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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

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EFFECT OF PARAMAGNETIC IONS ON THE MAGNETIC RELAXATION OF FLUORINE NUCLEI IN SOLUTION

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The effect of paramagnetic ions on the relaxation times of certain nuclei is currently used in the study of various processes occurring in solutions. The nuclei on which observations are made are usually

Fig. 1

Fig. 2

the nuclei of atoms that form part of neutral molecules of the solvent. In most works these are protons (proton paramagnetic resonance) and, much more rarely, nuclei of heavy hydrogen and the oxygen isotope O^{17}. We have found no data in the literature on the effect of paramagnetic ions on the relaxation in solutions of fluorine nuclei. In works (1, 2) only the relaxation of fluorine nuclei in the absence of paramagnetic substances was considered.

In the present work the effect of the ions Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Mn^{2+}, and Cr^{3+} on the relaxation times of fluorine nuclei in solutions was studied. The concentration of fluorides in the various solutions was 4-14 g-mol/l. The paramagnetic ions were introduced into the solution in the form of nitrates. Measurements were carried out on an apparatus described earlier (3), at a resonance frequency of 12.5 MHz. Figure 1 gives graphs characterizing the effect of different concentrations of Cu^{2+} (1), Mn^{2+} (2), and Fe^{3+} on the transverse relaxation time of fluorine nuclei in a 14 M solution of potassium fluoride. The other ions (Co^{2+}, Ni^{2+}, and Fe^{3+}) affect the relaxation of fluorine nuclei very weakly, so that under the conditions of our experiments this effect was difficult to detect.

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

The effect of Cu^2+, Mn^2+, and Fe^3+ ions on the relaxation of fluorine nuclei is different and is not in accord with their static magnetic moments. The greatest relaxation efficiency is found for the divalent copper ion ($\mu = 2.0$ Bohr magnetons) and a considerably smaller one for the divalent manganese ion ($\mu = 5.9$ Bohr magnetons). Possibly this discrepancy is explained by the different contact interaction of copper and manganese ions with fluoride, but for its final clarification a special detailed investigation of the entire mechanism of the relaxation process is necessary.

Manganese ions and especially copper ions affect the relaxation of fluorine nuclei by several orders of magnitude more strongly than they affect proton relaxation. The product of the concentration of paramagnetic ions and the transverse relaxation time of fluorine nuclei ($N \cdot T_2$) for solutions of manganese and copper salts is, respectively, $1 \cdot 10^{-6}$ g-ion/sec and $4 \cdot 10^{-8}$ g-ion/sec, whereas the analogous quantities for protons are, respectively, $1 \cdot 10^{-5}$ g-ion/sec and $6 \cdot 10^{-4}$ g-ion/sec.

Fig. 3

Fig. 4

The considerably greater effectiveness of the influence of copper and manganese ions on the relaxation of fluorine nuclei, as compared with their influence on protons, can be explained by the possibility that negatively charged fluorine ions ($r = 1.3$ Å) approach the paramagnetic centers more closely than water molecules ($r = 2.8$ Å), and also by the presence of a stronger contact interaction between the paramagnetic ions and fluorine.

The strong influence of copper ions on the relaxation times of fluorine nuclei can be used to determine small amounts of copper ions in solution. Calculation shows that, with a measurement error of 1%, copper can be detected from its effect on the relaxation of fluorine nuclei at a concentration of 10^{-8} g-ion/l. The low relaxation efficiency of trivalent iron ions ($\mu_{\text{st}} = 5.9$ Bohr magnetons), which under the conditions of our experiments were present as negatively charged complex particles, can likewise be explained by the impossibility of approach of the relaxing nuclei present in solution (negatively charged fluorine ions) to the paramagnetic ions. Evidently, exchange between fluorine ions located in the first coordination sphere and ions present in solution is very small. The effectiveness of copper ions decreases sevenfold when potassium fluoride in the solution is replaced by ammonium fluoride. The relaxation efficiency of the other ions ($\mathrm{Mn}^{2+}, \mathrm{Fe}^{3+}$) remains constant.

A series of experiments showed that the decrease in the relaxation efficiency of copper ions in ammonium fluoride solutions is explained by their binding into an ammine complex. The change, during complex formation, in the effectiveness of the influence of paramagnetic ions on the relaxation of fluorine nuclei was followed for certain copper complexes.

Figures 2 and 3 give curves characterizing the formation of copper complexes with ethylenediamine (Fig. 2) and glycol (Fig. 3). As is evident, in both cases the stepwise character of complex formation and the composition of the individual complex groups are clearly revealed. Copper complexes with the indicated ligands were previously studied by the method of proton paramagnetic resonance (p.p.r.) ([4,5]). It is interesting to note that both complex-formation curves in the region of low ligand concentrations have an identical character with

observations both on fluorine nuclei and on protons. In regions of higher ligand concentrations, a sharp increase is observed in the effectiveness of the influence of both glycolate (4) and ethylenediamine (5) copper complexes on proton relaxation; at the same time, the effectiveness of these complexes with respect to fluorine nuclei does not increase but, on the contrary, decreases. Particular attention should be paid to the very low relaxation effectiveness of the coordination-saturated, negatively charged glycolate complex.

These experiments on fluorine nuclei indicate the need to take into account changes in the rate of ligand exchange and the effective charge of the complex particle when explaining the increase in the effectiveness of the influence of a paramagnetic complex on proton relaxation.

The high sensitivity of fluorine nuclei to changes in the concentration of paramagnetic ions in the course of complex formation makes it possible to determine the concentrations of paramagnetic ions by a volumetric method.

As an illustration, Fig. 4 gives the titration curve of copper ions contained in reagent-grade potassium fluoride with a solution of Trilon B. The copper concentration found by this titration ($1.3 \cdot 10^{-5}$) agrees well with the results of chemical analysis ($1.4 \cdot 10^{-5}$).

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