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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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ASSOCIATION OF COMPLEX COPPER IONS IN SOLUTIONS

STUDY BY THE METHOD OF PARAMAGNETIC RESONANCE

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In studying the hyperfine structure of electron paramagnetic resonance (EPR) spectra of dilute solutions of complex copper ions, we encountered anomalous behavior which could not be explained on the basis of the theory of spectra and, as further study showed, is a consequence of association of the complex particles.

Fig. 1

In Figs. 1-3 are presented oscillograms of EPR curves obtained at an oscillating magnetic-field frequency $\nu_0 = 9395$ MHz and at room temperature for solutions of certain amine complexes of divalent copper. The narrow lines to the left of the curves are signals from the free radical α,α-diphenyl-β-picrylhydrazyl, used for calibration of the constant magnetic field H_0. Fig. 1 refers to 0.15 M solutions of monoethanolamine complexes. Earlier, by the method of proton magnetic resonance, it had been shown (^{1}) that in solutions monoethanolamine forms strong inner-complex compounds with Cu^{2+} ions, the most stable being complexes with coordination number three, presumably corresponding to the formula CuEtm_3^-, where Etm^- is the monoethanolamine ion $\mathrm{NH_2CH_2CH_2O}^-$. The sufficiently large excesses of monoethanolamine taken by us for preparing the solutions (see below) ensured the formation precisely of these complexes, which we shall conventionally denote CuEtm_3^-. The oscillograms of Figs. 1*a*–*e* show changes in the form of the spectra that occur when the solvent is changed in the sequence methanol (Fig. 1*a*)—ethanol (Fig. 1*b*)—propanol (Fig. 1*v*)—isopropanol (Fig. 1*g*)—butanol (Fig. 1*d*)—benzyl alcohol (Fig. 1*e*).

The alcohols used as solvents have approximately the same dipole moment, $\sim 1.7D$, but their dielectric constant decreases from the value $\varepsilon \simeq 33$ for methanol to $\varepsilon \simeq 13$ for benzyl alcohol. Under conditions of strong fields, which are realized at the chosen value of the frequency ν_0, the spectra should consist of four hyperfine-structure components corresponding to the spin value of the Cu^{63}/Cu^{65} nuclei, equal to 3/2. For a solution of $CuEtm_3^-$ in methyl alcohol (Fig. 1*a*) all components proved to be resolved. The spectrum has a noticeable asymmetry: the rightmost hyperfine component, corresponding to the value $I_z = +3/2$ (I_z is the nuclear magnetic quantum number), is broader and therefore less—

less intense than the others. Asymmetry of hyperfine-structure spectra has repeatedly been observed for solutions of magnetically anisotropic complexes ([2,3]) and arises when the characteristic frequency of Brownian rotation of the complexes, ν_c, is lower than the Larmor frequency ν_0. The asymmetry of the spectra increases upon a further decrease of ν_c and, conversely, disappears if $\nu_c > \nu_0$. These conclusions of work ([4]) will be used in the further discussion.

On going from a solution in methyl alcohol to a solution in ethyl alcohol ($\varepsilon \simeq 24$)*, the picture changes sharply (Fig. 1). An exchange curve with $g_{\text{eff}} \sim 2.09$** is superimposed on the hyperfine-structure spectrum, which coincides with the position of the hyperfine component $I_z = -\frac{1}{2}$ (second from the left). In addition, the hyperfine structure itself becomes sharply asymmetric—the width of the hyperfine components increases rapidly with increasing I_z. Owing to this, the hyperfine component $I_z = +\frac{3}{2}$ (which should be the farthest to the right) is strongly broadened and is not detected. The intensity of the exchange peak, as compared with the intensity of the hyperfine structure, increases for the solution in propyl alcohol ($\varepsilon \simeq 20$), remains approximately at the same level for the solution in isopropyl alcohol ($\varepsilon \simeq 18$), and slowly decreases on going to solutions in butyl ($\varepsilon \simeq 17$) and benzyl ($\varepsilon \simeq 13$) alcohols (Fig. 1 – , respectively).

