

INVESTIGATING THE NEW INTERACTION MODEL BETWEEN Cu(II) AND PVA BY THE PROTON RELAXATION METHOD

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An aqueous PVA-Cu²⁺ solution at pH = 3 is in the hydrated form and becomes green at pH ≥ 6 with a decrease in viscosity. The structure of the copper ion is suggested to be that of a polynuclear complex at pH > 6. For the green solution the polynuclear chains of the copper complex are believed to be surrounded by the PVA chains with the hydrophobic backbones facing toward the inside and the hydrophilic OH groups oriented toward the outside facing the bulk water. The proton spin-lattice relaxation rate 1/T_{1p} and the spin-spin relaxation rate 1/T₂ of CH and CH₂ in PVA and H₂O for aqueous PVA-Cu²⁺ solutions at pH = 3, can be explained by the two site exchange model in the region of the fast exchange limit. The dipolar correlation time τ_c is dominated by the reorientational process with a dipolar correlation time of 2.11 × 10⁻¹¹ s. When the pH rises from pH=3 to pH=12.5, the variation of 1/T_{1p} and 1/T_{2p} of CH and CH₂ in PVA with Cu²⁺ ion concentration in aqueous PVA-Cu²⁺ solution at pH = 12.5 can be explained in terms of the relaxation by an inclusive model of the polynuclear copper complex and PVA. Furthermore, the frequency (or field) dependence of 1/T_{1p}, 1/T_{2p} of CH in PVA for aqueous PVA-Cu²⁺ solution at pH = 12.5 suggests that the dipolar relaxation is dominated by the electron-spin relaxation with the electron spin relaxation time T_{1e} = 1 ~ 2 × 10⁻¹⁰ s. The invariance of 1/T_{1p} and 1/T_{2p} of H₂O with the variation of the Cu²⁺ ion concentration in aqueous PVA-Cu²⁺ solution at pH = 12.5 supports the hypothesis that the water is not directly bound to the Cu²⁺ ion.

INTRODUCTION

An aqueous solution of Cu(II) ion and Poly (vinyl alcohol) (PVA) shows green coloration at pH > 6, with a decrease in viscosity. Using Evan's method, Yokoi et al¹ showed that the effective magnetic moments μ_{eff} determined for aqueous PVA-Cu²⁺ solutions were 1.81 μ_B at pH = 3.0 and 1.33 μ_B at pH > 6. The result indicates the formation of a polynuclear copper(II) complex with a fairly strong antiferromagnetic interaction at pH > 6. This polynuclear complex Cu(OH)₂ is believed to be of the type [Cu_n(OH)_{2n-2}]²⁺. The invariance of line width at half height (Δν_{1/2}=1/T₂ π) for bulk water at various concentrations of Cu²⁺ at room temperature for aqueous PVA-Cu²⁺ solutions at pH > 6, suggests that all the Cu(II) ions, in the form of cupric hydroxide, are surrounded by helical PVA chains with

their hydrophobic backbones facing toward the complex and the hydrophilic OH groups facing outside toward the bulk water¹.

In the high frequency case, the proton longitudinal relaxation is caused primarily by the dipolar interaction between the nuclei and the paramagnetic spin while the transverse relaxation depends on the dipolar interaction as well as the isotropic hyperfine interaction between the proton and the paramagnetic ion. Therefore, knowledge of the proton relaxation rate may provide a probe to elucidate the binding and relaxation of Cu²⁺ and PVA.

It is the purpose of this work to obtain structural information on the [Cu_n(OH)_{2n-2}]²⁺-PVA system in aqueous solution. We measured the viscosity and the relaxation rates as a function of Cu²⁺ concentration at pH=12.5 in order to further confirm that the water isn't directly bound to the Cu²⁺ ion.

Studies of the field dependence of $1/T_{1p}$ and $1/T_{2p}$ for $-C^1H-$ of PVA at 90 and 300 MHz allows us to estimate the electron spin relaxation time at 90 (i.e. $T_{1e}(90)$) and 300 MHz (i.e. $T_{1e}(300)$) in aqueous PVA-Cu²⁺ solution at pH = 12.5 with $[Cu^{2+}] = 0.01$ M. Some concluding remarks are given in the last section.

EXPERIMENTAL SECTION

Chemicals

Hydrolyzed (98.9%) PVA with weight average molecular weight $M_w = 27,000$ (the number average molecular weight $M_n = 14,000$) was purchased from Aldrich Chemical Company. The triad tacticity of PVA with mm 22%, mr 50% and rr 28% were derived from the methine carbon peak in C¹³ measurements² on a Bruker AM-400 NMR spectrometer. The concentration of PVA was expressed in terms of the monomeric residues. All other reagents were of analytical grade or higher and were used without further purification.

Viscosity

The viscosity of a 0.2 M PVA solution prepared with the distilled-deionized water was measured at 25°C in capillary viscometers of the Ubbelohde type. The temperature was controlled to within $\pm 0.02^\circ C$.

