# ESR Investigation of Copper Ions on Several Kinds of Cation Exchange Resins

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Copper ions on several kinds of cation exchange resins were investigated by means of ESR spectroscopy. It was found that the motion of copper ions is restricted in the network of the ion exchange resin, and that the mobility of copper ions is closely connected with the chemical interaction of the copper ions with the fixed ionic groups of the resins. The mobility of copper ions is in the order of; on the sulfonic group>on the phosphonic group>on the carboxylic group>on the iminodiacetate group. This sequence is the reverse of the selectivity for the copper ion. The effect of the water molecules involved in ion exchange resins is also considered, and the copper species on each ion exchange resin are assumed.

It is interesting to investigate the physico-chemical properties of hydrated ion-exchange resin by NMR, ESR, and IR measurements, because it can be considered as a concentrated electrolyte solution. Studying the behavior of ion-exchange resin may also be helpful in making clear the behavior of a concentrated electrolyte solution.

With this in view, Zundel *et al.*[1] investigated in detail by infrared measurements the water molecules involved in ion exchange resins, and several recent reports have been concerned with the water molecules in ion exchange resins, which were investigated by the NMR technique.[2]

However, only a few studies using ESR measurements have been reported.[3] By ESR measurements, although the measurable ions are limited in such substances as Cu(II), Mn(II), VO(II), and Fe(III), the behavior of ions on ion exchange resin can be directly observed instead of the water molecules.

In this paper, we will describe the results of the investigation of copper ions on several kinds of cation exchange resins by ESR measurements. The bonding of copper ions with fixed ionic groups, the mobility of the copper ions, and the effect of water molecules will be discussed. It will be concluded that the mobility of copper ions with fixed ionic groups, and that water molecules also influence the mobility of copper ions and the bonding of copper ions when copper ions are exchanged on ion exchange resin of either the sulfonic- or phosphonic-acid type.

## Experimental

*Materials.* Cation exchange resins used were as follows, Dowex 50W X-2, 4, 8, and 16(sulfonic-acid-type cation exchange resin), Amberlite IRC 50(carboxylic-acid-type cation exchange resin), and Dowex A-1 (chelating ion-exchange resin containing an iminodiacetate group). These ion exchange resins were conditioned by the usual method.

*Preparation of Samples.* Wet ion exchange resin/10 m*l*, Na form was equilibrated with 20 m*l* of a copper nitrate solution of $10^{-3}$ mol/*l* for 24 hr, then it was collected by filtration, washed thoroughly with distilled water, and kept in a desiccator in which the relative humidity was 100%.

*Measurements.* A Japan Electron Optics Co., Ltd. ESR spectrometer model JES. ME 3X was used at room temperature or at 77°K. The modulation frequency was 100 kHz, and the modulation width was 5 gauss.

## Results and Discussion

The ESR line shape of copper ions on each ion exchange resin showed a well-resolved spectrum at 77°K, suggesting that the copper ions were homogeneously dispersed. Moreover, at room temperature, the ESR line consists of an asymmetric single line or a line consisting of $g_{//}$ and $g_{\perp}$ components. This suggests that the motion of copper ions was affected. It was found that the motion of copper ions was affected by the fixed ionic groups and also by the amount of water in the ion exchange resins.

*(1-1) The Influence of the Amount of Water in the Ion Exchange Resins on the Motion of Copper Ions.* Figure 1 shows the influence of the amount of water in Dowex 50 W on the ESR line shape of copper ions. The ESR spectrum shows an asymmetric single line, not a symmetric one, when the ion exchange resin is full of water. With the decrease in the amount of water in the ion exchange resin, the ESR spectra show $g_{//}$ and $A_{//}$ components. The change in these spectra is very similar to that in the spectra of copper ions obtained by Kneubühl[4] in glycerin. He discussed the influence of the viscosity of the solvent on the motion of copper ions and showed that the increase in viscosity causes a slower Brownian motion, resulting in the ESR spectra with $g_{//}$ and $A_{//}$ components of copper ions. This suggests that the decrease in the amount of water in ion exchange resin causes a slower Brownian motion of copper ions on ion exchange resin. In other words, the decrease in the amount of water from the network of the ion exchange resin results in an increase in the microscopic viscosity and a large correlation time, $\tau_c$.

