carbonyl fluoride complexes. Chemical oxidation of *cis*-Mo(CO)$_2$(dpe)$_2$ (dpe = 1,2-bis(diphenylphosphino)ethane) with NO$^+$PF$_6^-$ actually produces Mo(CO)$_2$(dpe)$_2$F.[43] Electrochemical oxidation of *cis*-Mo(CO)$_2$(dpe)$_2$ in CH$_2$Cl$_2$ occurs via two one-electron oxidation steps.[44] Controlled potential oxidative electrolysis in the presence of deliberately added fluoride, as might be expected, produces the stable seven-coordinate complex Mo(CO)$_2$(dpe)$_2$F (identified by infrared spectrum and comparison of other properties with an authentic sample) which has been well-characterized.[43] This example confirms our contention that electrochemical synthesis should provide a general route to preparation of carbonyl fluoride complexes.

Registry No. LiTFA, 2923-17-3; TFA$^-$, 14477-72-6; [B][Cr(CO)$_5$F] [B = dibenzo-18-crown-6-K], 101565-51-9; [B][Cr(CO)$_5$Cl] [B = dibenzo-18-crown-6-K], 101629-47-4; [B][Cr(CO)$_5$Br] [B = dibenzo-18-crown-6-K], 101565-52-0; [B][Cr(CO)$_5$I] [B = dibenzo-18-crown-6-K], 101565-53-1; Cr(CO)$_6$, 13007-92-6; Cr(CO)$_5$F, 101565-54-2; Cr(CO)$_5$F$^+$, 101565-55-3; Mo(CO)$_2$(dpe)$_2$F, 101565-56-4; *cis*-Mo(CO)$_2$(dpe)$_2$, 17523-42-1; F$^-$, 16984-48-8; Et$_4$NF, 665-46-3; Pt, 7440-06-4; Au, 7440-57-5; C, 7440-44-0.

---

[43] Snow, M. R.; Wimmer, F. L. *Aust. J. Chem.* **1976**, *29*, 2349.

[44] Wimmer, F. L.; Snow, M. R.; Bond, A. M. *Inorg. Chem.* **1974**, *13*, 1617.

Interaction Modes between Heavy Metal Ions and Water-Soluble Polymers. 1. Spectroscopic and Magnetic Reexamination of the Aqueous Solutions of Cupric Ions and Poly(vinyl alcohol)

Hiroshi Yokoi,* Satoshi Kawata, and Masamoto Iwaizumi

Contribution from the Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai 980, Japan. *Received September 16, 1985*

Abstract: The interaction mode between cupric ions and poly(vinyl alcohol) (PVA) in aqueous solutions has been reexamined in detail by EPR, NMR, magnetic susceptibility, and optical absorption techniques. Cupric ions exist as the olated polynuclear complex of Cu(OH)$_2$ solubilized by PVA at pH >6 and as ordinary hydrated ions at pH <6. This solubilization mechanism at pH >6 is of an inclusion type due to hydrophobic interaction, where Cu(OH)$_2$ is included by PVA chains with hydrophobic backbones toward the inside and with hydrophilic OH groups toward the outside of bulk water. This is a new interaction mode in the chemistry of polymer–metal complexes.

The polymer–metal complex has been the subject of increasing interest recently in the fields of catalytic reactions and metal ion separations,[1] in connection with biochemistry and environmental chemistry. Poly(vinyl alcohol) (PVA) is a simple synthetic water-soluble polymer. Aqueous solutions of cupric ions and PVA show a green coloration at pH >6,[2–4] with a remarkable decrease of viscosity.[5,6] This was interpreted by Kuhn et al. as a result of the formation of stable mononuclear copper(II) complexes with hydroxyl groups of PVA.[3] Curiously, the validity of this interpretation has not been questioned but generally accepted.[7] From the standpoint of coordination chemistry, it seems unlikely that alcoholic OH groups deprotonate at pH <7 to coordinate to cupric ions, even in the polymer domain, because the OH groups are generally assumed to have pK_a ~ 16.[8]

The purpose of this paper is to reinvestigate the aqueous solutions of cupric ions and PVA by spectroscopic and magnetic techniques and to report a new interaction mode between cupric ions and PVA, contradicting the above interpretation. This new interaction mode is very suggestive in considering the interaction between heavy metal ions and various natural macromolecules.

