AQUEOUS SOLUTIONS OF VO^{2+}

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Highly concentrated aqueous solutions of $VOCl_2$ are investigated by the EPR method. The dependence of EPR line shape on concentration and temperature is in agreement with the predictions of the exchange-narrowing theory. An exchange frequency $\omega_e \approx 5 \times 10^{10}$ sec^{-1} is estimated for a concentration of 6 M.

1. Liquid solutions of vanadyl (VO^{2+}) salts are convenient systems in which to test the existing theories of paramagnetic relaxation in solutions.[1-3]

Using the method proposed in [4] we have investigated the behavior of EPR (electron paramagnetic resonance) line width in aqueous solutions of $VOCl_2$ over the temperature range 278 to 390° K at concentrations from M = 6 M to M = 1 M at the frequency ν = 9430 Mc.

As was shown earlier in a qualitative way,[5] pronounced exchange interactions between the VO^{2+} ions are observed in this range of concentrations. Kubo and Tomita[3] have developed the most complete theory of exchange effects in EPR. Hence the following discussion will be based, for the most part, on the results of [3] and [6], in which the effect of exchange on the magnetic dipole-dipole interaction[3] and on the hyperfine interaction[6] is considered. It can be shown[6] that with very strong exchange, when the exchange narrowing predominates over motional narrowing, the absorption line has the Lorentz shape with half-width (at half-height) $\Delta\omega_{1/2}$

$$\Delta\omega_{1/2} = \Delta\omega_{ss} + \Delta\omega_{\mathrm{hf}} + \Delta\omega_z^a, \tag{1}$$

where $\Delta\omega_{ss}$ is the dipole contribution to the half-width,[3]

$$\Delta\omega_{ss} = \hbar^{-2}g^4\beta^4 S(S+1)\sum_j \langle r_{ij}^{-6}\rangle \omega_e^{-1}\left[\tfrac{3}{5}E_0 + E_1 + \tfrac{2}{5}E_2\right], \tag{2}$$

$\Delta\omega_{\mathrm{hf}}$ is the contribution to the half-width from the hyperfine interaction[6]

$$\Delta\omega_{\mathrm{hf}} = \tfrac{1}{3}I(I+1)\left(a^2 + \tfrac{1}{2}b^2\right)\omega_e^{-1}\left[E_0 + E_1\right], \tag{3}$$

and $\Delta\omega_z^a$ is the contribution of the anisotropic part of the Zeeman energy[6]

$$\Delta\omega_z^a = \tfrac{1}{15}(\Delta g\beta H/\hbar)^2\tau_c\left[\tfrac{4}{3} + (1 + \omega_0^2\tau_c^2)^{-1}\right]. \tag{4}$$

Here

$$a = (A + 2B)/3, \qquad b = 2(A - B)/3, \qquad \Delta g = g_{\parallel} - g_{\perp},$$

$$E_k = (\pi/2)^{1/2}\exp(-k^2\omega_0^2/2\omega_e^2),$$

$$\omega_e = \left[\tfrac{2}{3}J^2 S(S+1)\right]^{1/2}, \quad J^2 = N^{-1}\sum_{j\neq k} J_{jk}^2;$$

ω_e is the exchange frequency, J^2 is the mean value of the square of the exchange integral effective at one ion, and τ_c is the correlation time of Brownian motion. Equations (2) and (3) are obtained under the conditions of strong exchange $\omega_e^2\tau_c^2 \gg 1$ and coincidence of exchange frequencies for $\Delta\omega_{ss}$ and $\Delta\omega_{\mathrm{hf}}$.[6]

We note that the contribution $\Delta\omega_z^a$ does not depend on exchange, since the anisotropic part of the Zeeman energy is neutralized only by thermal motion and not by exchange.

2. Experimentally, the concentration dependence of the half-width of the EPR line in $VOCl_2$ solutions in concentration region I (6 to 2 M) differs in an essential way from that in region II (1 to 0.001 M).