Figure 2 shows the effect of the DVB (divinylbenzene) content in the resin on the Brownian motion. It shows

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[1] G. Zundel, "Hydration and Intermolecular Interaction", Academic Press, 1969, and literature cited in.

[2] for example, a) J. E. Gordon, *J. Phys. Chem.*, **66**, 1150 (1962); b) R. W. Creekmore and C. N. Reilley, *Anal. Chem.*, **42**, 570 (1970); c) L. S. Frankel, *Anal. Chem.*, **42**, 1638 (1970).

[3] a) R. J. Faber and M. T. Rogers, *J. Amer. Chem. Soc.*, **81**, 1849 (1959). b) C. Heitner-Wirguin and R. Cohen, *J. Phys. Chem.*, **71**, 2556 (1967). c) C. Heitner-Wirguin, and R. Cohen, *Inorg. Chim. Acta*, 3: 4, 647 (1969).

[4] F. K. Kneubühl, *J. Chem. Phys.*, **33**, 1074 (1964).

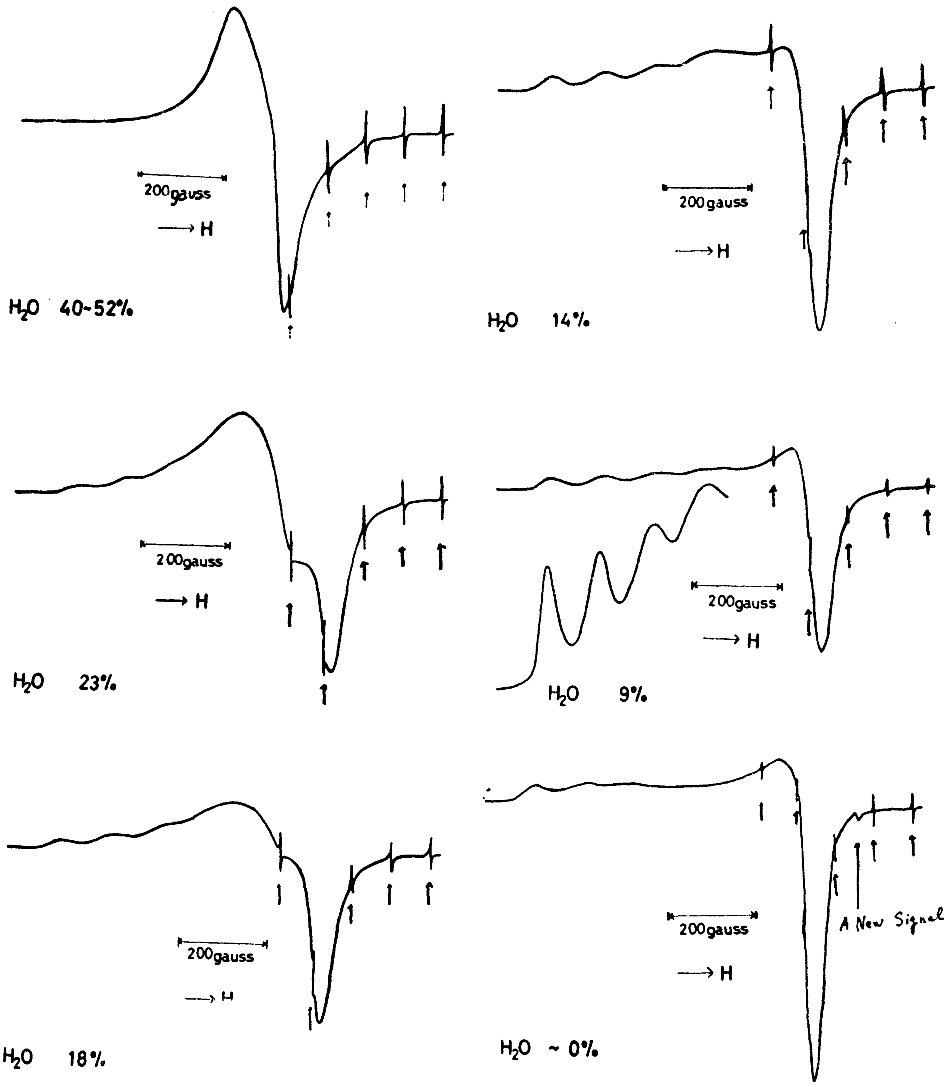

Fig. 1. ESR spectra of copper ions sorbed on Dowex 50W X-8, containing various amount of water. The arrows show the absorption signal of $Mn^{2+}$ as standard.

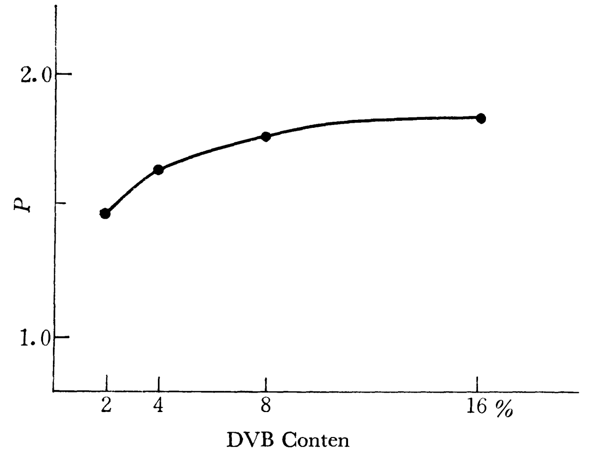

Fig. 2. Influence of DVB content on the motion of copper ion sorbed on Dowex 50W.

that the Brownian motion becomes slower with the increase in the DVB content. P indicates the ratio of the half maximum line width in the lower magnetic field to that in the higher magnetic field.[5] When P is equal to unity, the movement of copper ions is as fast as in an aqueous solution, while when P is larger than unity, the movement is slower than in an aqueous solution. The amount of copper ions sorbed was about 0.02 mmol/m*l* ion exchange resin. In this concentration range, the influence of dipolar interaction or electron exchange interaction is negligible. There are several points to be considered with regard to the effects of the increase in DVB content—the decrease in the amount of water in the ion exchange resin per unit of volume or per unit of weight, the increase in the number of sulfonic groups per unit of volume, and the decrease in the average pore diameter of the network. This last effect, however, seems to have little influence on the motion of copper ions, since the average pore diameter is about 16.9 Å for the ion exchange resin containing 15% of DVB,[6] this value is sufficiently large for the

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[5] S. Fujiwara, S. Katsumata, and T. Seki, *J. Phys. Chem.*, **71**, 115 (1967).

[6] M. Senō and T. Yamabe, This Bulletin **37**, 754 (1965).