¹H NMR relaxation time measurement

PVA and CuCl₂ were prepared in D₂O solvent. The pH was varied by adding NaOD or DCl to the solution. The proton magnetic resonance studies were performed on a Bruker AM-400 operated at 9.4 T, a Bruker AM-300 operated at 7.0 T and a Bruker MSL-90 operated at 2.1 T. The following two relationships were used to calculate the observed proton relaxation rates, $1/T_{1p}$ and $1/T_{2p}$,

$$1/T_{1o} = (1/T_1)_{Cu} - (1/T_1)_o$$

$$1/T_{2p} = \pi [(\Delta\nu_{1/2})_{Cu} - (\Delta\nu_{1/2})_o]$$

Here $(T_1)_{Cu}^1$ and $(T_1)_o^1$ are the spin-lattice relaxation rates with and without Cu(II) and, $(\Delta\nu_{1/2})_{Cu}$ and $(\Delta\nu_{1/2})_o$, in Hz, are the full width at half-height with and without Cu(II). T_1 values were measured accurately ($\pm 10\%$) with the $180^\circ - \tau - 90^\circ$ pulse sequence.

THEORY

Proton relaxation in the Cu²⁺-PVA solution at pH = 3.0 (Two site exchange model)

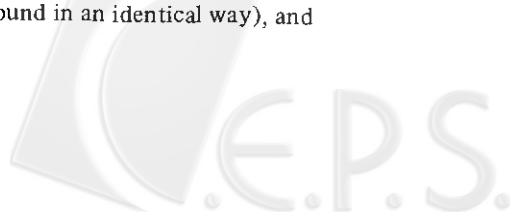
Cupric ions exist as ordinary hydrated ions at pH 3.0 in aqueous PVA-Cu²⁺ solution. The proton spin-relaxation measurements in aqueous solutions of Cu²⁺ and PVA at pH 3.0 are interpreted by assuming the water molecules undergo fast exchange between bulk solutions and the coordination spheres of the Cu²⁺ ion in the PVA-Cu²⁺ solution. The paramagnetic contributions to $1/T_{1p}$ and $1/T_{2p}$ due to water in the first coordination sphere of the Cu²⁺ ions were obtained from the observed $1/T_{1p}$ and $1/T_{2p}$ by subtracting out the values of the corresponding rates measured in diamagnetic solution ($(1/T_{1,2})_D$). Contributions from the outer-sphere relaxation effects were found to be negligible (i.e. $(1/T_{1,2})_{outer\ sphere} \ll (1/T_{1,2})_{inner\ sphere}$

$$\begin{aligned} (1/T_i)_p &\equiv 1/T_i - (1/T_i)_D \\ &= 1/T_i)_{inner\ sphere} + (1/T_i)_{outer\ sphere} \\ i &= 1, 2, \end{aligned} \quad (1)$$

$(1/T_i)_{inner\ sphere}$ is interpreted using the Luz-Meiboom³ and Swift-Connick⁴ equations, which here reduces to:

$$\begin{aligned} (1/T_i)_{inner\ sphere} &= \frac{pq}{T_{iM} + \tau_M} \\ i &= 1, 2, \end{aligned} \quad (2)$$

Here q is number of water molecules coordinated to each Cu²⁺ ion, (i.e. q is the average number of ligands bound in an identical way), and



$$P = \frac{[\text{paramagnetic metal ion}]}{[\text{ligand}]}$$

$$= \frac{[\text{Cu}^{2+}]}{[\text{H}_2\text{O}]} = \frac{[\text{Cu}^{2+}]}{55.6}$$

τ_M is the residence lifetime for nucleus in the paramagnetic environment (i.e. τ_M is the residence lifetime of a coordination water molecule) and T_{1M} and T_{2M} are the relaxation times of the bound protons.

The values of $1/T_{1M}$ and $1/T_{2M}$ are given by the Solomon-Bloembergen equations^{5,6,7}, which represent the sum of dipolar and scalar contributions:

$$\frac{1}{T_{1M}} = \frac{2}{15} \frac{\mu_{\text{eff}}^2 \gamma_I^2}{r^6} \left(\frac{3\tau_c}{1 + \omega_I^2 \tau_c^2} + \frac{7\tau_c}{1 + \omega_S^2 \tau_c^2} \right) + \frac{2}{3} \frac{S(S+1)A^2}{h^2} \left(\frac{\tau_e}{1 + \omega_S^2 \tau_e^2} \right) \quad (3)$$

$$\frac{1}{T_{2M}} = \frac{1}{15} \frac{\mu_{\text{eff}}^2 \gamma_I^2}{r^6} \left(4\tau_c + \frac{3\tau_c}{1 + \omega_I^2 \tau_c^2} + \frac{13\tau_c}{1 + \omega_S^2 \tau_c^2} \right) + \frac{1}{3} \frac{S(S+1)A^2}{h^2} \left(\tau_e + \frac{\tau_e}{1 + \omega_S^2 \tau_e^2} \right) \quad (4)$$

where $\mu_{\text{eff}}^2 = \gamma_e^2 h^2 S(S+1)$ and ω_I and ω_S are respectively the Larmor frequencies of the proton and electron. μ_{eff} is the effective electronic magnetic moment of Cu^{2+} , γ_I and γ_e are the gyromagnetic ratios of the proton and the electron, respectively, and r is the ion-proton distance. The parameter A is the isotropic hyperfine coupling constant and S is the total electron spin of the Cu^{2+} ion ($S = 1/2$).