In the present paper we limit ourselves to a consideration of the results pertaining to region I. These concentrations are characterized by a complete absence of any kind of hyperfine structure (hfs). In this region the shape and width of the single EPR are strongly concentration dependent (see the table). For the highest concentration M = 6 M the ratio $r = \langle\Delta H^4\rangle^{1/4}/\langle\Delta H^2\rangle^{1/2} = 1.49$ indicates a Lorentz shape for the absorption line. The smallest value of the width at these concentrations occurs at M = 6 M and is 175 oe, signifying strong exchange interaction in the sample (so-called "exchange narrowing"). The line gradually widens with dilution and at M ~ 2 M acquires a wide plateau-like shape with r = 1.20, which is close to the value 1.16 computed for this ratio for an idealized rectangular-shaped absorption line.

From this it can be seen that Eqs. (1) — (4) for the half-width $\Delta\omega_{1/2}$ of a Lorentz absorption line

Concentration, M	r	ΔH, oe	g-factor
6	1.49	174	1.963±0.005
5	1,36	251	1,963±0.005
4	1.30	347	1,963±0.005
3	1,26	502	—
2	1.20	653	—

in the case of strong exchange are suitable for the description of EPR in 5 — 6 M solution. An additional substantial argument in support of their applicability is the very weak dependence of the line width on temperature in the highly concentrated solutions. Thus, at a concentration of 6 M the width decreases from 175 to 160 oe as the temperature increases from 293 to 323° K, and with further heating it remains unchanged. Such a dependence can be explained on the basis of Eqs. (1) — (4) when it is realized that only the contribution from the anisotropic part of the Zeeman energy [Eq. (4)] depends on the temperature (through the correlation time τ_c). When τ_c becomes short enough with increasing temperature so that $\Delta\omega_z^2$ is negligible relative to $\Delta\omega_{ss} + \Delta\omega_{hf}$, the line width does not depend strongly on the temperature in accordance with Eqs. (2) and (3). In this temperature range the behavior of concentrated $VOCl_2$ solutions is completely analogous to that of paramagnetic solids having strong exchange interaction (free radicals, many magnetically concentrated ionic salts of elements of the first transition group, etc.).[7]

Using Eqs. (2) and (3) we can estimate from the temperature independent part of the half-width the exchange frequency ω_e, a parameter difficult to measure by other means. Taking $\Delta H = 160$ oe at $M = 6$ M, $A = 200$ oe, $B = 76$ oe, $I = 7/2$, and $S = 1/2$ we obtain $\omega_e \approx 5 \times 10^{10}$ rad/sec. Here we have used the values for the hyperfine coupling constants A and B obtained earlier in [8] from EPR spectra of super-cooled ethanol solutions of hydrated complexes of $VOCl_2$. Dilute liquid solutions in ethanol and water have isotropic hyperfine coupling constants $a = 110$ oe and $a = 117$ oe, respectively. The small difference between these values leads to the expectation that the use of the measurements of A and B in supercooled ethanol solutions is adequately justified. The strong exchange condition $\omega_e^2\tau_c^2 \gg 1$ for our solutions is apparently satisfied, since the viscosity of concentrated aqueous solutions of $VOCl_2$ is rather large (at room temperature the viscosity of a 6 M solution amounts to 141 centipoise).

When the concentration becomes somewhat lower than 2 M, traces of resolved hfs can be seen on the wide plateau-shaped absorption line. However, the dipole width of each peak in the concentration range 2 to 1 M is comparable to the hfs constant $a = (1/3)(A + 2B)$. Hence the hfs is either not resolved at all (2 M) or there are only traces of a resolved structure (1 M). In this case the relations $\Delta H \sim 2Ia = 7 \times 117 = 819$ oe should be satisfied. Experiment gives the somewhat larger value $\Delta H = 930$ oe for a 1 M solution, as was to be expected.

In discussing the results obtained at intermediate concentrations (2 — 1 M), we are limited to purely qualitative considerations, since existing theories[1-3,6] do not treat this case.

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190