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Complex formation of partially phosphorylated poly(vinyl alcohol), with metal ions in aqueous solution

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The complex formation of Cr(III), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) ions with partially phosphorylated poly(vinyl alcohol) (P-PVA) in aqueous solution is studied by means of potentiometric titration and electronic as well as e.s.r. spectroscopy. The titration data and spectroscopic results suggest that bivalent and trivalent metal ions bind with two and three phosphoric acid groups in P-PVA at pH <3.5, respectively. Overall formation constants, log K, for the bivalent metal ion and P-PVA are about 4.6. The electronic and e.s.r. spectroscopic results indicate that cupric ion forms a polynuclear complex of $Cu(OH)_2$ solubilized by unreacted hydroxyl groups in P-PVA at pH >6.2. Copyright © 1996 Elsevier Science Ltd.

(Keywords: partially phosphorylated poly(vinyl alcohol); metal complex; complexation; formation constant)

INTRODUCTION

Partially phosphorylated poly(vinyl alcohol) (P-PVA) has attracted considerable interest because of its non-inflammability[1,2], metal complexes[3], anionic polyelectrolyte hydrogels[4], and cation exchange resins[5,8]. We have reported the thermal stability of Ni(II)-P-PVA[6] and ion conductor of molecular composites of P-PVA with polyether and metal cations[7]. Quite recently, we reported P-PVA about polyelectrolyte gels and selective cation exchanger[9]. It was shown that the cation exchange resin separates Fe(III) ions from other metal ions completely. The metal–P-PVA complexes may be useful as metal selective absorbents, noninflammable material, and artificial teeth. In the present work, the complex formation of phosphoric acid groups in P-PVA and metal ions are studied by potentiometric titration and spectroscopic measurements in order to get detailed information regarding complex formation of P-PVA with metal ions.

EXPERIMENTAL

Material

The poly(vinyl alcohol) ($DP = 2000$) (PVA) of an analytical grade was completely hydrolysed by alkali in methanol[8]. The highly phosphorylated poly(vinyl) alcohol) (P-PVA) was prepared and purified by the procedure described in the previous paper[8]. The degree of phosphorylation was determined by pH titration and the molybdenum blue method. All of the other reagents used here were analytical reagent grade.

pH titration

All titrations were carried out under a nitrogen atmosphere in a glass vessel maintained at 25°C. The vessel was fitted with a glass electrode/calomel electrode system, a titration burette, and a nitrogen gas inlet. Sample solutions were adjusted to 0.01 mol dm^{-3} for the unit concentration of phosphoric acid group, 0.002 mol dm^{-3} for the metal ion concentration, and ionic strength was 0.1 using potassium chloride: thus, the proportion of metal ion concentration to phosphoric acid group was 5. Titration of the aqueous P-PVA solution in the presence or absence of metal ion was performed by using 0.10 N KOH aqueous solution.

Measurements

The electronic spectra were recorded on a JASCO UVIDEC-505 spectrophotometer at room temperature. A Valian E-109E ESR spectrometer (X-band) was used for e.s.r. spectra of the frozen solutions at 77 K.

RESULTS AND DISCUSSION

The degree of phosphorylation of the prepared P-PVA was 15 mol%. The titration curve of the aqueous P-PVA solution revealed that one proton of the phosphoric acid group in P-PVA was dissociated at pH 3.5–4.0 ($pka_1 \simeq 2.84$). The complex formation of the phosphoric acid group in P-PVA with metal ion may proceed

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through the following steps:

$$\mathrm{Mt}^{m+} + \mathrm{HL}^- \xrightleftharpoons{b_1} \mathrm{MtL}^{m-2} + \mathrm{H}^+ \tag{1}$$

$$\mathrm{MtL}^{m-2} + \mathrm{HL}^- \xrightleftharpoons{b_2} \mathrm{MtL}_2^{m-4} + \mathrm{H}^+ \tag{2}$$

$$\mathrm{MtL}_2^{m-4} + \mathrm{HL}^- \xrightleftharpoons{b_3} \mathrm{MtL}_3^{m-6} + \mathrm{H}^+ \tag{3}$$

