

THE OVERHAUSER EFFECT IN LIQUID SOLUTIONS OF Cr(V) AND Mo(V) COMPLEX COMPOUNDS

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Dynamic polarization of the protons of the solvent in liquid solutions of Cr(V) and Mo(V) complex compounds in organic solvents in a magnetic field of 3300 Oe is observed. The largest increase of proton polarization due to the Overhauser effect was -50 for the Cr(V) complex and -6.7 for the Mo(V) complex. It is found that a scalar sIS interaction between unpaired electrons of the complexes and protons of the solvent exists besides the main dipole-dipole mechanism of electron-nuclear coupling (a is the hyperfine splitting constant). A temperature at which the contributions from the dipole-dipole and scalar interactions compensate each other and the effect vanishes has been found to exist for the Cr(V) compound.

Up to now, the Overhauser effect in liquid solutions of paramagnetic ions was investigated in detail only for Mn^{2+} ions in the S-state. The small number of investigations^[1-3] of dynamic nuclear polarization (DNP) in liquid solutions of compounds of transition-group elements is apparently due to the difficulty of saturating the electronic transitions in such systems. At the same time, the Overhauser effect is employed more and more for the investigation of electron-nuclear interactions in solutions of free radicals in different solvents. It is known that solutions of both free radicals and of alkali metals have relatively long electron-paramagnetic relaxation times and are therefore convenient objects for such investigations. The corresponding relaxation times of the paramagnetic ions are usually short, and considerable microwave powers are necessary to saturate the electronic transitions. An increase of the power of the microwave source entails a number of experimental difficulties connected essentially with the microwave heating and with the difficulty of maintaining the sample temperature constant.

In this paper we present the results of an investigation of the dynamic polarization of protons in liquid solutions of the charged complexes Cr(V) and Mo(V) in organic solvents.

The experiments were performed in a setup specially constructed for this purpose and in a magnetic field of 3300 Oe. To obtain large saturating magnetic fields, the resonator employed was a helical microwave slow-wave system with a sample volume 0.8 mm^3 . The helix served simultaneously as the inductance of the tank circuit of an autodyne detector for the NMR signal, constructed in accordance with the Robinson circuit^[4]. The maximum microwave source power was 15 W. The homogeneity of the magnetic field inside the volume of the sample was of the order of 5×10^{-6} . The apparatus is described in greater detail in^[5].

The complex compound Cr(V) was obtained by heating a saturated solution of the hexavalent chromium salt $(NH_4)_2Cr_2O_7$ in ethylene glycol. The largest concentration of Cr(V), according to the measurements of the EPR signal amplitude, are obtained when the color of

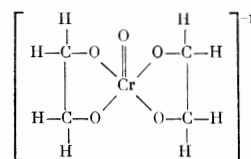
the solution changes from dark brown to dark green. The concentration was decreased by diluting the obtained complex with ethylene glycol.

The EPR spectrum of the ethylene glycol solution of the Cr(V) complex (0.03 mole/one) (see Fig. 1a) has the following parameters:

$$g = 1.981, \quad \delta H = 3.2 \text{ Oe}, \quad a_1 = 17.6 \text{ Oe},$$

where δH —width between the extremal points of the first derivative of the absorption curve, and a_1 —hyperfine structure (hfs) constant of the odd isotope Cr^{53} (9.5%) with $I = 3/2$.

We have shown in^[6] that in strongly diluted solutions ($N < 0.005$ mole/one) central EPR lines splits into a 9-component additional hyperfine structure with a binomial distribution of the intensity of the components and with a constant $a_2 = 0.64$ Oe from the 8 protons contained in the ligands of the complex. This has allowed us to assume that the complex has the following structure:



The complex of pentavalent Mo was obtained by dissolving $MoCl_5$ in dioxane^[7]. The EPR spectrum of the solution of $[MoOCl_5]^{2-}$ (0.002 mole/one) in dioxane (Fig. 1b) has the following parameters:

$$g = 1.94, \quad \delta H = 11 \text{ Oe}, \quad a = 58 \text{ Oe},$$

where a —averaged hfs constant for Mo^{95} (16.5%) and Mo^{97} (9.4%).

The concentration of the paramagnetic centers in the investigated Cr(V) and Mo(V) solutions was estimated by comparing the areas under the curves of the EPR signals from the investigated sample and from the standard, both being simultaneously introduced into the resonator and having identical volumes. The standard was a DPPH solution (0.05 mole/one) in benzene.

