Solution spinning of high T_c oxide superconductor: 1. Effect of propionic acid on the interaction between poly(vinyl alcohol) and copper (II) acetate

Hisayo Tomita*
Suzuka Junior College, 1250 Shono-cho, Suzuka, Mie 513, Japan

and Tomoko Goto
Department of Materials Science & Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan
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As basic research for the solution spinning of high T_c oxide superconductor, the interaction between poly(vinyl alcohol) (PVA) and copper (Cu) (II) acetate in aqueous solution and in the solid state with and without propionic acid was studied. The interaction between PVA and Cu (II) ions in aqueous solution was extremely weak or non-existent. Complex formation of PVA with Cu (II) was observed in the solid state. The complex was changed from the co-ordination of the Cu (II) ion to the hydroxy groups on PVA to the Cu (II) ion complexing with two acetate ions and the hydroxy groups of PVA by adding propionic acid.

(Keywords: PVA; copper (II) acetate; propionic acid; solution and solid states)

INTRODUCTION

Polymer–metal complexes are of increasing interest in the field of functional polymeric materials. In the textile industry, organic fibre containing metal or metal oxide has become of major interest for antimicrobial fibres for medical use.

Poly(vinyl alcohol) (PVA) is a simple synthetic water-soluble polymer, and the copper (Cu) (II) complex of PVA at $pH > 7$ has been studied by many investigators[1–6]. However, the interaction between PVA and the Cu (II) ion in solution and in the solid state at $pH < 7$ has not been disclosed.

One of the authors has studied the preparation of high T_c oxide superconducting long filaments using textile fibre spinning technology for the precursor of the oxide. The Ba–Y–Cu oxide filament is prepared by dry-spinning starting from a homogeneous aqueous solution containing acetates of Ba, Y and Cu, PVA and propionic acid[7–9]. The superconducting properties of the heated filament depend on the spinning dope as well as on the spinning conditions and heat treatment. The addition of propionic acid is the key to obtaining a stable viscous homogeneous spinning dope. The effect of propionic acid on the interaction between PVA and Cu (II) acetate in aqueous solution and in the solid state is studied in this paper.

EXPERIMENTAL

PVA (degree of polymerization, $\bar{P} = 1700$) was supplied by Nitivy Co. Ltd, and had a degree of saponification of 85 mol%, as determined by ^{1}H n.m.r. All other reagents were of analytical grade and were used without further purification.

Aqueous solutions for ultraviolet/visible (u.v./vis.) spectroscopy contained $0 \sim 1.0 \text{ mol l}^{-1}$ PVA, $0.5 \times 10^{-2} \sim 5.5 \times 10^{-2} \text{ mol l}^{-1}$ Cu (II) acetate and 0 or 0.8 ml l^{-1} propionic acid. U.v./vis. spectra were recorded on a Jasco Ubest 35 in the region of $200 \sim 1000$ nm. The viscosity of the solution was measured with an Ostwald viscometer at $30 \pm 0.1°C$.

The interaction between PVA and the Cu (II) ion in the solid state was also examined. The sample films were cast at 80°C on a polypropylene substrate after deaerating the solution. A Hitachi 285 was used for i.r. spectroscopy. X-ray diffraction and d.s.c. (Rigaku Denki Co. Ltd) were used to investigate the structure of the films. ^{1}H n.m.r. spectra were recorded on a Varian XL-200 (200 MHz).

RESULTS AND DISCUSSION

Interaction between PVA and the Cu (II) ion in aqueous solution

The interaction between PVA and the Cu (II) ion in aqueous solution was examined by spectroscopy and viscosity measurements. *Figure 1* shows u.v./vis. absorption spectra of aqueous Cu (II) acetate solutions and mixed solutions of Cu (II) acetate and PVA with and without propionic acid. The maximum absorption band for these spectra is observed at 770 nm, due to the aqueous Cu (II) ion, while a solution with $pH > 7$ showed two absorption bands at 260 and 640 nm for the complex between PVA and the Cu (II) ion, as previously reported[2]. The present spectra of the aqueous Cu (II)