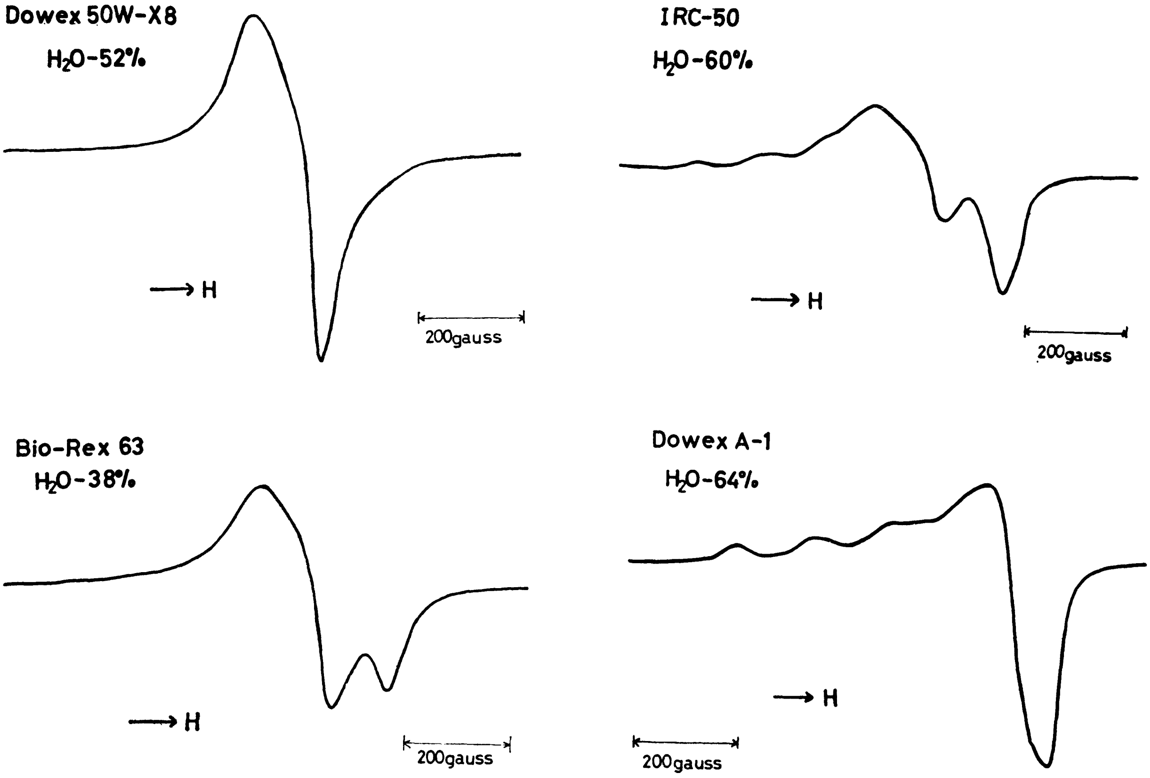


Fig. 3. ESR spectra of copper ions sorbed on various kinds of ion exchange resins at room temperature. The arrows show the absorption signal of $Mn^{2+}$ as standard.

copper ion radius. On the other hand, the other two factors are important, because the decrease in the amount of water is responsible for the slow Brownian motion of copper ions mentioned above, and because the increase in the number of sulfonic groups causes the increase in the amount of counter ions per unit of weight or per unit of volume of the ion exchange resins. The latter results in the decrease in the number of water molecules per cation; therefore, the copper ions are tightly attached to the sulfonic groups. A similar result was obtained by Creekmore and Reilley.[2b] They observed line broadening of the NMR spectra of $Na^+$ on Dowex 50 W.

*(1-2) Influence of Fixed Ionic Groups on the Motion of Copper Ions on Ion Exchange Resins.* Figure 3 shows the line shape of the copper ion on various ion exchange resins, which were equilibrated with a relative humidity of 100% at room temperature. The amount of copper ions sorbed was about 0.02 mmol/m*l* ion exchange resin. As can be seen from the figure, the motion of copper ions sorbed is affected more strongly by the kind of fixed ionic group than by the amount of water in the resin. For example, Dowex A-1, containing about 64% of water, shows $g_{//}$ and $A_{//}$ components in its ESR spectrum, suggesting a very slow motion, while Dowex 50W, containing about 52% of water, shows an asymmetric single line spectrum and no $g_{//}$ and $A_{//}$ components. From this comparison, it can be said that the mobility of copper ions decreases in the order of; on the sulfonic group>on the phosphonic group>on the carboxylic group>on the iminodiacetate group. This sequence is the reverse of the selectivity of copper ions. In other words, the stronger the chemical interaction of a fixed ionic group with copper ions, the slower the Brownian motion of the copper ions. This will be discussed in detail in the following section (2). In the higher concentration region of copper ions, we also observed the influence of the difference in the mobility of copper ions on the ESR line shape. In the iminodiacetate group, the line shape changed little except for a little line broadening, even in the higher concentration region of copper ions, while in sulfonic groups P approached to unity with increase in the copper ion concentration, as is shown in Fig. 4. This difference can be interpreted as follows. As the mobility of copper ions on sulfonic groups is less restricted in the network of ion exchange resin, copper ions can interact with each other by collision in the higher concentration region of copper ions. Therefore, the asymmetry due to a slow Brownian motion in the lower concentration region is averaged out by such strong interaction as electron exchange, resulting in a symmetric single line of the ESR spectrum.