We were able to establish that both dipole-dipole and scalar interactions between the electron spins of the complexes and the solvent protons take place in the investigated systems. These interactions are well described by the expression of Abragam and Solomon^[8]

$$A = |\gamma_s / \gamma_I| f S \rho, \quad (1)$$

where $A = (I_Z - I_0)/I_0$ is the factor characterizing the relative increase of the equilibrium nuclear magnetization I_Z upon irradiation as compared with the nuclear magnetization in thermal equilibrium with the lattice ($H_{1S} = 0$); $|\gamma_s / \gamma_I|$ —ratio of the electronic gyromagnetic factor to the nuclear factor, equal to 652 for the Cr(V) glycol complex and 640 for the $[\text{MoOCl}_5]^{2-}$ complex; $f = (1 - T_1/T_{10})$ —leakage factor, showing the fraction of the nuclear transitions in which the electron spins take part; f is usually expressed in terms of the ratio of the nuclear longitudinal relaxation (T_1) at a given paramagnetic-ion concentration to the relaxation time of the pure solvent (T_{10}).

For the concentrations of the paramagnetic centers investigated in this paper we have $f \approx 1$, since $T_{10} \approx 0.5$ sec and $T_1 \approx 4 \times 10^{-2}$ sec; the saturation parameter is

$$S = \frac{\gamma_s^2 H_{1S}^2 T_{1S} T_{2S}}{1 + (\Delta\omega T_{2S})^2 + \gamma_s^2 H_{1S}^2 T_{1S} T_{2S}}$$

where H_{1S} is the intensity of the microwave magnetic field, and T_{1S} and T_{2S} are the spin-lattice and spin-spin relaxation times. Since we have used a sufficiently small modulation of the magnetic field compared with the EPR line width, the term $(\Delta\omega T_{2S})^2$ was disregarded by us.

The nature of the electron-nuclear interactions and the character of the molecular motions is characterized by the coefficient

$$\rho = \left[\tau_e \frac{1 + \omega_s^2 \tau_c^2}{1 + \omega_s^2 \tau_e^2} - \sigma \tau_c \right] \times \left\{ \tau_e \frac{1 + \omega_s^2 \tau_c^2}{1 + \omega_s^2 \tau_e^2} + \sigma \tau_c [1.4 + 0.6(1 + \omega_s^2 \tau_e^2)] \right\}^{-1}, \quad (2)$$

where

$$\sigma = \frac{1}{4} \frac{\hbar^2 \gamma_s^2 \gamma_I^2}{\hbar^{-2} \langle A_{IS}^2 \rangle} \left\langle \frac{1}{r_0^6} \right\rangle$$

determines the ratio of the intensity of the dipole-dipole interaction to the scalar interaction, r_0 is the average distance between the nucleus and the electron spin, and τ_e and τ_c are the correlation times of the scalar and the

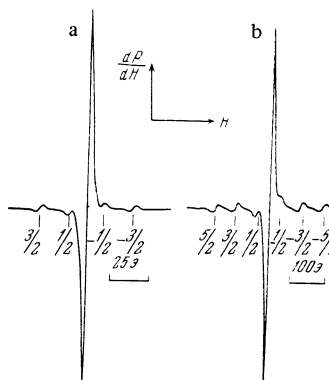


FIG. 1. EPR spectra of ethylene glycol complex of Cr(V), (a) and of the $[\text{Mo}]\text{Cl}_5^{2-}$ complex in dioxane (b).

dipole-dipole interactions. Here, $\tau_e^{-1} = \tau_s^{-1} + \tau_h^{-1}$, where τ_s —correlation time of the electron spins and τ_h —the lifetime of the protons in the first coordination sphere of the complex.

The purpose of our measurements was to determine the quantity ρ . From expression (2) we see that in a pure dipole-dipole interaction ($\sigma \rightarrow \infty$) and under the condition of fast molecular motion compared with the frequency of the irradiation source ($\omega_s \tau_c \ll 1$) the maximum value is $1/2$, and in pure scalar interaction ($\sigma \rightarrow 0$) the maximum value is $\rho = 1$.

If we denote by A_{max} the maximum possible increase of the polarization at infinitely large power ($S = 1$), calculated in accordance with equation (1), then the reciprocal increase of the nuclear polarization can be written in the form

$$A^{-1} = A_{\text{max}}^{-1} [1 + \alpha P^{-1}], \quad (3)$$

where^[9]

$$\alpha = \frac{1 + (\Delta\omega T_{2S})^2}{\gamma_s^2 T_{1S} T_{2S} \beta}, \quad (4)$$

$P = H_{1S}^2 \beta^{-1}$ is the power of the radiation source.

Extrapolation of the linear dependence of the experimental values of A^{-1} on P^{-1} makes it possible to determine A_{max} and ρ .