The dipolar and scalar relaxation mechanisms are modulated by the correlation times τ_c and τ_e as given by Eq. (5) and (6)

$$\frac{1}{\tau_c} = \frac{1}{T_{1e}} + \frac{1}{\tau_M} + \frac{1}{\tau_R} \quad (5)$$

$$\frac{1}{\tau_e} = \frac{1}{T_{1e}} + \frac{1}{\tau_M} \quad (6)$$

where T_{1e} is the longitudinal electron spin relaxation time, τ_M is the mean lifetime of a bound water molecule, and τ_R is the reorientational correlation time of the hydrated Cu(II) complex. Thus in the case of rapid chemical exchange ($T_{1,2M} \gg \tau_M$) and in the absence of significant outer sphere effects, the inverse spin-lattice and transverse relaxation time due to the presence of paramagnetic ion (i.e. Cu^{2+}) becomes

$$\frac{1}{T_{1p}} = \frac{P_q}{T_{1m}}$$

$$= \frac{[\text{Cu}^{2+}]_q}{55.6} \left\{ \frac{2}{15} \frac{\mu_{\text{eff}}^2 \gamma_I^2}{r^6} \left(\frac{3\tau_c}{1 + \omega_I^2 \tau_c^2} + \frac{7\tau_c}{1 + \omega_S^2 \tau_c^2} \right) + \frac{2}{3} \frac{S(S+1)A^2}{h^2} \frac{\tau_e}{1 + \omega_S^2 \tau_e^2} \right\} \quad (7)$$

$$\frac{1}{T_{2p}} = \frac{P_q}{T_{2m}}$$

$$= \frac{[\text{Cu}^{2+}]_q}{55.6} \left\{ \frac{1}{15} \frac{\mu_{\text{eff}}^2 \gamma_I^2}{r^6} \left(4\tau_c + \frac{3\tau_c}{1 + \omega_I^2 \tau_c^2} + \frac{13\tau_c}{1 + \omega_S^2 \tau_c^2} \right) + \frac{1}{3} \frac{S(S+1)A^2}{h^2} \left(\tau_e + \frac{\tau_e}{1 + \omega_S^2 \tau_e^2} \right) \right\} \quad (8)$$

In the limit of $\omega_S^2 \tau_c^2 \gg 1$ and $\omega_S^2 \tau_e^2 \gg 1$, Eq. (7) and (8) become

$$\frac{1}{T_{1p}} = \frac{[\text{Cu}^{2+}]_q}{55.6} \left\{ \frac{2\mu_{\text{eff}}^2 \gamma_I^2}{15r^6} \times \frac{3\tau_c}{1 + \omega_I^2 \tau_c^2} \right\} \quad (9)$$

$$\frac{1}{T_{2p}} = \frac{[\text{Cu}^{2+}]_q}{55.6} \left\{ \frac{\mu_{\text{eff}}^2 \gamma_I^2}{15r^6} \left(4\tau_c + \frac{3\tau_c}{1 + \omega_I^2 \tau_c^2} \right) + \frac{S(S+1)A^2}{3h^2} \tau_e \right\} \quad (10)$$

Paramagnetic shifts for the two site exchange model at the fast exchange rate

As a result of the hyperfine interaction, the proton resonance frequency in the coordination sphere of the paramagnetic ion may differ from that

of water in the bulk. The relevant equation has been given by Bloembergen^{5b,8}.

$$\frac{\Delta\omega}{\omega_1} = \frac{H_0 - H^*}{H^*} = pq \left[Ah \frac{Y_c}{Y_l} \left(\frac{S(S+1)}{3kT} \right) \right] \quad (11)$$

where H^* and H_0 are the magnetic fields at which the resonance of the bonded and free molecules, respectively, are observed at frequency ω_1 , and T is the absolute temperature.

Proton relaxation in the aqueous PVA-Cu²⁺ solution at pH 12.5

The environment of the copper ion in aqueous PVA-Cu²⁺ solution at pH 12.5 is suggested to be the polynuclear complex, $[\text{Cu}_n(\text{OH})_{2n-2}]^{2+}$. This polynuclear complex is presumably surrounded by PVA chains with their hydrophobic backbones facing toward the complex and with their hydrophilic OH groups facing toward the bulk water molecules.