$$\mathrm{MtL}^{m+} + \mathrm{HL}^- \xrightleftharpoons{B} \mathrm{MtLn}^{m-2n} + n\mathrm{H}^+ \tag{4}$$

where HL^- represents a phosphate anion $-\mathrm{PO_3H}^-$ in P-PVA, and b_1, b_2, b_3, and B are equilibrium constants for equations (1) to (4). These equilibrium constants were estimated using a modified Bjerrum's method[10]. For the present complexation, there are three successive formation constants, k_1, k_2, and k_3 as given below:

$$k_1 = \frac{[\mathrm{MtL}^{m-2}]}{[\mathrm{Mt}^{m+}][\mathrm{L}^{2-}]} \tag{5}$$

$$k_2 = \frac{[\mathrm{MtL}_2^{m-4}]}{[\mathrm{MtL}^{m-2}][\mathrm{L}^{2-}]} \tag{6}$$

$$k_3 = \frac{[\mathrm{MtL}_3^{m-6}]}{[\mathrm{MtL}_2^{m-4}][\mathrm{L}^{2-}]} \tag{7}$$

$$K = k_1 \cdot k_2 \cdot k_3 = \frac{[\mathrm{MtL}_3^{m-6}]}{[\mathrm{Mt}^{m+}][\mathrm{L}^{2-}]^3} \tag{8}$$

where Mt^{m+} is the bivalent or trivalent metal ion and L^{2-} is the ligand; MtL^{m-2}, MtL_2^{m-4}, and MtL_3^{m-6} refer to the three complex species. In the complex formation between the polymeric ligand and metal ion, it is found that the value of pH when the coordination occurs is lower than the pka_2 value of the polymeric ligand. Considering the equilibrium of equations (1)–(3), the product $b_1 \cdot b_2 \cdot b_3$ was represented by 'B'. The relationship between B and K is $B = k_j \cdot ka_2$, where 'j' is 1–3 and 'ka_2' is the second acid dissociation constant of phosphoric acid group in P-PVA. Therefore, we can write B, b_1, b_2, and b_3 as follows:

$$B = b_1 \cdot b_2 \cdot b_3, \quad b_1 = k_1 \cdot ka_2, \quad b_2 = k_2 \cdot ka_2,$$
$$b_3 = k_3 \cdot ka_2 \tag{9}$$

Using Bjerrum's method[11], we defined the average number of ligands bound per metal ion, $\bar{n}$, which is expressed as

$$\bar{n} = \frac{[\mathrm{MtL}^{m-2}] + 2[\mathrm{MtL}_2^{m-4}] + 3[\mathrm{MtL}_3^{m-6}]}{[\mathrm{Mt}^{m+}] + [\mathrm{MtL}^{m-2}] + [\mathrm{MtL}_2^{m-4}] + [\mathrm{MtL}_3^{m-6}]} \tag{10}$$

$$\bar{n} = \frac{k_1[\mathrm{L}^{2-}] + 2k_1 \cdot k_2[\mathrm{L}^{2-}]^2 + 3k_1 \cdot k_2 \cdot k_3[\mathrm{L}^{2-}]^3}{1 + k_1[\mathrm{L}^{2-}] + k_1 \cdot k_2[\mathrm{L}^{2-}]^2 + k_1 \cdot k_2 \cdot k_3[\mathrm{L}^{2-}]^3} \tag{11}$$

Based on electroneutrality and mass balance, we can obtain the useful relationship equation (12) from equations (10) and (11):

$$\bar{n} = \frac{b_1 \cdot \frac{[\mathrm{HL}^-]}{[\mathrm{H}^+]} + 2b_1 \cdot b_2 \cdot \left(\frac{[\mathrm{HL}^-]}{[\mathrm{H}^+]}\right)^2 + 3b_1 \cdot b_2 \cdot b_3 \cdot \left(\frac{[\mathrm{HL}^-]}{[\mathrm{H}^+]}\right)^3}{1 + b_1 \cdot \frac{[\mathrm{HL}^-]}{[\mathrm{H}^+]} + b_1 \cdot b_2 \cdot \left(\frac{[\mathrm{HL}^-]}{[\mathrm{H}^+]}\right)^2 + b_1 \cdot b_2 \cdot b_3 \cdot \left(\frac{[\mathrm{HL}^-]}{[\mathrm{H}^+]}\right)^3} \tag{12}$$

