Physical Chemistry

A. A. Popel, R. A. Dautov, A. V. Zakharov

1963

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

Physical Chemistry

A. A. Popel, R. A. Dautov, A. V. Zakharov

The Influence of the Symmetry of a Paramagnetic Complex on the Proton Relaxation Time

(Presented by Academician B. A. Arbuzov, November 5, 1962)

The change in the longitudinal (T_1) and transverse (T_2) relaxation times of protons that occurs upon binding into a complex of paramagnetic ions is used to determine the composition and stability of the complexes formed ([1]). However, very little attention is paid in this connection to the possible dependence of T_1 and T_2 on the symmetry of the complex particle. The gradual replacement, in the course of complex formation, of water molecules in the first coordination sphere by other ligands leads to a lowering of the symmetry of the complex particle.

A sharp breaking of symmetry may be expected when the pH of the solution is changed, owing to partial replacement of water molecules or other ligands by hydroxyl ions. In a number of cases such replacement may lead to the paramagnetic ion (the central ion of the complex) ceasing to be a center of inversion symmetry. There are no systematic data on the influence of pH on the relaxation times of solutions. Pearson et al. ([2]) observed changes in the proton T_2 with pH in solutions of complex chromium salts and related these changes to the rate of proton exchange. The anomalous values of T_2 observed by them in the pH range 1.5–5 were not explained.

In the present work, the influence of pH on the proton T_2 in aqueous solutions of certain paramagnetic salts of elements of the iron group was investigated. The influence of pH on the proton T_2 was studied in solutions of halide and nitrate salts of copper, cobalt, nickel, iron, manganese, and chromium.

Fig. 1

The transverse relaxation times of protons (T_2) were measured by the spin-echo method ([3]) at a frequency of $\simeq$ 17 MHz. The error of the measurements was $\pm 5\%$.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

Figure 1 shows the dependence of the proton T_2 on pH in solutions of copper bromide $CuBr_2$ (the concentration of copper ions in the solution was 0.4 mole). As can be seen from the figure, in the pH range 0.5-3 the proton T_2 decreases sharply, indicating an increase in the relaxation efficiency of copper ions. At the same time, a change in the symmetry of the complex is observed in connection with the appearance of a hydroxyl ion in the coordination sphere. The conclusion that the symmetry of the complex is lowered is confirmed by a change in the effective g-factor. The numerical values of the g-factor of copper ions, found from electron paramagnetic resonance spectra, increase with increasing pH of the solutions.

Dependences of the effective g-factors for Cu^{2+} on pH in aqueous solutions of copper bromide (0.4 mole):

$-\lg[H^+]$	−0.35	0.0	1.85
g_{eff}	2.177	2.181	2.188

A change in symmetry is also indicated by a change in the color of the solution from blue to brownish-yellow. An analogous increase in relaxation efficiency is observed in solutions of halide salts of trivalent chromium CrCl (0.08 mg) in the pH region 1.5-3 (Fig. 2). In the indicated pH interval the color of the solution changes, passing from violet (pH 1-1.5) to green (pH 2.5-3). In the case of solutions of chromium and copper nitrates, an increase in pH does not lead to an increase in the relaxation efficiency of the ions. Apparently, the lowering of symmetry should be associated with the formation of mixed hydroxo-halide complexes. Thus, a sharp increase in the relaxation efficiency of Cu^{2+} and Cr^{3+} ions is accompanied by a change in the symmetry of the complex particle.

Fig. 2

Fig. 3

The influence of symmetry on relaxation efficiency may be explained as follows: lowering of symmetry (absence of a center of inversion symmetry) causes changes in the orbital splittings of the ions under consideration. The latter leads to a change in the electronic relaxation time [(4)]. With lowering of symmetry there also occurs a change in the degree of covalency and of the contact interaction [(5)]. Thus, lowering of symmetry leads to changes in the parameters on which [(6)] the value of the transverse relaxation time of protons depends.

The validity of the considerations expressed here is confirmed by the absence of similar changes in the proton T_2 in solutions of salts of divalent manganese $MnCl_2$(10^{-3} M) (Fig. 3) and trivalent iron [7]. As is known, both these ions are in an S-state with orbital moment equal to zero.

The change in the efficiency of the influence of a paramagnetic ion on the proton T_2 as a function of pH is not limited only to the phenomenon considered above. A change in T_2 is also possible depending on the rate of proton exchange as a function of pH. With increasing acidity the exchange rate usually increases, the consequence of which is a shortening of the transverse relaxation time T_2. Such an influence of acidity was clearly observed in strongly acidic solutions of a number of the salts studied (see AB, Fig. 2).

Kazan State University
named after V. I. Ulyanov-Lenin

Received
31 X 1962

CITED LITERATURE

1. B. M. Kozyrev, A. I. Rivkind, ZhETF, **27**, issue 1 (7), 69 (1954); A. I. Rivkind, DAN, **100**, No. 5, 933 (1955); **102**, No. 6, 1107 (1955).

2. R. A. Pearson, J. Palmer et al., Zs. Electrochem., **64**, No. 1, 110 (1960).

3. E. L. Hahn, Phys. Rev., **80**, 580 (1950).

4. N. S. Garif' yanov, E. I. Semenova, DAN, **140**, No. 1, 157 (1961).

5. N. Bloembergen, Phys. Rev. Letters, **7**, No. 3, 90 (1961); G. W. Ludwig, H. H. Woodbury, Phys. Rev. Letters, **7**, No. 6, 240 (1961).

6. K. A. Valiev, ZhETF, **41**, issue 5 (11), 1956 (1961).

7. A. A. Popel' , R. A. Dautov, V. D. Korepanov, *Paramagnetic Resonance*, collection, p. 195, Kazan, 1960.

Note: Figure translations are in progress. See original paper for figures.