(a) $1/T_{1,2p}$ of water:

In this inclusive type model, some water molecules are bound to the exterior site of the PVA helix, while most of water molecules stay away from the copper center of the $[\text{Cu}_n(\text{OH})_{2n-2}]^{2+}$ complex. This is a typical one site model.

$$\frac{1}{T_{1,2p}} \equiv \frac{1}{T_{1,2}} - \left(\frac{1}{T_{1,2}} \right)_D \approx 0 \quad (12)$$

(b) $1/T_{1,2p}$ of CH and CH₂ in PVA:

From Eq. (3) and (4), the $1/T_{1p}$ and $1/T_{2p}$, of nuclear CH and CH₂ bonded to a paramagnetic ion $[\text{Cu}_n(\text{OH})_{2n-2}]^{2+}$ are given by Eq. (13) and (14).

$$\frac{1}{NT_{1p}} = \frac{q}{[L]} \left[\frac{2\mu_{\text{eff}}^2 Y_l^2}{15r^6} \left(\frac{3\tau_c}{1+\omega_l^2\tau_c^2} + \frac{7\tau_c}{1+\omega_n^2\tau_c^2} \right) + \frac{2}{3} \frac{S(S+1)A^2}{h^2} \frac{\tau_c}{1+\omega_n^2\tau_c^2} \right] \quad (13)$$

$$\frac{1}{NT_{2p}} = \frac{q}{[L]} \left[\frac{1}{15} \frac{\mu_{\text{eff}}^2 Y_l^2}{r^6} \left(4\tau_c + \frac{3\tau_c}{1+\omega_l^2\tau_c^2} + \frac{13\tau_c}{1+\omega_n^2\tau_c^2} \right) + \frac{1}{3} \frac{S(S+1)A^2}{h^2} \left(\tau_c + \frac{\tau_c}{1+\omega_n^2\tau_c^2} \right) \right] \quad (14)$$

where $N < N_0$. In these equations, N is the molar concentration of paramagnetic ion while its saturated concentration is denoted by N_0 , $[L]$ is the ligand concentration. For the case of $\omega_s^2\tau_e^2 \gg 1$, $\omega_s^2\tau_c^2 \gg 1$ and where the paramagnetic shift is small, i.e. $A \approx 0$, Eq. (13) and (14) reduce to the following form:

$$\frac{1}{NT_{1p}} = \frac{q}{[L]} \frac{2\mu_{\text{eff}}^2 Y_l^2}{15r^6} \frac{3\tau_c}{1+\omega_l^2\tau_c^2} \quad (15)$$

$$\frac{1}{NT_{2p}} = \frac{q}{[L]} \left\{ \frac{\mu_{\text{eff}}^2 Y_l^2}{15r^6} \left(\frac{3\tau_c}{1+\omega_l^2\tau_c^2} + 4\tau_c \right) \right\} \quad (16a)$$

$$= \frac{1}{2} \frac{1}{NT_{1p}} + \frac{4\mu_{\text{eff}}^2 Y_l^2 \tau_c}{15r^6} \frac{q}{[L]} \quad (16b)$$

Equation (17) and (18) were obtained by substituting ω_1 (90 MHz) = 5.65×10^8 rad/s, ω_1 (300 MHz) = 1.88×10^9 rad/s into Eq. (15) and (16b).

$$\frac{1}{NT_{2p(90)}} - \frac{1}{2} \frac{1}{NT_{1p(90)}} = \frac{\tau_c(90)}{\tau_c(300)} \quad (17)$$

$$\frac{1}{NT_{1p(90)}} = \frac{\tau_c(90)}{\tau_c(300)} \times \frac{1+3.53 \times 10^{18} \tau_c^2(300)}{1+3.19 \times 10^{17} \tau_c^2(90)} \quad (18)$$

where $\tau_c(90)$, $\tau_c(300)$ are the dipolar correlation time (cf. Eq. (5)) at 90 and 300 MHz.

(c) Paramagnetic shifts for one site exchange model:

Similar to Eq. (11) the paramagnetic shift for the one site model is given by Eq. (19).

$$\frac{\Delta\omega_M}{\omega_1} = \frac{H_0 - H^*}{H^*} = Ah \frac{Y_c}{Y_l} \left[\frac{S(S+1)}{3kT} \right] \quad (19)$$

RESULTS AND DISCUSSION

Viscosity

The variation of the viscosity with pH in an aqueous solution of PVA-Cu²⁺ with $[\text{PVA}] = 0.2$ M is shown in Fig. 1. In the measured pH ranges, the viscosity decreases with an increase of pH from 3.0 to 7.0 and then flattens at pH larger than 7.0. This result is similar to the report of Hojo et. al⁹. Fig. 2 shows the dependence of reduced viscosity $\eta_{sp/c}$ on