Experimental Section

Spectroscopic and Magnetic Measurements. A Varian E-4 EPR spectrometer (X-band) was used to measure EPR spectra of aqueous sample solutions at room temperature and of their frozen solutions at 77 K. All the EPR sample solutions contained 2.50 mM Cu^{2+}, 50 mM PVA (polymer residue concentration), and 0.10 M NaClO$_4$. The pH adjustment was done throughout this work without any buffer. A JEOL Model JNM-FT90Q FT NMR spectrometer was used in ^{1}H NMR studies and in magnetic susceptibility measurements by the Evans method at room temperature.[9] Aqueous solutions for ^{1}H NMR measurements contained 100 mM PVA and Cu^{2+} at various concentrations. In the application of the Evans method, 2% *tert*-butyl alcohol was used as an indicator. Visible and UV spectra were recorded at room temperature on a Shimadzu UV-240 spectrophotometer, using quartz 10- and 1-mm cells.

Chemicals. Hydrolyzed (100%) PVA with the average molecular weight 14 000 was purchased from Aldrich Chemical Co. The concentration of PVA was expressed in terms of the monomeric residues. All other reagents were of reagent grade or higher and were used without further purification.

Results and Discussion

EPR and Magnetic Susceptibility. Figure 1 shows EPR spectra both of an aqueous Cu^{2+}–PVA solution at pH 3.0 at room temperature and of its frozen solution at 77 K. These spectra were

---

[1] Pittman, C. U., Jr. In *Polymer-Supported Reaction in Organic Synthesis*; Hodge, P., Sherrington, D. C., Eds.; Wiley: New York, 1980; Chapter 5. Akelah, A.; Sherrington, D. C. *Chem. Rev.* **1981**, *81*, 557. Skorobogaty, A.; Smith, T. D. *Coord. Chem. Rev.* **1984**, *53*, 55. Sahni, S. K.; Reedijk, J. *Coord. Chem. Rev.* **1984**, *59*, 1.

[2] Saito, S.; Okayama, H. *Kolloid Z. Z. Polymn.* **1954**, *139*, 150.

[3] Kuhn, W.; Toth, I. *Z. Naturforsch.* **1963**, *18A*, 112. Kuhn, W.; Toth, I.; Kuhn, H. J. *Makromol. Chem.* **1963**, *60*, 77.

[4] Gelfman, A. Ya.; Kvyatkovskaya, E. F.; Ruzan, R. G.; Skorobogatov, B. S. *Vysokomol. Soedin.* **1963**, *5*, 1534.

[5] Hojo, N.; Shirai, H.; Sakata, K.; Fukuda, M. *J. Chem. Soc., Jpn. Ind. Chem. Sect.* **1970**, *73*, 1862.

[6] Hojo, N.; Shirai, H.; Hayashi, S. *J. Polym. Sci.* **1974**, *C-47*, 299.

[7] Hojo, N.; Shirai, H. *J. Chem. Soc. Jpn.* **1972**, *96*, 1316.

[8] Riddick, J. A.; Bunger, W. B. In *Techniques of Chemistry*, 3rd ed.; Weissberger, A., Ed.; Wiley-Interscience: New York, 1970; Vol. 2, pp 146.

[9] Evans, D. F. *Proc. Chem. Soc.* **1958**, 115. Evans, D. F. *J. Chem. Soc.* **1959**, 2003. Loliger, J.; Scheffold, R. *J. Chem. Educ.* **1972**, *49*, 646.

