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V. M. Berdnikov, K. I. Zamaraev

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Abstract

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V. M. Berdnikov, K. I. Zamaraev

Investigation by N.M.R. and E.P.R. Methods of Electron-Exchange Interactions in Aqueous Solutions of Copper Ammine Complexes

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Paramagnetic complex metal ions with an unfilled $3d$ shell are active catalysts of oxidation–reduction reactions occurring in the liquid phase ([1,2]). In ([3]) the suggestion was made that the catalytic activity of these compounds may be associated with electron-exchange interactions (electron exchange). Since these interactions must lead to changes in the magnetic properties of the system, methods of magnetic radiospectroscopy can be used to study them.

Until recently, studies of exchange in solution had been carried out only for hydrated ions, which are catalytically only weakly active. With the aid of the e.p.r. method it was established that the effective exchange frequency for these ions is small, so that exchange in them is observed comparatively rarely and only in highly concentrated solutions (see the review in ([4])). The n.m.r. method, as far as we know, has not been used to study electron-exchange interactions in solutions.

It seemed of interest to study the exchange interaction in a solution of some complex ion possessing higher catalytic activity and to compare the data obtained with the results of studies of hydrated ions. As the object of study in the present work, copper ammine was chosen; it is an active catalyst of the decomposition reaction of hydrogen peroxide, the oxidation of phenols, etc. ([1]). The investigations were carried out by means of n.m.r. and e.p.r. methods.

It follows from theory ([5]) that electron exchange in aqueous solutions containing paramagnetic ions can lead to a nonlinear dependence between the concentration of these ions and the width $1/T_2$ of the n.m.r. spectra of water protons, whereas in the absence of exchange this dependence should be linear. The proton-resonance spectra of an aqueous solution of copper ammines containing 7.8 mole/liter NH_4NO_3 were recorded on an INM-3 spectrometer. The copper concentration in the form of $Cu(NO_3)_2$ was varied within the range from 0.0005 to 0.1 mole/liter. The mean coordination number of the complexes, $\bar{n}$, was varied in the interval from 4.3 to 5 by adding the necessary amount of NH_4OH*. The change in $\bar{n}$ was monitored by measuring the pH of the medium (see ([6])). Analysis of the spectra obtained showed that, in copper–ammonia solutions, the dependence between $1/T_2$ and the copper concentration $[Cu]_0$ at constant $\bar{n}$ is

Fig. 1. Plot of the dependence of the width of the proton-resonance spectrum on the copper concentration, $\bar{n} = 4.3$

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linear only in the interval $[Cu]_0$ from 0.0005 to 0.003 mole/liter, and becomes nonlinear at higher concentrations–

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* NH_4NO_3 was introduced into the solution in order to lower the pH and to prevent precipitation of copper hydroxide at small values of $\bar{n}$.

copper concentrations. As an example, Fig. 1 shows the plot of this dependence for solutions having $\bar{n} = 4.3$. It should be noted that, according to (7), for the hydrated copper ion no deviations from the linear dependence between $1/T_2$ and $[Cu]_0$ are observed up to $[Cu]_0 = 1.8$ mol/liter.

At a constant value of $\bar{n}$, the relative concentrations of ammine complexes of different composition cannot change when $[Cu]_0$ changes; consequently, the violation of proportionality between $1/T_2$ and $[Cu]_0$ cannot be associated with a shift of the chemical equilibrium. Therefore the observed deviations from the linear dependence between these quantities make it possible to conclude that electron exchange interactions arise already in highly dilute solutions of copper ammine complexes.

It was of interest to verify this conclusion also by means of another radiospectroscopic method–the e.p.r. method. From the works of (8) and others it is known that exchange interactions must change the shape of e.p.r. lines; moreover, for spectra possessing hyperfine structure (h.f.s.), the character of these changes depends on the ratio between the exchange frequency ν_e and the frequency ν_p corresponding to the hyperfine splitting. At $\nu_e < \nu_p$, the h.f.s. components, as ν_e increases, must first broaden and then, at $\nu_e \sim \nu_p$, merge into a single line. A further increase in ν_e must lead to narrowing of this line.

