INVESTIGATION OF THE DIFFUSION MOVEMENT
OF WATER MOLECULES IN SOLUTIONS OF PARAMAGNETIC
IONS BY PROTON RESONANCE MEASUREMENT

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The frequency dependence of the relaxation times of proton spins in aqueous solutions containing
\[ \text{[Cr(CN)\textsubscript{6}]^{3-}} \] complexes has been measured by means of the spin-echo spectrometer. Analysis of the
experimental data has shown that relaxation of proton spins is due to dipole-dipole interactions be-
tween the proton and the paramagnetic \[ \text{[Cr(CN)\textsubscript{6}]^{3-}} \] ions, excited by transla
tional diffusion of water molecules in relation to these ions. This circumstance makes it possible to determine the diffusion
coefficient of water molecules in the vicinity of the \[ \text{[Cr(CN)\textsubscript{6}]^{3-}} \] complexes, which is higher than the
diffusion coefficient of the molecules in pure water (at the same temperature). \[ \text{[Cr(CN)\textsubscript{6}]^{3-}} \] com-
plexes are thus found to be negatively hydrated.

PURPOSE OF THE INVESTIGATION

In aqueous solutions of paramagnetic particles, the relaxation rate of the protons is composed of translational
and rotational contributions. When the paramagnetic particles do not bind water on their surface, the relaxation rate
of the protons is primarily determined only by the magnetic interaction between the paramagnetic particles and the
freely moving water molecules. By investigating relaxation in such solutions, information may be obtained regarding
the character of the diffusion movement of the water molecules in relation to the paramagnetic particles.

Certain inorganic complexes of \( \text{Cr}^{2+} \) were used for the measurements. The experimentally found relationships
between relaxation rate and frequency were analyzed by means of the equations of Solomon [1], [2], and Pfeifer [3],
[4]; it was thus possible to show that in solutions of \[ \text{[Cr}^{3+}(\text{CN})\textsubscript{6}]^{3-} \] ions in water, the dependence of relaxation rate
on frequency satisfies the equations for a purely translational contribution if realistic values are assumed for the cor-
relation time of diffusion \( T_d \) and for minimum distance of the protons from the center of the ion. This is justified by
the supposition that the length of the activated jumps of the water molecules in the vicinity of the ion during the dif-
fusion process has an order of magnitude of the distance between the water molecules. The coefficient of diffusion of
the water molecules in the immediate vicinity of the ions was found to be approximately 1.6 times greater than
that in pure water.

The quantitative treatment of the frequency dependence of relaxation rates in solutions of \[ \text{[Cr(}\text{SCN})_{6}]^{3-} \] and
[\( \text{[Cr(NH\textsubscript{3})\textsubscript{6}]^{3+}} \] ions presents certain difficulties, because there is also a certain contribution from rotation in conse-
quence of the mutual replacement of part of the ligands by water molecules, and in addition, it is possible that water
molecules are bonded to the surface of the complex, due to the formation of hydrogen bridges.

THEORY

In the analysis of the relaxation of protons in aqueous solutions of paramagnetic particles, the shape of which
we shall consider henceforth to be spherical, two cases must in principle be distinguished:

Case 1: The particle offers fairly strong obstruction to the movement of a water molecule in the first layer of
the hydrate shell, so that the mean time of stay \( T_h \) of the protons in this layer is high compared with the mean time
of stay $\tau_w$ in equilibrium positions in the structure of the water. If the influence of the particle on the movement of the more remote water molecules is then taken into account by the introduction of an effective diffusion coefficient we obtain two regions with different relaxation mechanisms, formed by the water of the first layer of the hydrate shell and the "freely" diffusing water. Denoting the respective relaxation rates by $T_{IH}^{-1}$ and $T_{IWIT}^{-1} + T_{I0}^{-1},$ $T_{IWIT}^{-1}$ being the so-called translational contribution and $T_{I0}^{-1},$ the relaxation time of water without paramagnetic particles (the number of the latter in 1 cm$^3$ is denoted by $N$), then according to the Chapman-Kolmogorov equations (cf., for example, [5]), for the resulting relaxation rate in dilute solutions ($mN_1 \ll N$) and under the condition that $T_{IH} \ll T_{IWIT},$ we obtain

$$\frac{1}{T_I} = \frac{mN_1}{N} \frac{1}{T_{IH}} + \frac{1}{T_{IWIT}} + \frac{1}{T_{I0}}.$$  

Here, $m$ is the number of molecules of water in the first hydrate shell of an ion, and $N$ is the total number of molecules of water in 1 cm$^3$.