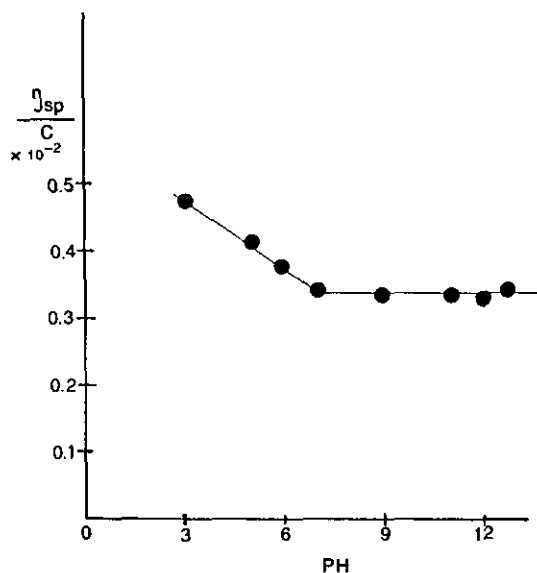


Fig. 1 Typical viscosity plots for the PVA-Cu²⁺ solution with various pH values at 25°C with [PVA] = 0.2 M and [Cu²⁺] = 0.01 M. The viscosity of the solution is divided by the viscosity of the solvent to obtain the relative viscosity η_r . The specific viscosity, $\eta_{sp} = \eta_r - 1$, expresses the incremental viscosity attributable to the polymeric solute. The concentration C is expressed in grams per 100 ml of solution. The unit of η_{sp}/c is deciliters per gram.

Cu²⁺ ion concentration at various pH values of the solution. The reduced viscosity is independent of the Cu²⁺ concentration at pH = 3.26 and decreases linearly with an increase in Cu²⁺ ion concentration at pH > 7.0.

The latter fact is consistent with the result shown in Fig. 1, suggesting that Cu(OH)₂ is an assembly of hydrophobic particles and the hydrophobic interaction between Cu(OH)₂ and the interior hydrophobic part of PVA helix produces the solubilization of Cu(OH)₂ by PVA. This result supports the decrease in the viscosity of aqueous PVA-Cu²⁺ solution at pH > 7¹.

(I) The relaxation behavior at pH=3.0 of the aqueous PVA-Cu²⁺ solution

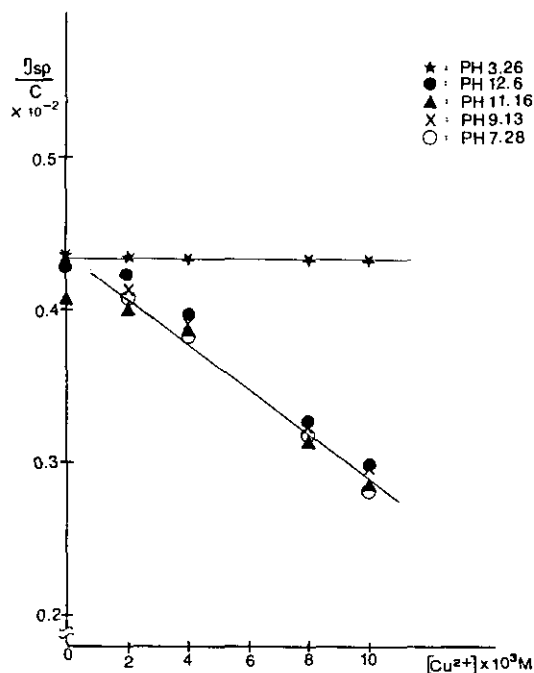


Fig. 2 Dependence of the reduced viscosity η_{sp}/c of a PVA-Cu²⁺ solution on the concentration of Cu²⁺ with various pH values at 25°C with [PVA] = 0.2 M.

Cu²⁺ is in the hydrated form at pH = 3.0 in Cu²⁺-PVA aqueous solution. The coordination waters are presumably in the limit of fast exchange with bulk water. This can be explained in terms of two site model in the fast exchange limit. Eq. (9) and (10) indicate that the [Cu²⁺] ion concentration, the reorientational correlation time τ_c (which relates to the viscosity η of the solution through the Stokes-Einstein relation) and μ_{eff}^2 determine the relaxation rates. Fig. 2 shows that the viscosity is independent of Cu²⁺ ion concentration at pH = 3.26. Thus, the only variable in Eq. (9), (10) is the copper ion concentration. Fig. 3, shows the observed proton values of $1/T_{1p}$ and $1/T_{2p}$ for H₂O at pH 3.0 versus [Cu²⁺]. The result is consistent with our expectation. For the Cu(H₂O)₆²⁺ complex, the distance r between the proton and the central Cu²⁺ may be calculated from crystallographic data. The literature value is $2.45 \pm 0.16 \text{ \AA}^{10}$. The viscosity (η) of the