where $[\mathrm{HL}^-]$ can be estimated from the observed pH value. The relationships between $\bar{n}$ and $-\log([\mathrm{HL}^-]/[\mathrm{H}^+])$ for the bivalent and trivalent metal ions are shown in *Figure 1* and *Figure 2*. By putting the observed values of $([\mathrm{HL}^-]/[\mathrm{H}^+])$ and $\bar{n}$ into equation (12), several simultaneous equations are derived for each of the modified Bjerrum's plots, and then the value of b_1, b_2, and b_3 under various conditions can be estimated by solving three simultaneous equations. Approximate values of b_1, b_2, and b_3 are easily read from the modified Bjerrum's plots at $\bar{n} = 1/2$, 1.0 and 1.5.

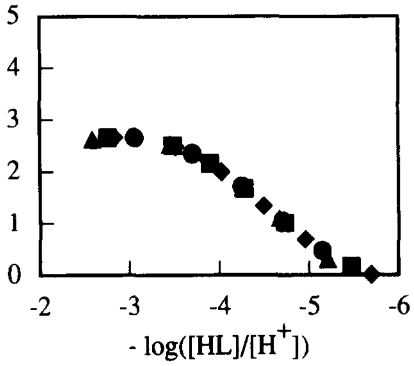

Figure 1 Modified Bjerrum plots for bivalent metal ion-P-PVA. ■, Co(II); ▲, Ni(II); ●, Cu(II); ◆, Zn(II)

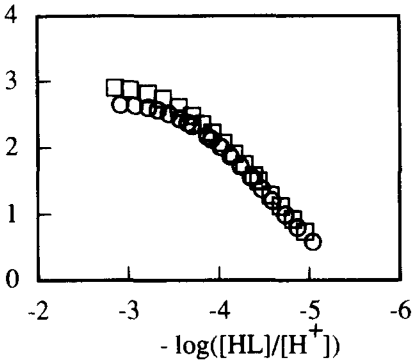

Figure 2 Modified Bjerrum plots for trivalent metal ion-P-PVA. ○, Fe(III); □, CR(III)

From the formation curves shown in *Figure 1* and *Figure 2*, it was estimated that the coordination numbers of P-PVA for the bivalent and trivalent metal ions are 2 and 3 for one metal ion, respectively.

The values of the constants, b_1, b_2, b_3, B, k_1, k_2, k_3, and K, which were estimated by the methods mentioned above are summarized in *Table 1*. The successive stability constants, k_1, k_2, and k_3 and overall stability constant, K, were obtained from equation (9). The second acid dissociation constant of P-PVA, referred to as ka_2 was determined using a modified Henderson-Hasselbach's equation[12] on the basis of the titration data for aqueous P-PVA solution.

Overall formation constants $\log K$ for all bivalent metal-P-PVA complexes were about 4.6. These values are smaller than those of the other macromolecular metal complexes[13]. We have reported that the viscosity of the aqueous Cu(II)-P-PVA solution decreased with the complex formation induced by an increase of pH. This indicated that the polymer complex took a very compact structure as a whole: thus, Cu(II)-P-PVA complex was formed by the intramolecular chelation[14]. The steric

Table 1 Formation constants (kj) of Mt-P-PVA complexes

Mt	$\log b_1(\log k_1)$	$\log b_2(\log k_2)$	$\log b_3(\log k_3)$	$\log B(\log K)$
Co^{2+}	-5.273 (1.827)	-4.328 (2.772)	-	-9.601 (4.599)
Ni^{2+}	-5.282 (1.818)	-4.308 (2.792)	-	-9.590 (4.610)
Cu^{2+}	-5.219 (1.881)	-4.310 (2.790)	-	-9.529 (4.671)
Zn^{2+}	-5.241 (1.859)	-4.307 (2.793)	-	-9.548 (4.652)
Fe^{3+}	-5.338 (1.762)	-4.443 (2.657)	-3.533 (3.567)	-13.314 (7.986)
Cr^{3+}	-5.318 (1.782)	-4.364 (2.736)	-3.412 (3.688)	-13.094 (8.206)