Fig. 1. Plot of the dependence of the width of the proton-resonance spectrum on the copper concentration, $\bar{n} = 4.3$

The e.p.r. spectra of copper-ammonia solutions were recorded on an EPR-2 IKhF spectrometer with a wavelength of 3.2 cm. The temperature of the samples during the measurements was maintained within $25 \div 30°$. The concentration of copper in the form of $Cu(NO_3)_2$ and $CuCl_2$ was varied in the range from 0.047 to 3.2 mol/liter. When the anion was replaced, no changes in the e.p.r. spectra were observed. The value of $\bar{n}$ in all experiments was constant and equal to 4.9. Ammonium salts were not added to the solutions under investigation.

The e.p.r. spectrum of a solution having $[Cu]_0 = 0.047$ mol/liter consists of four superposed h.f.s. components (the nuclear spin of copper is $I = 3/2$). The

Fig. 2. Plot of the dependence of the effective extent of the EPR spectrum on copper concentration, $\bar{n} = 4.9$. a–$Cu(NO_3)_2$, b–$CuCl_2$.

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g-factor at the center of the spectrum is equal to 2.120 ± 0.006, and the splitting between the h.f.s. components is $\Delta H_p = 65 \pm 5$ oersted. These parameters agree well with the values of the g-factor and ΔH_p of copper pentaammine obtained in (9). With increasing copper concentration the h.f.s. components gradually broaden and at $[Cu]_0 \approx 0.1$ mol/liter merge into one line with a g-factor still equal to 2.120. A further increase in $[Cu]_0$ leads to narrowing of this line. Fig. 2 shows the plot of the dependence on $[Cu]_0$ of the effective width of the spectrum ΔH_c^*, measured as the distance between the points of maximum slope of the absorption curve. It is seen from the figure that, when $[Cu]_0$ changes from 0.047 to 3.2 mol/liter, the value of ΔH_c^* decreases monotonically from ~ 260 to 50 oersted. Thus, the results of analysis of the e.p.r. spectra confirm the conclusion made above that electron exchange arises already in dilute aqueous solutions of copper ammine complexes. We note that in solutions containing the hydrated copper ion, even at concentrations above 4 mol/liter, exchange narrowing of the e.p.r. spectrum is not observed.

In the interval of copper concentrations from 0.26 to 3.2 mol/liter, the dependence between ΔH_c^* and $[Cu]_0$ is well described by the equation:

$$\Delta H_c^* = \frac{a}{[Cu]_0} + b, \tag{1}$$

where $a = 43$ Oe $\cdot$ mol $\cdot$ l^{-1}, $b = 29$ Oe, or, in frequency units, $a = 2.2 \cdot 10^8$ mol/l$^{-1} \cdot$ sec^{-1}, $b = 1.4 \cdot 10^8$ sec^{-1}. The quantity $a/[Cu]_0$ characterizes the broadening of the line due to differences in local magnetic fields averaged by exchange. $a/[Cu]_0 \sim (\Delta\nu)^2/\nu$, where $(\Delta\nu)^2$ is the mean value of the square of the shift of the resonance frequency caused by local fields. The quantity

$$b = \lim_{\nu_e \to 8} \Delta H_c^*$$

is the intrinsic linewidth, due only to spin-lattice interaction, since anisotropic spin-spin interactions under conditions of infinitely rapid exchange are averaged to zero.

Fig. 2. Plot of the dependence of the effective extent of the EPR spectrum on the copper concentration, $\bar{n} = 4.9$. a–$Cu(NO_3)_2$, b–$CuCl_2$.

From formula (1) it follows that the effective exchange frequency $\nu_e = k[Cu]_0$, where k is a constant. Taking into account that at $[Cu]_0 \approx 0.1$ mol/l the

condition $\nu_e \sim \nu_p$ must be satisfied, it is not difficult to calculate that $k \sim 10^9$ l · mol^{-1} · sec^{-1}.

Thus, the results obtained indicate a sharp increase in the intensity of the electron exchange interaction upon passing from the catalytically weakly active hydrated copper ion to the highly active copper complex with ammonia. To test the assumption that this effect may be connected with catalytic activity, it is necessary to carry out analogous studies of other catalytically active complexes.

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Institute of Chemical Physics
Academy of Sciences of the USSR

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