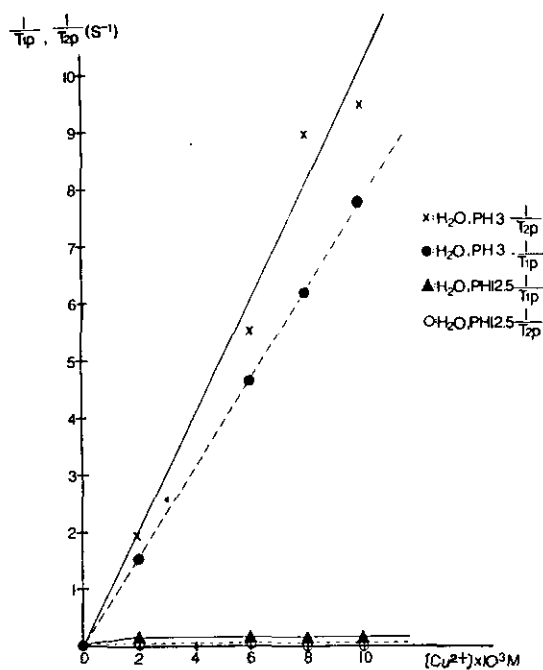


Fig. 3 Plots of $1/T_{1p}$ and $1/T_{2p}$ for the proton of water at pH 3.0 and pH 12.5 as a function of Cu^{2+} ion concentration at 25°C with $[\text{PVA}] = 0.2 \text{ M}$.

aqueous PVA- Cu^{2+} solution shown in Fig. 2 is 1.28 cps. The slope of the linear plot of $1/T_{1p}$ against $[\text{Cu}^{2+}]$ ion concentration at pH = 3.0 (shown in Fig. 3) is 777.91. Substituting $r = 2.45 \pm 0.16 \text{ \AA}$, $q = 5 \sim 6$ and $\omega_1(90 \text{ MHz}) = 5.65 \times 10^8 \text{ rad/s}$ into Eq. (9), we obtain $\tau_c = 2.11 \times 10^{-11} \text{ s}$. In accordance with the Stokes-Einstein relation, the overall reorientational correlation time τ_R of the Cu(II) complex is related to the radius of this complex by

$$\tau_R = \frac{4\pi\eta r^3}{3kT} \quad (20)$$

Substitution of $\eta = 1.28 \text{ cps}$, $k = 1.38 \times 10^{-23} \text{ J/K}$, $r = 2.45 \text{ \AA}$ and $T = 298^\circ\text{K}$ yields a τ_R of $1.92 \times 10^{-11} \text{ s}$. Thus, we have $\tau_c \cong \tau_R$. The reorientational motion determines the modulation process of dipolar relaxation. It is generally agreed that in aqueous solutions of Cu^{2+} ion, $\tau_c \sim 10^{-9} \text{ s}^{11}$ is large enough to make the scalar contribution to T_{1p}^{-1} negligibly small ($\omega_s^2\tau_c^2 \gg 1$) while for T_{2p} the large value of τ_c makes the scalar contribution dominant. Further-

more, the magnetic field strength is on the order of 2.1 T, $(\omega_s\tau_c)^2 = 61.5$ and $\omega_1^2\tau_c^2 = 1.42 \times 10^{-4}$ in aqueous PVA- Cu^{2+} solution at pH = 3.0 at 25°C . The error in $1/T_{1,2p}$ resulting from the neglect of the dispersion term $1 + \omega_s^2\tau_c^2$ in Eq. (7), (8), is less than 4%. Thus, we have shown the validity of Eq. (9) and Eq. (10) to interpret relaxation data in the aqueous PVA- Cu^{2+} solution at pH 3.0.

(II) The relaxation behavior in aqueous PVA- Cu^{2+} solution at pH 12.5

For $N < N_0$ all Cu^{2+} of $\text{Cu}(\text{OH})_2$ are presumed to be inclusive in the helical PVA chains. When the Cu^{2+} ion concentration is in excess of the saturation concentration, i.e. $N > N_0$, the $\text{Cu}(\text{OH})_2$ precipitates out of the solution. In this work, the saturation concentration N_0 of Cu^{2+} is about 0.012 M (Eq. 13, 14). All the Cu^{2+} ion concentrations were prepared below the saturation value N_0 .

(a) Variation of $1/T_{1p}$ and $1/T_{2p}$ of H_2O with Cu^{2+} ion concentration:

