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# *PARAMAGNETIC RESONANCE IN SOLUTIONS OF* $Cr^{3+}$ *SALTS*

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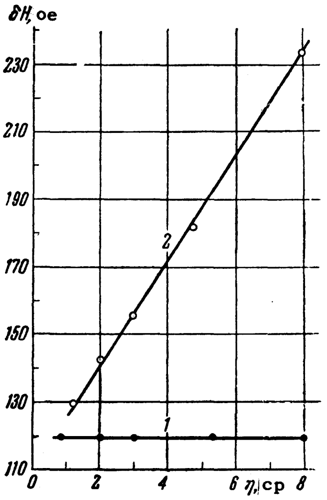
The influence of additions of $Al(NO_3)_3$ to aqueous solutions of $Cr(NO_3)_3$ on the EPR (electron paramagnetic resonance) spectrum of the latter is studied. The EPR line width is found to be independent of the macroscopic viscosity of the solution.

PREVIOUS measurements of the temperature dependence of the line width $\Delta H$ of paramagnetic resonance in violet-colored aqueous solutions of the nitrate of trivalent chromium[1] showed that this dependence could not be explained by the theory of paramagnetic relaxation presented by McConnell.[2] However changes in $\Delta H$ in solutions over a wide temperature range can always be ascribed not only to a direct dependence of the relaxation time on temperature, but also to a change in the initial splitting of the spin sublevels with temperature. This is made more probable by the fact that cases are known among solid chromium salts in which the trigonal field constant D changes gradually with temperature over a wide range of the latter.[3] Therefore it was of interest to look into the dependence of the EPR line width in solutions of chromium salts on the viscosity at constant temperature. In doing this we strove to create changes in the viscosity of the solution without any disturbance to the immediate surroundings of a $Cr^{3+}$ ion. It is to be noted that measurements of $\Delta H$ as a function of viscosity have hitherto been made only on solutions of $Mn^{2+}$ salts.[4,5]

We prepared two series of aqueous solutions. Samples of the first series contained 0.6 mole/liter of $Cr(NO_3)_3$ and varying concentrations of $Al(NO_3)_3$ (from 0 to 2.5 mole/liter). The second series consisted of samples containing 0.01 mole/liter of $Cr(NO_3)_3$ and the same concentrations of $Al(NO_3)_3$ as in the first series. The coefficient of viscosity $\eta$ of each sample was measured with an Ostwald viscosimeter at 295°K. The EPR measurements were carried out at the same temperature in a PÉ-1301 double-modulation radiospectrometer at 9346 Mc/sec. The line width was measured as the separation between the maximum and minimum of the first derivative of the absorption curve. The results obtained agree with the earlier data, within the limits of accuracy of the measurement (± 10%). Thus, for 0.6 mole/liter $Cr(NO_3)_3$ in water $\delta H = 130$ oe, which corresponds accurately to Kozyrev's data,[4] if it is assumed that the shape of the absorption line in $Cr(NO_3)_3$ solutions is Lorentzian.

It is certain that the predominant type of chromium ions in the violet aqueous nitrate solutions is $[Cr(H_2O)_6]^{3+}$. Since we added the nitrate of another trivalent ion, $Al^{3+}$, in order to increase the viscosity, we had grounds for believing that the concentration of $Cr^{3+}$ ions, holding in the first sphere not only water but also acid residues, will not increase here by any substantial amount. This found some confirmation in the measurements of the optical absorption spectrum of the solutions, made with an SF-2M spectrophotometer. It turned out that in the given series the location and intensity of the two observed absorption bands (the centers of which are at $\lambda_1 = 0.412\mu$ and $\lambda_2 = 0.580\mu$) do not depend on the $Al^{3+}$ ion concentration in the solution. At the same time, in going from the violet aqueous solutions of chromium nitrate to the green aqueous solutions of chromium chloride $[Cr(H_2O)_4Cl_2]Cl$, a shift of the centers of both absorption bands toward longer wavelengths is observed. This shift equals $0.020\mu$ and lies outside the limits of error of the experiment.

The results of our EPR measurements are presented in the figure. It can be seen from it that the more concentrated solution exhibits a slight widening of the EPR line with the increase in viscosity as the $Al^{3+}$ concentration is made greater. For an almost ninefold increase in viscosity, the line width increases correspondingly only 1.6 times. On the other hand, for the 0.01 mole/liter $Cr(NO_3)_3$ solutions (Curve 1) the line width remains unchanged for a ninefold increase in viscosity, within the limits of error. It is natural to attribute the weak dependence of $\delta H$ on $\eta$ observed in the 0.6 mole/liter $Cr(NO_3)_3$ solu-



tions (Curve 2) to the contribution to the width brought about by the magnetic dipole interaction between the $[Cr(H_2O)_6]^{3+}$ ions. This contribution is practically nil at a concentration of 0.01 mole/liter $Cr^{3+}$, where the line width is evidently completely determined by the spin-lattice relaxation. According to any of the theories on paramagnetic relaxation in liquid solutions,[2,6,7] the independence of the spin-lattice relaxation time of the macroscopic viscosity $\eta$ is rather unexpected. This independence can apparently be explained only by assuming that the correlation time $\tau_c$ is not connected with the macroscopic viscosity of the solution as a whole, but with the microscopic viscosity on the boundary between the paramagnetic complex and the solvent. This microviscosity apparently changes little with the ionic concentration, as was first proposed by Tishkov[8] in an analysis of the data on paramagnetic relaxation in parallel fields in solutions of $Mn^{2+}$ salts. Our measurements, having been made by a different method and on a different ion, confirm this hypothesis.

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[1] Avvakumov, Garif'yanov, Kozyrev, and Tishkov, JETP **37**, 1564 (1959), Soviet Phys. JETP **10**, 1110 (1960).

[2] H. M. McConnell, J. Chem Phys. **25**, 709 (1956).

[3] S. A. Al'tshuler and B. M. Kozyrev, Élektronnyi paramagnitnyi rezonans (Electron Paramagnetic Resonance), Fizmatgiz, 1961, p. 109.

[4] B. M. Kozyrev, Doctoral Dissertation, FIAN 1957

[5] Tinkham, Weinstein, and Kip, Phys. Rev. **84**, 848 (1951).

[6] S. A. Al'tshuler and K. A. Valiev, JETP **35**, 947 (1958), Soviet Phys. JETP **8**, 661 (1959).

[7] I. V. Aleksandrov and G. M. Zhidomirov, JETP **40**, 1720 (1961), Soviet Phys. JETP **13**, 1211 (196).

[8] P. G. Tishkov, Dissertation, Kazan' State Univ., 1961.

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