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Abstract

Full Text

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EFFECT OF PARAMAGNETIC IMPURITIES ON THE SPECTRA OF NUCLEAR MAGNETIC RESONANCE IN CERTAIN ORGANIC SUBSTANCES

(Presented by Academician A. E. Arbuzov, May 18, 1961)

Until now, the effect of paramagnetic impurities on proton resonance in liquids has been studied by methods of nuclear relaxation ($^{1-4}$).

It was of interest to determine how the presence of paramagnetic substances would affect individual lines of the fine structure of proton resonance, observed in organic liquids at high homogeneity of the field H_0. Some alcohols and glacial acetic acid were chosen as objects of investigation; the paramagnetic impurities used were: $MnCl_2$, $Mn(CH_3CO_2)_2 \cdot 2H_2O$, and $CuCl_2$. Proton-resonance measurements were carried out at a frequency of 30 MHz; the homogeneity of the field H_0 in the volume of the sample was of the order of 10^{-6}. At such homogeneity, ethyl alcohol CH_2CH_2OH gives three lines corresponding to the groups CH_3, CH_2, and OH, with relative intensities $3 : 2 : 1$ (Fig. 1a). All the lines in pure ethyl alcohol have the same width at half-height, corresponding to approximately 9 millioersteds. This width is due to the inhomogeneity and instability of the constant magnetic field. The true line width $1/T_2$ in pure alcohol, as is known, is incomparably smaller.

Fig. 1. Dependence of the NMR spectrum of C_2H_5OH on the concentration of Mn^{2+}

Upon adding anhydrous manganese chloride to the alcohol at a concentration N from 0.00065 mole/liter $MnCl_2$ to 0.4 mole/liter $MnCl_2$, a gradual change in the spectrum occurs. At first only a broadening of the lines is observed, the OH line changing most strongly (Fig. 1b). At a concentration $N = 0.004$ mole/liter, the OH line practically disappears (Fig. 1c). A further increase in the $MnCl_2$ concentration also leads to intense broadening of the CH_2 line (Fig. 1d), which

Fig. 2

Figure 2: Fig. 2

disappears at $N = 0.08$ mole/liter (Fig. 1e), and, finally, at a concentration $N = 0.4$ mole/liter the CH_3 line practically disappears (Fig. 1e).

The action of anhydrous copper chloride on the spectrum of C_2H_5OH is quite analogous to the action of manganese chloride, but the required concentrations of $CuCl_2$ are approximately fifteen times higher.

In addition to ethyl alcohol, the two-line spectra of ethylene glycol $HOCH_2CH_2OH$ and ethylene chlorohydrin $ClCH_2CH_2OH$ were studied; in the presence of $MnCl_2$, the line corresponding to the OH group first broadens and disappears, and then the line corresponding to the CH_2 group.

Finally, measurements were made in glacial acetic acid containing manganese acetate $Mn(CO_2CH_3)_2 \cdot 2H_2O$. Pure CH_3COOH gives two lines with an intensity ratio of $3:1$ (Fig. 2a). Dissolution of the paramagnetic substance leads to broadening of both lines (Fig. 2b), but the line corresponding to the OH group broadens more rapidly and disappears at $N \approx 0.015$ mole/liter (Fig. 2c). With a further increase in concentration, the CH_3 line continues to broaden—

···is obtained (Fig. 2g); however, it was not possible to achieve its complete disappearance because of the insufficient solubility of manganese acetate in CH_3COOH.

The results presented are of interest both from the standpoint of the theory of proton relaxation in liquids and from the standpoint of studying the structure of solutions. Since, in the presence of paramagnetic substances, the observed width of the fine-structure lines exceeds the width produced by the inhomogeneity of the field H_0, we are dealing with the true time T_2; in the presence of paramagnetic particles in the solution this time proves, generally speaking, to be different for each fine-structure line. The data we obtained for ethyl alcohol show that the quantity $1/T_2$ for each individual fine-structure line is approximately proportional to the square of the magnetic moment of the ion and also, apparently (if the relative intensity of the fine-structure lines is taken into account), inversely proportional to the cube of the distance between the paramagnetic ions and the protons of the given group. The latter dependence agrees with measurements of proton resonance in various Fe^{3+} complexes[3].

Fig. 2. Dependence of the NMR spectrum of CH_3COOH on the concentration of Mn^{2+}

It is also interesting to note the following. From work[4] it is known that the proton spin-lattice relaxation time T_1 for C_2H_5OH containing 0.02 mole/liter Mn^{2+} is 0.03 sec.; from our measurements it follows that the relaxation time T_2 at the indicated Mn^{2+} concentration for the CH_3 group is ~ 0.015 sec., and for the remaining groups it is incomparably shorter. It follows from this that the widths of the fine-structure lines in ethyl alcohol containing Mn^{2+} are determined mainly not by the spin-lattice interaction, but by the spin-spin interaction ($T_1 \gg T_2$).

Especially great prospects may be expected from the observed phenomenon in studying the structure of solvates in solutions. First of all, in each specific case one can judge which group of the solvating molecule adjoins the paramagnetic particle. In particular, from our measurements it follows that an alcohol molecule adjoins the paramagnetic particle by the OH group, while an acetic-acid molecule adjoins by the group

$$-\mathrm{C}=\mathrm{O}.$$

By carrying out more accurate quantitative measurements, it will undoubtedly be possible to estimate the distance between the paramagnetic particle and the nearest group of the solvating molecule.

It may be supposed that by other methods as well, for example by spin echo, it is possible to detect the existence of several proton relaxation times in solutions, analogous to those measured by us. However, our method has obvious advantages not only in its simplicity and visual character, but also in the fact that, in principle, it makes it possible to determine any number of T_2 times corresponding to different groups of protons.

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