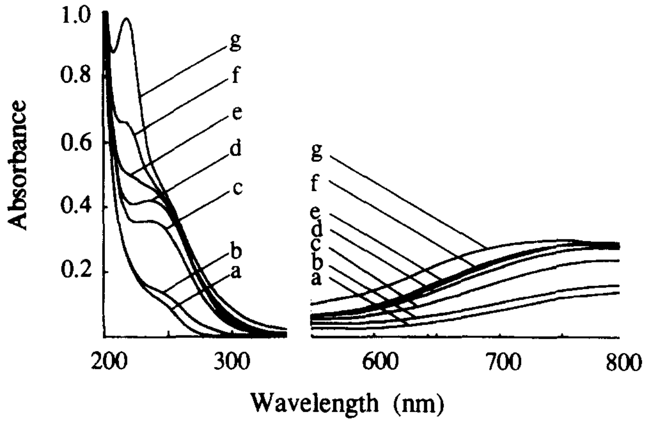

Figure 3 Electronic spectra for Cu(II)-P-PVA complex at various pH: a, 2.78; b, 3.12; c, 5.42; d, 6.29; e, 7.05; f, 7.71; g, 8.57 at 25°C, $\mu = 0.1$ (KCl). Cell length, 0.1 cm (200–300 nm) and 5 cm (550–800 nm)

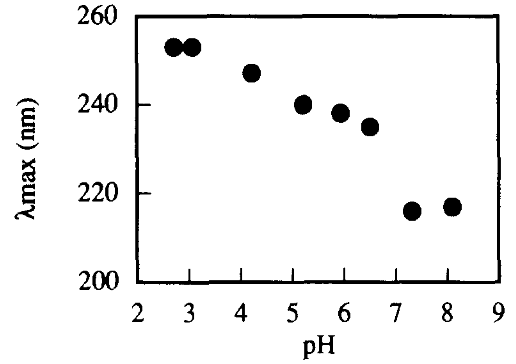

Figure 4 Relationship between λ_{max} and pH for Cu(II)-P-PVA complex

hindrance by bulky phosphoric acid group on P-PVA polymer chain taking the compact structure prevents the complex formation and lowers the $\log K$ value. The successive formation constants, *ki*, increased about 10 times with increasing *i*. This phenomenon is probably due to the chelate effect in the intramolecular complex formation, which is generally known when the complex of metal ion with polymeric ligand is formed[15]. The formation constants, $\log k_1$, $\log k_2$, $\log k_3$, and $\log K$ increase in the order of Cu(II) > Zn(II) > Ni(II) > Co(II), which agrees with the Irving–Williams series for stability constants of many bivalent metal complexes[13].

U.v.-visible absorption spectra of aqueous Cu(II)-P-PVA solutions at various pH are shown in *Figure 3*.

In the pH range from 2.5 to 3.0, the absorption spectrum of aqueous Cu(II)-P-PVA solution gave two absorption bands at 780 nm and 253 nm. As $\bar{n}$ was increased with increasing pH, both the hyperchromic and the blue shift were observed. The absorption bands

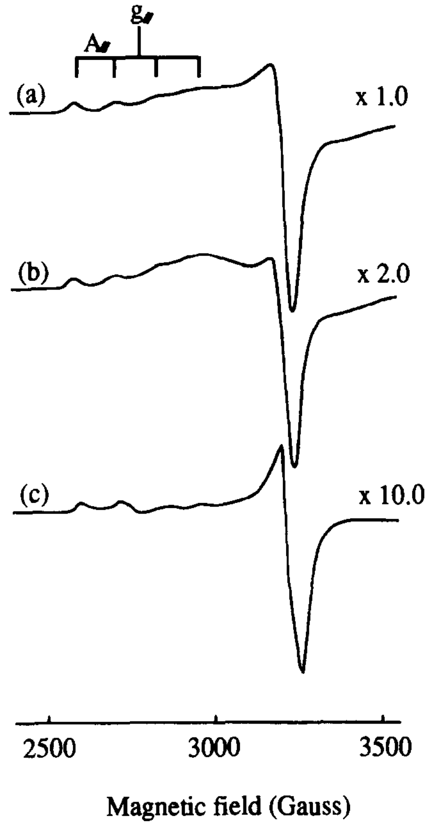

Figure 5 E.s.r. spectra of Cu(II)-P-PVA at 77 K: (a) pH 2.78; (b) pH 4.31; (c) pH 8.57

