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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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INVESTIGATION OF THE SOLVATION OF PARAMAGNETIC IONS IN ALCOHOL-WATER SOLUTIONS BY MEANS OF HIGH-RESOLUTION N.M.R.

(Presented by Academician A. E. Arbuzov, 23 V 1963)

In works ([1]-[3]) and others, the solvation of paramagnetic ions in alcohol-water solutions was investigated by means of optical spectra.

In the present work, the method of high-resolution n.m.r. has been applied to the study of this question. We used the effect of selective broadening of the lines of the n.m.r. spectrum of ethyl alcohol under the action of paramagnetic ions, described in works ([4], [5]). As the concentration of paramagnetic ions in alcohol increases, the lines of the n.m.r. spectrum broaden to unequal degrees. First the line of the OH group broadens, then that of the CH_2 group, and finally that of the CH_3 group. In mixed alcohol-water solutions a process of hydration occurs, i.e., displacement of alcohol molecules from the solvation shell of the paramagnetic ion by water molecules. In this case, naturally, the lines of the n.m.r. spectrum of the alcohol should narrow. It may be expected that the narrowing of the alcohol lines with increasing water content in the solution will also proceed differently: first the CH_3 line should narrow, then CH_2, etc. From the relative narrowing of the lines one can judge the hydration process occurring in the solution. Measurements were carried out on an n.m.r. spectrometer with a resolution of $\sim 5 \cdot 10^{-8}$, at a frequency of 30 MHz.

Solutions of paramagnetic salts $Cu(NO_3)_2 \cdot 3H_2O$, $CuCl_2$, $MnCl_2$, $Cr(NO_3)_3 \cdot 9H_2O$ in deuterated alcohol C_2H_5OD with the addition of various amounts of heavy water were investigated. Deuterated alcohol and heavy water were used in order to exclude the proton peak of water, which, being superimposed on the alcohol spectrum, distorts it. The deuterium resonance lies in much higher magnetic fields; therefore the lines from D_2O and the OD group of the alcohol were not observed.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

Fig. 1

Deuteration of the alcohol was carried out by us under laboratory conditions. The purity of the deuterated alcohol obtained was above 98% (as established by means of n.m.r. spectra).

For each paramagnetic salt a series of mixed alcohol–water solutions was prepared. The content of heavy water was varied from 5 to 70% in steps of 5%. The molarity of the paramagnetic substance in all solutions of a given series remained constant.

As a measure of the hydration process occurring in solution, the ratio of the amplitudes of the lines of the CH_3 and CH_2 groups, A_{CH3}/A_{CH2}, was taken. This ratio decreases with increasing water content in the solution. Beginning with a certain definite percentage of water content, further decrease of A_{CH3}/A_{CH2} ceases. This means that the alcohol is practically completely

displaced from the solvate shell of the paramagnetic ion. The value of A_{CH3}/A_{CH2} thereby becomes close to the ratio $3:2$ for pure alcohol.

Figure 1 shows the dependences of A_{CH3}/A_{CH2} on the percentage content of D_2O for solutions of the paramagnetic salts $CuCl_2$ and $Cu(NO_3)_2 \cdot 3H_2O$. As is seen from the graphs, in $CuCl_2$ solutions with concentrations 10^{-1} mol/l (Fig. 1, 1) and $5 \cdot 10^{-2}$ mol/l (Fig. 1, 2), practically complete displacement of alcohol from the solvate shell of Cu^{2+} occurs at a water content of $\sim 55\%$. In a $5 \cdot 10^{-2}$ mol/l solution of $Cu(NO_3)_2 \cdot 3H_2O$ (Fig. 1, 3), it occurs at a water content of $\sim 60\%$.

Fig. 2

Fig. 3

The hydration number determined from the graphs for Cu^{2+} is approximately 120 in all three cases. For a $4 \cdot 10^{-3}$ mol/l $MnCl_2$ solution, the curve of A_{CH3}/A_{CH2} versus the percentage water content is more gently sloping (Fig. 2). Complete displacement of alcohol occurs at $\sim 60\%$.

Calculations showed that, for all the investigated solutions of Cu^{2+} and Mn^{2+}, alcohol is practically completely displaced from the solvate shell of the paramagnetic ion when approximately 4 molecules of water are introduced per one molecule of alcohol.

We also carried out measurements at +60°. It was found that, for all solutions, as the temperature is raised the alcohol is displaced more readily (complete displacement occurs when approximately 2 water molecules per alcohol molecule are introduced into the solution), i.e., the strength of the alcohol solvates decreases with increasing temperature more rapidly than the strength of the aqueous ones. After the solutions were kept for 3 hours at +60° and cooled to room temperature, the effectiveness of the paramagnetic ions increased compared with solutions that had not been heated. The nature of this peculiar hysteresis phenomenon requires further study.

For a $6 \cdot 10^{-2}$ mol/l solution of $Cr(NO_3)_3 \cdot 9H_2O$, the measurements showed a more complex picture of solvation. The A_{CH3}/A_{CH2} curve proceeds very gently and "saturation" is not reached (Fig. 3).

The different slopes of the curves in Figs. 1-3 indicate unequal strengths of the solvates. The greater the slope of the curves, the stronger the solvation. This agrees with known data on the strength of the solvate shells of the ions studied. Thus, the lifetime of a water molecule in the first sphere of the Mn^{2+} ion is of the order of 10^{-8} sec ([6]). Therefore it is natural that molecules entering the first sphere of Mn^{2+} do not have time to become completely oriented, whereas in the stronger copper solvates much better orientation can be achieved and, correspondingly, we obtain a steeper slope of the A_{CH3}/A_{CH2} curve. In the Cr^{3+} ion, the first solvate sphere is exceptionally strong: the lifetime of a water molecule in it is measured in hours ([7]). Therefore, in our experiments the hydration process of Cr^{3+} is practically registered only in the second sphere, which gives an even smaller strength of hydrates than in the case of Mn^{2+}.

Thus, the high-resolution NMR method can be successfully used to study the solvation of paramagnetic ions in ternary and more complex systems.

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