0002-7863/86/1508-3358$01.50/0

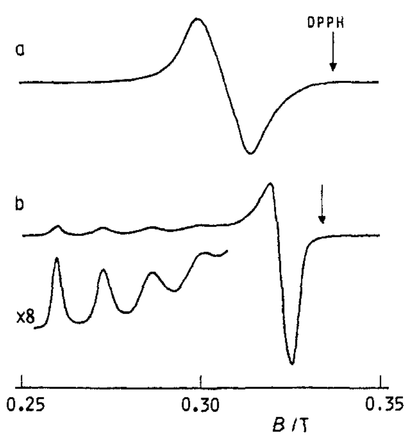

Figure 1. X-Band EPR spectra of aqueous Cu^{2+}–PVA solutions at pH 3.0 ([Cu^{2+}] = 2.50 mM; [PVA polymer residue] = 50.0 mM; [NaClO$_4$] = 0.10 M): (a) observed at room temperature (g_0 = 2.17); (b) observed at 77 K ($g_{\parallel}$ = 2.420; $|A_{\parallel}|$ = 0.0138 cm^{-1}).

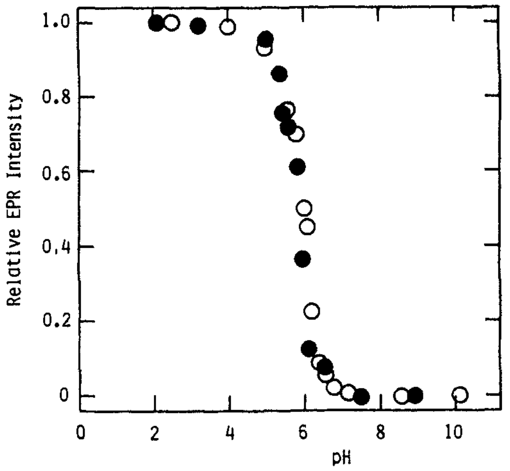

Figure 2. pH dependence of the intensities of room temperature EPR spectra for aqueous Cu^{2+} solutions with PVA (●) and without PVA (○) (the same respective concentrations of Cu^{2+}, PVA, and NaClO$_4$ as in Figure 1).

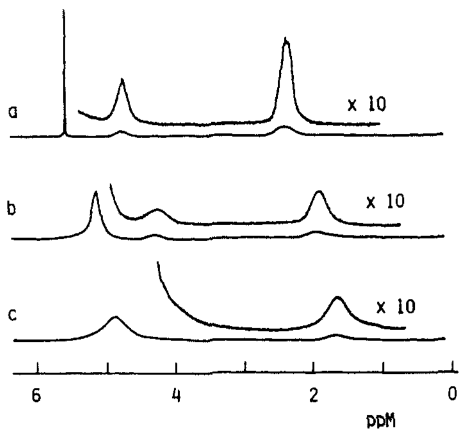

Figure 3. ^{1}H NMR spectra of aqueous Cu^{2+}–PVA solutions with [PVA polymer residue] = 100 mM at pH 3.0 at room temperature with the following Cu^{2+} concentrations (mM): (a) 0; (b) 40.0; (c) 100.