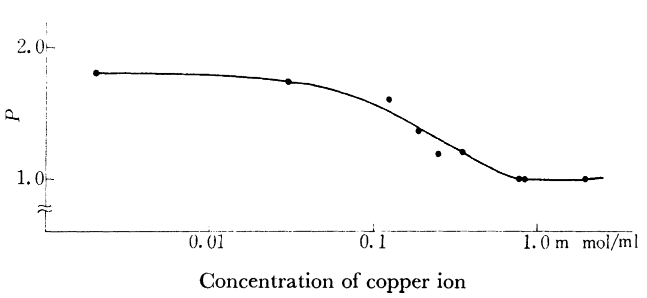


Fig. 4. Concentration dependence of copper ions on P.

Furthermore, a narrowing of the line width was observed. When P is equal to unity, the line width, $\varDelta H_{pp}$, was 110 gauss a value which was consistent with that reported as the exchange narrowed line width by Fujiwara and Hayashi.[7] On the other hand, in iminodiacetate groups, the mobility of copper ions is too restricted for copper ions to move around; therefore, an increase in copper ions only causes dipolar interaction, resulting in line broadening.

TABLE 1.

| Ion Exchange resin | $g_{//}$ | $g_{\perp}$ | $A_{//}$ $\times 10^{-4}$ cm$^{-1}$ | *d–d* band maxima |
|---|---|---|---|---|
| Dowex 50W (hydrated) | 2.408 | 2.087 | 135 | ~800m$\mu$ |
| (dehydrated)[a] | 2.438 | 2.09 | 114 | —— |
| Bio-Rex 63 (hydrated) | 2.381 | 2.08 | 134 | ~800m$\mu$ |
| (dehydrated)[a] | 2.419 | 2.08 | 113 | —— |
| Amberlite IRC 50 (hydrated) | 2.338 | 2.07 | 145 | ~690m$\mu$ |
| (dehydrated)[a] | 2.323 | 2.066 | 146 | —— |
| Doxew A-1 (hydrated) | 2.275 | 2.07 | 151 | ~710m$\mu$ |
| (dehydrated)[a] | 2.282 | 2.074 | 149 | —— |
| Copperacetatemonohydrate[b] | 2.344 | 2.053<br>2.093 | 80 | |
| Zinc-doped Copperacetate-monohydrate[c] | 2.344 | 2.052<br>2.082 | 147 | |

All *g*- and *A*-values were obtained at 77°K and amount of copper ion sorbed was about 0.02 mmol/m*l* ion exchange resin.

a) ion exchange resin was dehydrated in vacumm at $10^{-3}$ mmHg for 24 hr at room temperature, at 50°C and at 100°C, but it was not observed the influence of dehydration temperature on *g*- and *A*-values.

b) see Ref. 10.

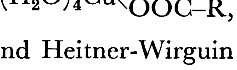
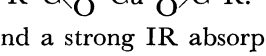
c) see Ref. 11.