A plot of the ^1H relaxation rate $1/T_{1p}$ and $1/T_{2p}$ of water against the Cu^{2+} ion concentration for a PVA- Cu^{2+} solution at pH 12.5 is shown in Fig. 3. At pH 12.5, the Cu^{2+} ion is in the form of a polynuclear complex. The observed values $1/T_{1p}$ and $1/T_{2p}$ of H_2O at this pH value confirm their independence from the Cu^{2+} ion concentration. Fig. 1 and Fig. 2 show the same reduced viscosity for pH = 7.3 and pH = 12.6 in PVA- Cu^{2+} aqueous solutions. Hence μ_{eff} at pH = 12.6 should be the same as that at pH = 7.0, i.e. $\mu_{\text{eff}} = 1.33 \mu_B$ at pH = 12.5 and $\mu_{\text{eff}} = 18.1 \mu_B$ at pH = 3.0¹. By varying the pH from 3.0 to 12.5 in aqueous PVA- Cu^{2+} solution, the Cu^{2+} ion structure changes from a hydrated type ion to a polynuclear $\text{Cu}(\text{OH})_2$ complex, $[(\text{Cu}_n(\text{OH})_{2n-2})]^{2+}$. Consequently, μ_{eff} decreases from $1.81 \mu_B$ to $1.33 \mu_B$ and the reduced viscosity $\eta_{\text{sp}/c}$ of solution decreases about 30% from 43.1 dl/gram to 29.9 dl/gram (at $[\text{Cu}^{2+}] = 0.01 \text{ M}$). It is shown in Fig. 3 that $1/T_{1p}$ (or $1/T_{2p}$) of aqueous PVA- Cu^{2+} solution with $[\text{Cu}^{2+}] = 0.01 \text{ M}$ at pH

12.5 is about 0.1 s^{-1} , which is much less than $1/T_{1p}$ (or $1/T_{2p}$) at pH 3.0. Likewise, the observed $1/T_{1p}$ and $1/T_{2p}$ at pH 12.5 can not be explained by Eq. (13) and (14). The drastic reduction in the relaxation rate suggests that chains of the $\text{Cu}(\text{OH})_2$ polynuclear complex (i.e. $[\text{Cu}_n(\text{OH})_{2n-2}]^{2+}$) are surrounded by PVA chains while H_2O is bound to the exterior site of the helical PVA chain so that its relaxation rates remain independent of the Cu^{2+} concentration. This fact can be explained by Eq. (12) which describes relaxation by bulk water only.

(b) Field-dependent $1/T_{1p}$ and $1/T_{2p}$ of C^1H in PVA- Cu^{2+} solution at pH 12.5:

The appropriate dipolar correlation time τ_c can be determined by field-dependent relaxation studies. At 25°C , $1/T_{1p}$ and $1/T_{2p}$ of CH in aqueous PVA- Cu^{2+} solution at 90 and 300 MHz with $[\text{PVA}] = 0.2 \text{ M}$, $[\text{Cu}^{2+}] = 0.01 \text{ M}$ and pH 12.5 are shown in Table I. It indicates that $1/T_{1p}$ and $1/T_{2p}$ decrease with an increase of frequency (or field) from 90 to 300 MHz. This is due to the dispersion behavior ($\omega_1\tau_c \approx 1$) in the spectral densities of Eq. (15) and (16). When the field is increased, the increase of $\omega_1^2\tau_c^2$ leads to the decrease of $1/T_{1p}$ and $1/T_{2p}$ in Eq. (15) and (16a). The τ_c of CH in PVA was calculated from Eq. (17), (18) and found to be:

$$\tau_c(300) = 1.12 \times 10^{-10} \text{ s}$$

$$\tau_c(90) = 1.92 \times 10^{-10} \text{ s}$$

The paramagnetic shift measured between the solvation shell CH and the bulk CH at 300 MHz is 6.2 Hz. Substitution of $\Delta\omega = 6.2 \text{ Hz}$ into Eq. (11) yields A/\hbar of $4.9 \times 10^4 \text{ rad/s}$. The scalar terms $2/3S(S+1) (A/\hbar)^2(\tau_c/1 + \omega_s^2\tau_c^2)$ and $1/3S(S+1) A^2\tau_c/\hbar$ in Eq. (13) and (14) were estimated to be 7×10^{-6} and $6.7 \times 10^{-2} \text{ rad}^2/\text{s}$, respectively, with $\omega_s(300 \text{ MHz}) = 1.237 \times 10^{12} \text{ rad/s}$. Hence the hyperfine coupling between the electron and nuclear spin should be very small in comparison with the dipolar interaction. The $\omega_s^2\tau_c^2 = 1.92 \times 10^4 \gg 1$ and $\omega_1\tau_c = 0.21$ were calculated from $\omega_1(300 \text{ MHz}) = 1.88 \times 10^9 \text{ rad/s}$ and $\tau_c = 1.12 \times 10^{-10} \text{ s}$, thus the assump-

Table I $1/T_{1p}$ and $1/T_{2p}$ of CH in PVA for an aqueous PVA- Cu^{2+} solution, at frequencies of 90 and 300 MHz with $[\text{PVA}] = 0.2 \text{ M}$, $[\text{Cu}^{2+}] = 0.01 \text{ M}$ at pH 12.5 at 25°C .

MHz	$1/T_{1p}(\text{s}^{-1})$	$1/T_{2p}(\text{s}^{-1})$
	CH	CH
90	0.4475	12.35
300	0.2527	7.1942

tions for using Eq. (15) and (16) have been justified.