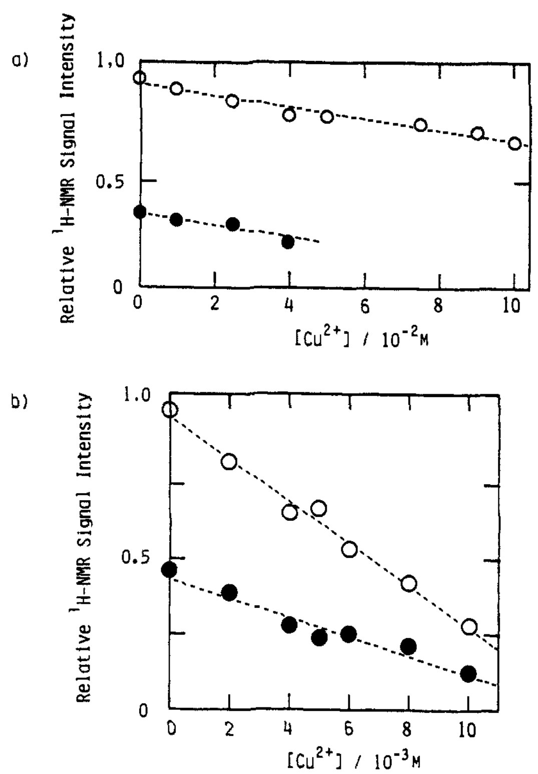

Figure 4. Plots of ^{1}H NMR signal intensities for CH$_2$ (○) and CH (●) in PVA against the concentration of Cu^{2+} at room temperature ([PVA polymer residue] = 100 mM): (a) pH 3.0; (b) pH 7.0.

almost identical with those of the corresponding solutions without PVA, indicating that both EPR spectra in Figure 1 are due to ordinary hydrated cupric ions. Interestingly, these EPR spectra were pH dependent not in line shape and position but in intensity. Plots of the intensities of room temperature EPR spectra against pH (Figure 2) show that the intensities decrease steeply in the pH range 5.5–6.5 and are reduced to almost zero at pH 7.0. Similarly, the frozen solution EPR spectra decreased steeply in intensity around pH 6.0 and disappeared near pH 8.0

The pH at the above sharp decay in EPR intensity is coincident with pH 5.9 at which cupric hydroxide is formed in aqueous Cu^{2+} solutions.[10] Similar plots for aqueous Cu^{2+} solutions without PVA (Figure 2) indicate that a sharp decay in EPR intensity for aqueous Cu^{2+} solutions parallels the formation or precipitation of apparently EPR-silent cupric hydroxide. The fact that both aqueous Cu^{2+} solutions with and without PVA are identical in the pH dependence of EPR intensity (Figure 2) means that cupric hydroxide is formed without precipitation in aqueous Cu^{2+}–PVA solutions at pH 6, leading to the conclusion that the PVA functions as a solubilizing agent for cupric hydroxide, as described later.

The effective magnetic moments (μ_{eff}) determined for aqueous Cu^{2+}–PVA solutions by magnetic susceptibility measurements were 1.81 ± 0.02 μ_B at pH 3.0 and 1.33 ± 0.02 μ_B at pH 7.0. The former obviously corresponds to hydrated cupric ions, whereas the latter is so small as to show the formation of a polynuclear copper(II) complex with a fairly strong antiferromagnetic interaction.[11] This polynuclear complex is nothing but cupric hydroxide, which has OH bridging groups capable of such a strong antiferromagnetic interaction. In conclusion, in aqueous Cu^{2+}–PVA solutions at pH >6, there exists no mononuclear copper(II) complex, but the cupric hydroxide solubilized by PVA, contrary to Kuhn's expectation.

^{1}H NMR. ^{1}H NMR studies of aqueous Cu^{2+}–PVA solutions have been carried out in order to elucidate the interaction mode between cupric ions or cupric hydroxide and PVA. ^{1}H NMR spectra of PVA in aqueous solutions with and without Cu^{2+} at pH 3.0 are shown in Figure 3, where slight paramagnetic shifts are observed for all ^{1}H NMR signals. The ^{1}H NMR signals of CH and CH$_2$ in PVA polymer residues at pH 3.0 and 7.0 were dependent upon the concentration of cupric ions not in line width but in intensity. These signal intensities linearly decreased with

---

(10) Ringbom, A. In *Complexation in Analytical Chemistry*; Wiley: New York, 1963; Chapter 2.