We investigated the DNP of the solvent protons in non-evacuated samples of the complex compounds (Cr(V) Mo(V) in the concentration range from 0.01 to 0.005 mole/one. At larger and smaller concentrations the polarization decreases, in the former case as a result of the shortening of the electron paramagnetic relaxation time τ_s , due to the dipole-dipole broadening, and in the latter case as the result of the decrease of the number of paramagnetic particles.

Figure 2 shows the results of an investigations of the DNP of the protons of the solvent of the 0.02 mole/1 solution ($\delta H = 2.9$ Oe) of the ethylene glycol complex of Cr(V). We saturated the EPR line with $g = 1.981$ of the even isotopes of Cr. A rather appreciable nuclear polarization with $A_{\text{max}} = -50$ and $\rho = 0.077$ is observed at 45°C (curve 1).

With decreasing solution temperature, the polarization decreases (curve 2), and is not observed at all at -15°C . With further decrease of the temperature, the sign of the polarization reverses and small positive polarization is observed at -30°C (curve 3), with $A_{\text{max}} = 2$ and $\rho = 3.1 \times 10^{-3}$.

Thus, the observed temperature dependence of the DNP is the opposite of that observed for the Mn^{2+} ion^[2],

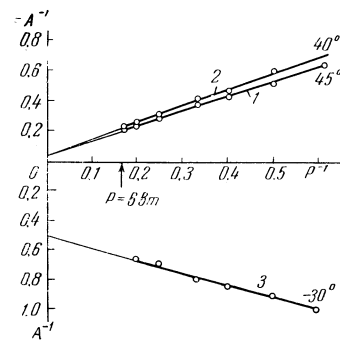


FIG. 2. Dependence of A^{-1} on P^{-1} for a solution of the complex Cr(V) (0.02 mole/one) in ethylene glycol.

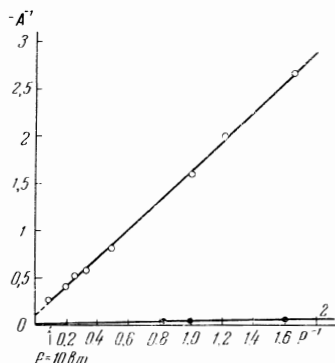


FIG. 3. Dependence of A^{-1} on P^{-1} for the solution of the complex $[\text{MoOCl}_5]^{2-}$ (0.04 mole/one) in dioxane at $T = 30^\circ\text{C}$ (curve 1) and a solution of DPPH in benzene (0.05 mole/one) at $n = 20^\circ\text{C}$ (curve 2).

indicating that the main mechanism of the electron-nuclear interactions is the dipole-dipole interaction between the $3d^1$ electrons and the protons of the solvent. The scalar $a\text{IS}$ interaction greatly decreases the negative nuclear polarization also at temperatures below 15°C , owing to the decrease of the Brownian motion in liquids, and becomes the predominant mechanism of the electron-nuclear coupling.

We also observed polarization of the solvent protons in a solution of the Mo(V) complex in dioxane. We saturated the EPR line with $g = 1.94$ of four Mo isotopes. At 37°C we observed in the solution of the $[\text{MoOCl}_5]^{2-}$ complex (0.04 mole/one) (with $\delta H = 11.7$ Oe) a small negative dynamic polarization with $A_{\text{max}} = -6.7$ and $\rho = 1.05 \times 10^{-2}$ (Fig. 3, curve 1). With decrease in temperature the polarization decreases, but no change in the sign of the polarization was observed all the way up to temperatures at which the NMR line begins to broaden noticeably as a result of the cessation of both the translational and the rotational motion. In our case the main mechanism of electron-nuclear interaction is thus the dipole-dipole coupling between the $4d^1$ electrons and the protons of the solvents. For comparison, Fig. 3 (curve 2) shows the dependence on P^{-1} for a DPPH solution (0.005 mole/one) in benzene, with $A_{\text{max}} = -80$ at $T = 25^\circ\text{C}$.

Since we used in our experiments a low- Q resonant system, and the investigated samples are not strong

electrolytes, it is possible to assume without danger incurring a large error that the microwave field intensity remains practically constant when the investigated sample is replaced by the standard solution of DPPH in benzene, for which the electron paramagnetic resonance times, taken from^[10], are $T_{1S} = 4.4 \times 10^{-7}$ and $T_{2S} = 0.6 \times 10^{-8}$ sec. From this we can determine the coefficient β and, using expression (4), estimate the electron relaxation times $\tau_S = \sqrt{T_{1S}T_{2S}}$, which are of the order of a $\times 10^{-8}$ and 6×10^{-9} sec, respectively, for the solution of the Cr(V) complex (0.02 mole/1) and the solution of the Mo(V) complex (0.04 mole/1).

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