*(2) Copper Species on Each Ion Exchange Resin.* Table 1 shows the *d–d* band absorption maxima and the *g*- and *A*-values of copper ions on hydrated ion exchange resins and on dehydrated ones. The values for hydrated ion exchange resins agree well with those obtained by Cohen and Heitner-Wirguin.[3c] They assumed that the copper species on hydrated Dowex 50W was $[Cu(H_2O)_6]^{2+}$ on the bases of a comparison of the *g*-values and *d–d* band absorption maxima of the aqueous solution of $[Cu(H_2O)_6]^{2+}$ with those of copper ions on Dowex 50W.[3b] However, as can be seen from Table 1, the *g*-values increased and the $A_{//}$ value decreased when Dowex 50W was dehydrated in a vacuum at $10^{-3}$ mmHg for 24 hr.[8] These changes may be due to a decrease in the coordination number of the water molecules around the copper ions. In Table 2, there are listed the *g*- and *A*-values of copper ions in $H_2O$-ethyleneglycol, those of copper *p*-toluenesulfonic acid in $H_2O$ and those of copper polystyrene sulfonic acid in $H_2O$; almost all were the same and coincided well with those of copper ions on hydrated Dowex 50W. In the media of sulfuric acid, however, the *g*-vaulues of copper ions increased slightly and the *A*-value decreased with the increase in the coordination of sulfuric acid. This can be interpreted as being due to the decrease in the number of water molecules around copper ions as a result of dehydration by sulfuric acid. This tendency of change in *g*- and *A*-values was consistent with the results on copper ions on hydrated and dehydrated Dowex 50W. Similar results were obtained by Zundel and Murr[9] by studying the infrared spectra. They concluded that, when the resin was hydrated, the copper ion was $[Cu(H_2O)_6]^{2+}$, and that when it was dehydrated, the copper ions was $[Cu(H_2O)_4]^{2+}$. It is difficult to estimate the coordination number of water molecules from the ESR data, but it seems reasonable, in view of the Jahn-Teller effect, to assume that the coordination number of water molecules decreases from six to four upon dehydration. As is well known, as a result of the Jahn-Teller effect one copper ion interacts with four ligands more strongly than with the other two ligands. Therefore, two among six water molecules coordinated with the copper ion are rather easily dehydrated. Similarly, copper ions on Bio-Rex 63 are $[Cu(H_2O)_6]^{2+}$ when hydrated and $[Cu(H_2O_4)]^{2+}$ when dehydrated. These results suggest that the sulfonic and phosphonic groups interact with copper ions only by means of electro-static force. Moreover the difference in the mobility of copper ions may be due to the difference in the charge number of the fixed ionic groups. The sulfonic group is one minus ion, while the phosphonic group can be two minus.

TABLE 2. *g*- AND *A*-VALUES OF COPPER ION VARIOUS FROZEN SOLUTION AT 77°K

| | Volume Ratio of Solvent | $g_{//}$ | $g_{\perp}$ | $A_{//}$ $\times 10^{4}$ cm$^{-1}$ |
|---|---|---|---|---|
| $Cu(NO_3)_2$/water-ethyleneglycol | 1:5 | 2.406 | 2.084 | 133 |
| $Cu(NO_3)_2$-*p*-toluenesulfonic acid/water | | 2.383 | 2.091 | 133 |
| $Cu(NO_3)_2$-polystyrenesulfonic acid/water | | 2.413 | 2.085 | 133 |
| $Cu(NO_3)$/water-sulfuric acid | 5:1 | 2.40 | 2.08 | 145 |
| | 1:5 | 2.44 | 2.10 | 123 |
| | 1:10 | 2.48 | 2.10 | 104 |
| | 1:500 | 2.48 | 2.10 | 98 |

Concentration of copper ion was about $10^{-3}$ mol/*l*.