(11) Willett, R. W. In *Magneto-Structural Correlations in Exchange Coupled System*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; Reidel: Boston, 1983; pp 389. Hodgson, D. J. *Prog. Inorg. Chem.* **1975**, *19*, 173. Brubaker, C. H., Jr.; Wicholas, M. *J. Inorg. Nucl. Chem.* **1965**, *27*, 59.

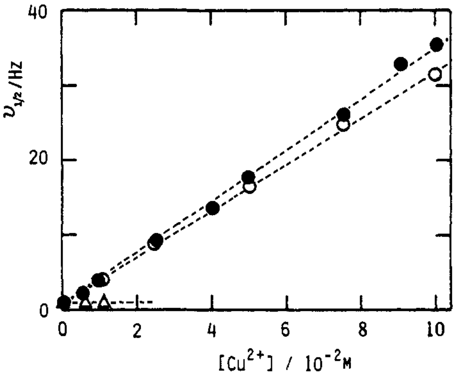

Figure 5. Plots of ^{1}H NMR line widths at half-height ($\nu_{1/2}$) for bulk water against the concentration of Cu^{2+} at room temperature: (●) C_{PVA} = 100 mM and pH 3.0; (○) C_{PVA} = 0 and pH 3.0; (△) C_{PVA} = 100 mM and pH 7.0.

a concentration increase of cupric ions at pH 3.0 and 7.0, as shown in Figure 4. These intensity changes at pH 7.0, however, are much more sensitive to the concentration of cupric ions than those at pH 3.0, where cupric hydroxide is never formed. This fact indicates that the interaction mode between cupric ions and PVA at pH 7.0 is different from that at pH 3.0 and that the interaction is much stronger at pH 7.0. In Figure 4b, the intercept of the two lines on the abscissa is estimated by extrapolation to correspond to a [PVA polymer residue]/$[Cu^{2+}]$ ratio of 7.2. This phenomenon is comparable to that in ^{1}H NMR studies of copper proteins,[12] in which only ^{1}H NMR signals due to protons in close proximity to cupric ions are broadened beyond detection. Consequently, each cupric ion in aqueous Cu^{2+}–PVA solutions at pH >6 is closely surrounded by 7.2 (CH–CH_2) units in a regular arrangement. A closer proximity of these protons to each cupric ion in the present case is indicated particularly by the fact that the Cu^{2+} has the subnormal μ_{eff} value of 1.33 μ_B, because the dipolar paramagnetic broadening of ^{1}H NMR signals is proportional to μ_{eff}^2. Interestingly, the above fact of about 7 (CH–CH_2) units around each cupric ion seems to be consistent with the fact that [PVA polymer residue]/$[Cu^{2+}]$ > 6 is necessary for keeping the solutions from precipitation.[5] On the other hand, at pH 3.0, there is a different kind of very weak interaction between cupric ions and PVA, as estimated by Figure 4a and the above-mentioned paramagnetic shifts of PVA ^{1}H NMR signals; details on this weak interaction will be reported elsewhere in the near future.

Plots of the ^{1}H NMR line widths of bulk water molecules against the concentration of cupric ions were also linear, as shown in Figure 5. At pH 3.0, both of the plots for aqueous Cu^{2+} solutions with and without PVA are almost identical, although the line widths are slightly broader in the former than in the latter case, owing primarily to a difference in viscosity. On the other hand, the ^{1}H NMR line widths of bulk water at various concentrations of cupric ions for aqueous Cu^{2+}–PVA solutions at pH 7.0 were definitely invariant, although experiments at higher concentrations of cupric ions could not be carried out in these solutions. This invariance of line width at pH 7.0 means that water molecules in the vicinity of cupric ions do not exchange easily with bulk water, suggesting that all cupric ions in the form of cupric hydroxide are surrounded by PVA chains in such a way that bulk water does not easily come close to the cupric ions.