**Case 2:** Retardation of the movement of the water molecules in the first layer of the hydrate shell may be ignored, i.e., $\tau_h \approx \tau_w.$ Consequently, the region of freely diffusing water may extend directly to the surface of the paramagnetic particle; that is

$$\frac{1}{T_I} = \frac{1}{T_{IWIT}} + \frac{1}{T_{I0}}.$$  

The proportion of translation in this equation $1/T_{IWIT}$ differs mainly from $1/T$ merely in the fact that for minimum distance of the freely diffusing water molecules from the center of the paramagnetic particle, a correspondingly reduced value must be introduced, i.e., one reduced approximately by the mean diameter of a water molecule.

Of course these two cases are limit cases, transition from the first to the second case occurring on decrease in the ratio

$$Q = \frac{\tau_h}{\tau_w}.$$  

Assuming

$$\gamma_s \gg \gamma, \quad \gamma H_0 \tau_c \ll 1, \quad I^4 \ll 6a^2I^2,$$

we get for the four relaxation rates $T_{IH}^{-1}$ and $T_{IWIT}^{-1}$ (cf. 1-4):

$$\frac{1}{T_{IH}} = \frac{\gamma^2 \tau_w^2 s (s + 1)}{15\rho_p^6} \left( 6\tau_c + \frac{14\tau_c}{1 + \omega_s^2 \tau_c^2} \right) + \frac{2}{3} s (s + 1) \left( \frac{\gamma}{h} \right)^2 \left[ \frac{\tau_A}{1 + \omega_s^2 \tau_A^2} \right].$$  

$$\frac{1}{T_{2H}} = \frac{\gamma^2 \tau_w^2 s (s + 1)}{15\rho_p^6} \left( 7\tau_c + \frac{13\tau_c}{1 + \omega_s^2 \tau_c^2} \right) + \frac{4}{3} s (s + 1) \left( \frac{\gamma}{h} \right)^2 \left[ \frac{\tau_A}{1 + \omega_s^2 \tau_A^2} \right].$$  

$$\frac{1}{T_{IWIT}} = \frac{1}{4} \gamma^2 \gamma_s^2 s (s + 1) \left( 6J_1(\gamma H_0) + 14J_1(\gamma_s H_0) \right)$$

$$\frac{1}{T_{IWIT}} = \frac{1}{4} \gamma^2 \gamma_s^2 s (s + 1) \left( 4J_1(0) + 3J_1(\gamma H_0) + 13J_1(\gamma_s H_0) \right).$$

Here, $l$ is the length of the activated jump of the water molecules during the diffusion process, $s$ and $\gamma_s$ are the spin and hydromagnetic ratio of the paramagnetic particle; $2\hbar$ is the Planck universal constant; $\gamma,$ the hydromagnetic ratio of a proton; $H_0,$ the strength of the applied field; $\rho_p,$ the distance of a proton of the first layer of the hydrate shell from the center of the paramagnetic particles; and $\tau_c,$ the correlation time of the dipole-dipole interaction.

$J_1(\omega)$ is proportional to $N_1$ and depends in a complex manner on $\omega,$ electron relaxation time $\tau_e,$ and the effective diffusion coefficient $D_{eff},$ which is equal to

$$D_{eff} = \frac{1}{2} \left( D_I + D_{10} \right).$$  

if the diffusion movements of the paramagnetic particle ($D_I$) and water molecule ($D_{10}$) are uncorrelated. $A$ denotes the constant of the scalar interaction, which is generally not large compared with the dipole-dipole interaction in the system, so that the contribution of the scalar interaction to the total relaxation rate may be ignored if the correlation