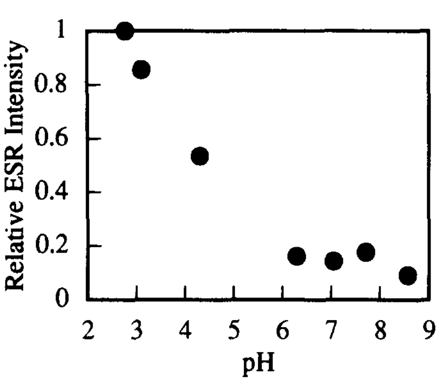

Figure 6 pH-dependence of intensity of e.s.r. spectra

at 780 nm and 253 nm correspond to the d-d band of Cu(II)-P-PVA complex and the $P\pi(0) \rightarrow dx^2 - y^2(Cu)$ charge transfer transition, respectively. This observation indicates that the phosphoric acid group in P-PVA complexes cupric ion at this pH.

A plot of the λ_{max} at the $P\pi(0) \rightarrow dx^2 - y^2(Cu)$ against pH for aqueous P-PVA-Cu(II) solution is shown in *Figure 4*. At pH >3.5, the blue shift of λ_{max} was observed, and the λ_{max} finally reached 218 nm at pH 7.0. Essentially the same shift of λ_{max} was observed in the Cu(II)-PVA system, indicating that the Cu(II)-P-PVA complex formed was similar to the Cu(II)-PVA one above pH 7.0[16,17].

Figure 5 shows the e.s.r. spectra for Cu(II)-P-PVA at pH of 2.78, 4.31, and 8.57. A plot of the signal intensity of e.s.r. spectra against pH for Cu(II)-P-PVA is shown in *Figure 6*. The shapes and e.s.r. parameters for three spectra almost resemble each other, but e.s.r. signal intensity decreased with increasing pH. The obtained e.s.r. parameters indicate that the Cu(II) complex takes square planar configuration, binding to four oxygens. In particular, at $pH < 3$, the Cu(II) ion binds to oxygen in the phosphoric acid group. The signal intensity decreased in the pH range 3–6, and then remained constant above pH 6. This indicates that a Cu(II) complex at $pH < 3$ differs from one at $pH > 6$. Further, the e.s.r. intensity at $pH > 6.2$ was similar to that for the hydrophobic interaction between the $Cu(OH)_2$ cluster and PVA[10]. The $Cu(OH)_2$ cluster may be formed in Cu(II)-P-PVA in a similar manner to the formation of the cluster in Cu(II)-PVA at $pH > 6.2$.

In conclusion, the complex between phosphoric acid groups on P-PVA and metal ions were formed at $pH < 3.5$, and the average ligand numbers for bivalent or trivalent metal ions were 2 or 3. The formation constants increased in order of Cu(II) > Zn(II) > Ni(II) > Co(II), which agreed with the Irving–Williams series for stability constants of many bivalent metal complexes. The overall formation constants for bivalent metal ion were about 4.6. The stability of complexes was lower than those of the other macromolecular metal complexes. This was explained by the steric hindrance by bulky phosphoric acid groups on the P-PVA polymer chain.

The e.s.r. spectra suggest that the planar complex between Cu(II) ion and two phosphoric acid groups on P-PVA is formed at $pH < 3.5$. The Cu(II)-P-PVA complex breaks with increasing pH, and Cu(II) ion forms a polynuclear complex of $Cu(OH)_2$ at $pH > 6.2$. The $Cu(OH)_2$ cluster may be solubilized by the hydrophobic interaction with P-PVA polymer chain as the Cu(II)-PVA complex.

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