Optical Absorption. Visible and UV spectra of aqueous Cu^{2+}–PVA solutions at different pH values at room temperature are shown in Figure 6. The solutions at pH >6 assume a green color and show two absorption bands at 263 and 625 nm, as previously reported. Besides these two bands, however, there is another shoulder-like band at 370 nm with pronounced tailing in the visible region, as seen in Figure 6. This tailing is responsible for the green coloration of aqueous Cu^{2+}–PVA solutions at pH >6, because an absorption at 625 nm alone corresponds to a blue color. It has been reported that absorptions around 370 nm are characteristic of antiferromagnetic binuclear copper(II) complexes such as the complexes of diamino alcohols and cupric acetate.[13,14] These facts suggest the possibility that the present absorption band at 370 nm may be due to the $p\pi(O) \rightarrow d_{x^2-y^2}(Cu)$ charge transfer transitions, where $p\pi$(O) denotes the $p\pi$ orbital on bridging OH groups in cupric hydroxide. Usually, cupric hydroxide is a light blue precipitate, but it is considered to become green when it is incorporated into PVA. The detailed mechanism for this green coloration, however, is quite uncertain at present. On the other hand, at pH 4.0, the visible and UV spectra of aqueous Cu^{2+} solutions with and without PVA were almost the same, indicating that the interaction between cupric ions and PVA at this pH is extremely weak or not present; in the comparison of these UV spectra, attention should be given to the fact that any commercially available PVA inevitably has some absorption in the UV region.

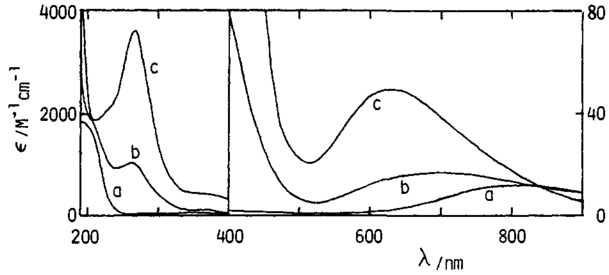

Figure 6. Visible and UV spectra of aqueous Cu^{2+}–PVA solutions at room temperature (same concentrations of Cu^{2+}, PVA, and $NaClO_4$ as in Figure 1): (a) pH 4.00; (b) pH 5.95; (c) pH 8.05.

Concluding Remarks. Cupric hydroxide, $Cu(OH)_2$, is believed to be of the type $[Cu_n(OH)_{2n-2}]^{2+}$ and can also be obtained as crystals.[15] $Cu(OH)_2$ as a whole molecule is almost neutral in charge, because n is generally large. Furthermore, $Cu(OH)_2$ coagulates and precipitates when formed in aqueous solutions. This suggests that $Cu(OH)_2$ is an assembly of hydrophobic particles and that hydrophobic interactions produce the solubilization of $Cu(OH)_2$ by PVA. This solubilization mechanism is convincingly supported by the above ^{1}H NMR result, demonstrating that the polynuclear complex of $Cu(OH)_2$ is surrounded by PVA chains with their hydrophobic backbones toward the complex and with their hydrophilic OH groups toward the outside of bulk water. PVA is well-known to react with iodine to give a complex with a characteristic blue color similar to that of a helical inclusion complex of amylose and iodine.[16] This suggests an analogous helical inclusion model for $Cu(OH)_2$, in which chains of $Cu(OH)_2$ are included in helical PVA chains; this is an efficient type of inclusion especially at small ratios of [PVA polymer residue]/$[Cu^{2+}]$. Recently, a spectrophotometric study of p-aminoazobenzene in aqueous Cu^{2+}–PVA solutions has been attempted to demonstrate the presence of hydrophobic domains in the solutions at pH >7,[17] since the dye is an indicator of hydrophobicity. The results supported the present model for the $Cu(OH)_2$–PVA complex which is also consistent with the decrease in the viscosity of aqueous Cu^{2+}–PVA solutions at pH >6. On the other hand, their visible and UV spectra are probably due to the olated polynuclear complex of $Cu(OH)_2$ included by PVA in a hydrophobic domain.