The presence of exchange peaks quite unambiguously indicates the formation of associates that include at least two complex copper ions, the residence time of the ions in the associated state exceeding the reciprocal of the Larmor frequency. In a 0.15 *M* solution of $CuEtm_3^-$ complexes in methyl alcohol (Fig. 1) exchange is absent; however, if the dielectric constant of the solution is lowered by replacing in it approximately half of the methanol with ether ($\varepsilon_{\text{ether}} \simeq 4.3$), association occurs and an exchange peak appears (Fig. 1) ***.

The fact that exchange peaks appear as a result of lowering the dielectric constant of the solutions testifies to the important role of Coulomb (electrostatic) interactions in the formation of associates.

The association of $CuEtm_3^-$ ions on going from the solution in isopropyl alcohol (Fig. 1) to solutions in butyl (Fig. 1) and benzyl (Fig. 1) alcohols weakens somewhat, whereas, judging from the values of ε of these alcohols, it should have continued to increase. It must be taken into account, however, that in the same order in which the dielectric constant of the solutions decreases (Fig. 1 –

Fig. 2

Figure 2: Fig. 2

), their bulk viscosity increases[****]. The latter circumstance, by decreasing the probability of collisions of ions, is most likely the cause that slows the formation of associated particles.

Association of equally charged complex ions under the action of Coulomb attractive forces may be represented as occurring at the expense of mutual polarization of the complexes when they approach one another. However, this is not sufficient for an unambiguous explanation of the available experimental facts.

The phenomenon of association was also observed by us for a number of other complex copper ions. In Fig. 2 an EPR oscillogram is shown, obtained for a 0.15 *M* aqueous solution of ammine complexes $Cu(NH_3)_4^{2+}$. The curve has a shape due to the presence of unresolved hyperfine structure. With a comparatively small increase in the viscosity of the solution, by replacing in the solvent ~ 25% (by volume) of the water with glycerin, the relaxation time increases, which leads to narrowing of the hyperfine components and to the appearance of a clearly noticeable hyperfine structure (Fig. 2b) (4). However, a quite different situation obtains if the complexes $Cu(NH_3)_4^{2+}$ are dissolved in a medium with a sufficiently low dielectric constant. 0.15 M solutions of $Cu(NH_3)_4^{2+}$ complexes were prepared in ~ 90% (by volume) aqueous methanol, in ~ 84% (by volume) aqueous ethanol, in ~ 65% (by volume) aqueous propanol, and in ~ 60% (by volume) aqueous dioxane ($\varepsilon_{\text{dioxane}} \simeq 2.2$). As a result of measurements, identical exchange curves were obtained for all these solutions, with $g_{\text{eff}} \sim 2.10$ and with width $\Delta H \sim 219$ Oe, one of which is presented in Fig. 2c. Since the hyperfine structure due to monomeric ions $Cu(NH_3)_4^{2+}$ is completely absent, it may be concluded that practically all the complex particles are combined into dimers or larger formations. Similar results were also obtained for solutions of ethylenediamine complexes $CuEn_2^{2+}$ (En is an ethylenediamine molecule, $NH_2CH_2CH_2NH_2$). In a 0.15 M solution of $CuEn_2^{2+}$ complexes in water (Fig. 2c), as well as in methanol, asso-

Fig. 2

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[*] All quoted values of ε refer to the solvent.

[**] The position of the exchange peak here and in the other oscillograms of spectra where it is present is marked by a vertical arrow.

[***] In preparing the latter solution, the content of the complex-forming agent—monoethanolamine—was also somewhat increased (see below, the procedure for preparing the solutions).

[****] The range of increase of viscosity (η) is characterized by the following values (in centipoises): for methanol $\eta_{20^\circ} = 0.55$; for benzyl alcohol $\eta_{15^\circ} = 7.76$.