The *g*- and *A*-values of copper ions on Amberlite IRC 50, which were not influenced by dehydration, suggest a strong interaction of copper ions with the carboxylic group. The form of the copper species can be assumed to be $[Cu(OOC-R)_2]_2$,  $(H_2O)_4Cu\langle\begin{matrix}OOC-R\\OOC-R\end{matrix}$, or  $R-C\langle\begin{matrix}O\\O\end{matrix}Cu\begin{matrix}O\\O\end{matrix}\rangle C-R$. Cohen and Heitner-Wirguin found a strong IR absorption at 1650 cm$^{-1}$ and attributed it to COO–M groups; they also found broad absorption maxima usually found for octahedral copper carboxylates, at 14300 cm$^{-1}$. They proposed the second form for copper species on IRC 50.[3c] However, the data obtained by them strongly suggest that copper ions form chelate bonding with carboxylic groups, but

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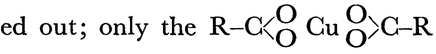
[7] S. Fujiwara and H. Hayashi, *J. Chem. Phys.*, **43**, 23 (1965).

[8] A new ESR signal always appeared at about 3360 gauss; the same magnetic field as in the absorption of DPPH, after the dehydration of the ion exchange resin. This will be reported elsewhere in more detail.

[9] G. Zundel and A. Murr, *Z. Phys. Chem.*, **54**, 59 (1967).

give weak evidence of coordination by four water molecules. We propose the last form for it for the following reasons. First, it should be noted that copper ions on the carboxylic group exists as a monomer, not a dimer, which is the first form, although copper ions generally form a dimer with acetic acid and other fatty acids. The $g$- and $A$-values have already been obtained for copper acetate monohydrate,10) which is a dimer form, and zinc-doped copper acetate monohydrate,11) X-ray-12) or $\gamma$-ray-13) irradiated copper acetate monohydrate, which are monomer forms.14) Moreover, the ESR spectrum of copper ions on the carboxylic group showed only a doublet spectrum and the $g$- and $A$-values are consitent with those of the monomer form, Second, no influence of dehydration on $g$- and $A$-values was observed, and these was a restricted motion of copper ions; these facts suggest that water molecules have little influence on the bonding or mobility of copper ions. If one copper ion is surrounded by four water molecules as Cohen *et al.* proposed, the copper ion is mobile, as are copper ions on the sulfonic group, by the rapid exchange of water molecules from coordination sphere to the outer sphere; furthermore, two of the water molecules around the copper ion are unstable upon dehydration, and the dehydration will cause a change in the $g$- and $A$-values. As has been mentioned above, however, the $g$- and $A$-values changed little upon dehydration. Therefore, the second form can be ruled out; only the  $\mathrm{R{-}C}{<}^{\mathrm{O}}_{\mathrm{O}}\,\mathrm{Cu}\,{}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{C{-}R}$ model can well explain these results.

The copper ion on Dowex A-1 was discussed in detail by Cohen and Heitner-Wirguin;3c) they assumed that the iminodiacetate group acts as a trivalent ligand when the copper ion is sorbed from a neutral solution. Considering the coincidence of our $g$- and $A$-values with those obtained by them, the small influence of the dehydration on the $g$- and $A$-values, the very slow motion of the copper ion, our results agree well with theirs.

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10) K. D. Bowers and J. Owen, *Rept. Progr. Phys.*, **18**, 304 (1955).

11) G. F. Kokoszka, H. C. Allen, Jr., and G. Gordon, *J. Chem. Phys.*, **42**, 3693 (1965).

12) A. Kawamori, *Bull. Am. Phys. Soc. Ser.* II, **14**, 599 (1969).

13) U. Sakaguchi, Y. Arata, and S. Fujiwara, *J. Chem. Phys.*, **53**, 464 (1970).

14) Strictly speaking, copper acetate monohydrate does not change its dimer form upon X-ray or $\gamma$-ray irradiation or by dopetion by zinc ions. However, the elctronic exchange interaction between copper ions disappears and the elctronic behavior of the copper ion is that of a monomer.