We conclude that the interaction between cupric ions and PVA at pH >6 is a hydrophobic interaction between the olated polynuclear complex of $Cu(OH)_2$ and PVA. This interaction mode

---

(12) Ulrich, E. L.; Markley, J. L. *Coord. Chem. Rev.* **1978**, *27*, 109. Cass, A. E. G.; Hill, H. A. O.; Smith, B. E.; Bannister, J. V.; Bannister, W. H. *Biochemistry*, **1977**, *16*, 3061.

(13) Kida, S.; Nishida, Y.; Sakamoto, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2428. Nishida, Y.; Numata, F.; Kida, S. *Inorg. Chim. Acta* **1974**, *11*, 189.

(14) Catterick, J.; Thornton, P. *Adv. Inorg. Chem. Radiochem.* **1977**, *20*, 291.

(15) Jaggi, V. H.; Osward, H. R. *Acta Crystallogr.* **1961**, *14*, 1041.

(16) Zwick, M. M. *J. Appl. Polymn. Sci.* **1965**, *9*, 2393.

(17) Narisawa, M.; Ono, K.; Murakami, K., presented at the 34th Annual Meeting of Polymer Science, Japan (Kyoto), 1985 (Polymer Reprints, No. 3, pp 491).

is of a new type in the chemistry of polymer–metal complexes. Similar studies involving other heavy metal ions are now in progress. Many natural macromolecules contain a large number of OH groups. The above new interaction mode between cupric ions and PVA is suggestive of the binding of heavy metal ions in nature.

Acknowledgment. The authors express their deep gratitude of Prof. H. Sugiyama for his unfailing guidance throughout the course of this work.

Registry No. PVA, 9002-89-5; $Cu(OH)_2$, 20427-59-2; Cu^{2+}, 15158-11-9.

Interaction Modes between Heavy Metal Ions and Water-Soluble Polymers. 2. Spectroscopic and Magnetic Reexamination of the Aqueous Solutions of Cupric Ions and Poly(acrylic acid)

Hiroshi Yokoi,* Satoshi Kawata, and Masamoto Iwaizumi

Contribution from the Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai 980, Japan. *Received September 16, 1985*

Abstract: The interaction between cupric ions and poly(acrylic acid) (PAA) in aqueous solutions has been reexamined by EPR, magnetic susceptibility, and optical absorption. Cupric ions exist in solutions at pH <3 as ordinary hydrated ions, and in the pH range 3–8, two mononuclear complexes with carboxyl groups of PAA are formed in equilibrium with other complex species; the two complexes have the same coordination structures as $Cu(OAc)^+$ and $Cu(OAc)_2$, where OAc^- denotes acetate anion. Around pH 4, two slightly different binuclear copper(II) complexes of the cupric acetate type are formed in high yields; at [PAA polymer residue]/$[Cu^{2+}] \lesssim 10$, about 90% of the cupric ions form such binuclear complexes. At pH >6, $Cu(OH)_2$ is gradually formed and complex species other than $Cu(OH)_2$ finally disappear at pH >9. $Cu(OH)_2$ does not deposit but remains in solution by hydrophobic interaction with PAA, as in the case with poly(vinyl alcohol).

Poly(acrylic acid) (PAA) is a familiar synthetic water-soluble polymer. In the preceding paper,[1] we found that there is a new interaction mode between cupric ions and poly(vinyl alcohol) (PVA). The difference between PAA and PVA in interaction with heavy metal ions is that PAA contains carboxyl groups as weak ligands for these ions. Various spectroscopic, equilibrium, and related studies of aqueous solutions of cupric ions and PAA have been reported.[2-10] Similar studies were carried out of aqueous Cu^{2+} solutions with PAA analogues, poly(methacrylic acid) and poly(L-glutamic acid).[5,6,10-14] However, the identification of copper(II) complexes formed in these solutions is still obscure, since aqueous Cu^{2+}–PAA solution systems involve interactions between cupric ions and PAA which cannot be fully clarified by these usual techniques. At present, the EPR method is considered the most useful technique for identification of unknown copper(II) complexes in solutions,[15] although this method is not applicable to apparently EPR-silent copper(II) complexes often formed in solutions. Therefore, in order to elucidate the intrinsic nature of complex formation in aqueous Cu^{2+}–PAA solutions, information on the quantitative contribution of cupric ions to every observed EPR spectrum is indispensable. Most EPR studies so far reported for aqueous Cu^{2+}–PAA[6] and Cu^{2+}–PVA[16] lack for these kinds of data.