Fig. 3

Figure 3: Fig. 3

ciation is absent; but if ethyl alcohol is used as the solvent, an exchange peak appears against the background of the hyperfine structure (Fig. 2d).

Fig. 3

Obviously, the more concentrated the solution, the greater the probability of association should be. This regularity can be clearly traced for aqueous solutions of CuEn_2^{2+} complexes, which permit the creation of high concentrations. On going from 0.15 to 0.3 M concentration of CuEn_2^{2+} complexes, an exchange peak appears on the oscillogram of the hyperfine structure (Fig. 2e). The height of the exchange peak increases with further increase in the concentration of aqueous solutions of CuEn_2^{2+}, so that for a 1.2 M solution (Fig. 2g) only an intense exchange curve is observed ($g_{\mathrm{eff}} \sim 2.07$; $\Delta H \sim 150$ Oe), without any signs of hyperfine structure.

Association of CuEtm_3^- complexes in alcoholic solutions (Fig. 1) is disrupted under the influence of small additions of water ($\varepsilon \simeq 80$), which cause an increase in the total dielectric constant. This is shown in Fig. 3a–c. In a 0.15 M solution of CuEtm_3^- complexes in butanol containing $\sim 5\%$ (by volume) water (Fig. 3b), the intensity of the exchange peak (relative to the hyperfine structure) is substantially lower than in the same solution but in absolute butanol (Fig. 3a)*. With still higher water content, $\sim 10\%$ (by volume), the exchange peak disappears completely and the curve assumes the asymmetric form shown in Fig. 3c. Evidently, the sharply asymmetric form of the curve in Fig. 3c may be regarded as immediately preceding the appearance of an exchange peak. And since, as noted, the increase in the asymmetry of the spectra is a consequence of a lowering of the characteristic frequency of Brownian rotation of the complexes ν_c, it may be concluded that the observed association is preceded by a lowering of the frequency ν_c. Apparently, as ε of the solutions decreases, associates are first formed with a lifetime t_i smaller than the reciprocal value of the Larmor frequency (i.e., $t_i < 1/\nu_0 \sim 10^{-10}$ sec). Such associates, continuously breaking down and forming again, must hinder the Brownian rotation of the complexes. With a further decrease in ε, the associates become stronger, and when the lifetime of the complexes in the associated state t_i begins to exceed $1/\nu_0 \sim 10^{-10}$ sec, exchange interaction becomes effective and an exchange peak appears on the hyperfine-structure oscillograms. The value $t_i = 1/\nu_0 \sim 10^{-10}$ sec is the lower limit of the lifetime of associates detectable by the presence of exchange peaks at an oscillating magnetic-field frequency of the order of 10^4 MHz.

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* This curve was shown in Fig. 1d. Here it is given again for convenience of comparison with Figs. 3b and 3c.

Method of Preparing the Solutions

All solutions were obtained by dissolving weighed portions of copper chloride or nitrate and specified volumes of the required reagents (monoethanolamine, concentrated aqueous ammonia, ethylenediamine) in the corresponding solvents. Usually, chloride $CuCl_2 \cdot 2H_2O$ was used. The exceptions were aqueous solutions of $CuEn_2^{2+}$ complexes, for the preparation of which the initial salt was nitrate $Cu(NO_3)_2 \cdot 3H_2O$. Based on a $0.15\,M$ concentration of the complexes, the following amounts of reagents were taken (as percentages of the total solution volume): for aqueous solutions of $CuEn_2^{2+}$, 5%; for a methanol-ether solution of $CuEtm_3^{2+}$, 15%; in all other cases, 10%.

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References Cited

1. A. I. Rivkind, ZhNKh, 2, 1263 (1957).
2. B. R. McGarvey, J. Phys. Chem., 60, 71 (1956).
3. T. Vänngard, S. Akerström, Nature, 184, 183 (1959).

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