The three terms on the right side of Eq. (5) represent possible processes by which the dipolar field seen by the proton may be interrupted. The proton chemical exchange between the CH molecule in the coordinate sphere and the bulk is slower at 298°K than the other process so that $1/\tau_M$ does not, in general, contribute to $1/\tau_c$ ¹². The overall re-orientational motion of the coupled pair between Cu^{2+} in the $\text{Cu}(\text{OH})_2$ polynuclear complex and CH in helical PVA of the aqueous PVA- Cu^{2+} solution at pH 12.5 with $[\text{PVA}] = 0.2 \text{ M}$ seems to be very slow in comparison with electronic relaxation. Thus the dipolar correlation time is dominated by the electron spin relaxation processes. Hence we have $T_{1e}(300) = 1.21 \times 10^{-10} \text{ s}$, $T_{1e}(90) = 1.92 \times 10^{-10} \text{ s}$. Both $T_{1e}(300)$ and $T_{1e}(90)$ are approximately equal within experimental error.

(III) Variation of $1/T_{1p}$ and $1/T_{2p}$ of CH and CH_2 with $[\text{Cu}^{2+}]$ ion concentration

According to Eq. (9) and (10) and Eq. (15) and (16a), the plots of $1/T_{1p}$ and $1/T_{2p}$ for the protons of CH and CH_2 in PVA polymer residues at pH 3.0 and 12.5 against the concentration of Cu^{2+} at 25°C should have linearly increasing slopes. All the data of $1/T_{1p}$, $1/T_{2p}$ at pH 3.0 and 12.5 shown in Fig. 4 and 5 are in agreement with our explanation.



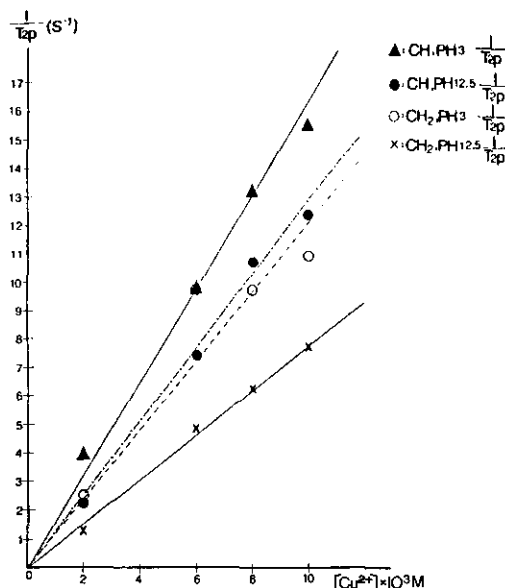


Fig. 4 Plots of $1/T_{2p}$ for the proton of CH and CH_2 in PVA polymer residue at pH 3.0 and pH 12.5 against the concentration of Cu^{2+} at 25°C.

CONCLUSION

1. For aqueous PVA- Cu^{2+} solution at pH 3.0 the dipolar correlation rate of H_2O was dominated by the rotational correlation rate with a dipolar correlation time of 2.11×10^{-11} s. From the field dependence of CH in aqueous PVA- Cu^{2+} solution at pH 12.5, the dipolar correlation rate determined by an electron spin relaxation process with $T_{1e} \cong 1 \sim 2 \times 10^{-10}$ s.
2. The invariance of $1/T_{1p}$, $1/T_{2p}$ of H_2O with variations of the Cu^{2+} ion concentration in aqueous PVA- Cu^{2+} solutions at pH = 12.5 supports the hypothesis that water is not directly bound to the Cu^{2+} ion.

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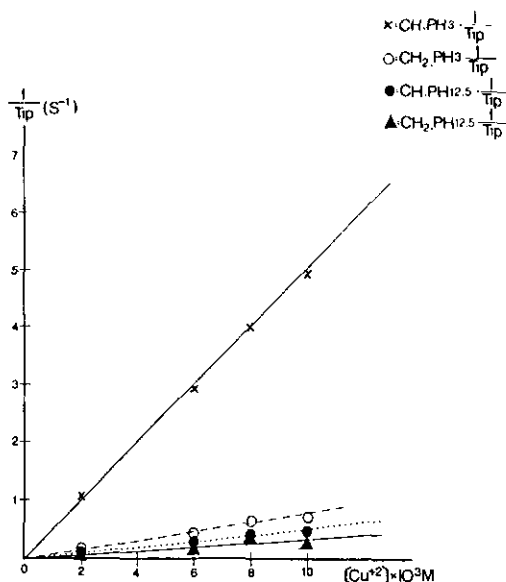


Fig. 5 Plots of $1/T_{1p}$ for the proton of CH and CH_2 in PVA polymer residue at pH 3.0 and pH 12.5 against the concentration of Cu^{2+} at 25°C.

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Key Word Index— PVA, Cu^{2+} , Proton Relaxation.

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