The purpose of this paper is to reexamine aqueous Cu^{2+}–PAA solutions by EPR, magnetic susceptibility, and optical absorption techniques and to elucidate the interaction mode between cupric ions and PAA in detail.

Experimental Section

Spectroscopic and Magnetic Measurements. A JEOL Model JES-FE2XG EPR spectrometer was used to measure EPR spectra of aqueous sample solutions at room temperature and of the frozen solutions at 77 K. All the EPR sample solutions contained 2.50 mM cupric ions, 0.10 M $NaClO_4$, and 10.0–100 mM PAA (polymer residue concentration). Hereafter, the concentration of PAA is expressed as R = [PAA polymer residue]/$[Cu^{2+}]$. The real intensities of room temperature EPR spectra were obtained by double integration of the observed first-derivative spectra with a NEC PC-9801 computer. The room temperature EPR spectra were measured under a constant condition of the spectrometer by using the same sample tube in order to enable their EPR intensities to be compared exactly with each other. The pH adjustment was done throughout this work without any buffer. A JEOL Model JNM-FX90Q

---

(1) For Part 1, see: Yokoi, H.; Kawata, S.; Iwaizumi, M. *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) Wall, H. P.; Gill, S. J. *J. Phys. Chem.* **1954**, *58*, 1128.

(3) Gregor, H. P.; Luttinger, L. B.; Loebel, E. M. *J. Phys. Chem.* **1955**, *59*, 34.

(4) McLaren, J. V.; Watts, J. D.; Gilbert, A. *J. Polym. Sci.* **1967**, *C-16*, 1903.

(5) Kotliar, A. M.; Morawetz, H. *J. Am. Chem. Soc.* **1955**, *77*, 3692.

(6) Noji, S.; Yamaoka, K. *Macromolecules*, **1979**, *12*, 1110.

(7) Yamaoka, K.; Masujima, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1819.

(8) Nishikawa, H.; Tsuchida, E. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1545.

(9) Yamada, R.; Tamura, K.; Harada, S.; Yasunaga, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3413.

(10) Marinsky, J. A. *Coord. Chem. Rev.* **1976**, *19*, 125.

(11) Katchalsky, A.; Spitnik, P. *J. Polym. Sci.* **1947**, *2*, 432.

(12) Leyte, J. C.; Zuiderweg, L. H.; van Reisen, M. *J. Phys. Chem.* **1968**, *72*, 1127. Marinsky, J. A.; Anspach, W. M. *J. Phys. Chem.* **1975**, *79*, 439.

(13) Yamaoka, K.; Masujima, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1286. Masujima, T.; Yamaoka, K. *Biopolymers* **1980**, *19*, 477.

(14) Koide, M.; Tsuchida, E. *Makromol. Chem.* **1981**, *182*, 359.

(15) Peisach, J.; Blumberg, W. E. *Arch. Biochem. Biophys.* **1974**, *165*, 691. Yokoi, H.; Addison, A. W. *Inorg. Chem.* **1977**, *16*, 1341. Yokoi, H.; Hanaki, A. *Chem. Lett.* **1984**, 481.

(16) Sumita, O.; Fukuda, A.; Kuze, E. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1801.

0002-7863/86/1508-3361$01.50/0