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* To whom correspondence should be addressed

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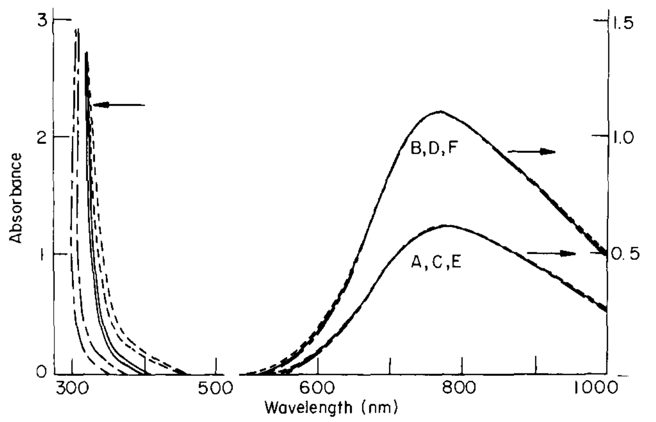


Figure 1 U.v./vis. spectra of aqueous Cu (II) acetate solution at room temperature: (— – —, A) Cu (II) solution, 2.5×10^{-2} mol l^{-1}; (— – —, B) Cu (II) solution, 5.0×10^{-2} mol l^{-1}; (– – –, C) PVA + Cu (II) solution, 1.0 mol l^{-1} PVA, 2.5×10^{-2} mol l^{-1} Cu (II) acetate; (– – –, D) PVA + Cu (II) solution, 1.0 mol l^{-1} PVA, 5.0×10^{-2} mol l^{-1} Cu (II) acetate; (——, E) PVA + Cu (II) + propionic acid solution, 1.0 mol l^{-1} PVA, 2.5×10^{-2} mol l^{-1} Cu (II) acetate, 2 ml l^{-1} propionic acid; (——, F) PVA + Cu (II) + propionic acid solution, 1.0 mol l^{-1} PVA, 5.0×10^{-2} mol l^{-1} Cu (II) acetate, 4 ml l^{-1} propionic acid

Table 1 Molar absorption coefficients of various Cu (II) acetate solutions at 770 nm

Solution[a]	pH	ε (l mol^{-1} cm^{-1})
Cu (II)	5.8	25
Cu (II) + propionic acid	4.3	24
PVA + Cu (II)	5.5	25
PVA + Cu (II) + propionic acid	4.3	26

[a] PVA, 1 mol l^{-1}; propionic acid, 0.8 ml l^{-1}

Table 2 Intrinsic viscosity values and Huggins constants of various PVA solutions at 30°C

Solution[a]	pH	$[\eta]$	K'
PVA	5.0	0.7	0.9
PVA + propionic acid	4.3	0.7	0.9
PVA + Cu (II)	5.5	0.7	0.9
PVA + Cu (II) + propionic acid	4.3	0.7	1.0

[a] Cu (II) acetate, 2.5×10^{-2} mol l^{-1}

acetate solution with and without PVA are almost identical and do not change by adding propionic acid, indicating that the interaction between PVA and the Cu (II) ion at pH $\leqq 5.8$ is extremely weak or non-existent. The molar absorption coefficient (ε) was calculated from the linear slope of the absorbance at 770 nm (λ_{max}) and the concentration of Cu (II) acetate (*Table 1*). The ε values of the aqueous Cu (II)–PVA solution with and without propionic acid are almost identical to those of the corresponding Cu (II) acetate solution.

These solutions were dialysed against the solution using a Visking tube. As the absorbance in the visible region of the spectra of the solution in this tube was not detected, the Cu (II) ions in PVA solution could be washed away during the dialysis. The intrinsic viscosity of the solution was evaluated from experimental data using the Huggins equation:

$$\eta_{sp}/C = [\eta] + K'[\eta]^2 C$$

where η_{sp} is the specific viscosity, C is the concentration of PVA (g dl^{-1}), $[\eta]$ is the intrinsic viscosity (dl g^{-1}) and K' is the Huggins constant. The resulting values are presented in *Table 2*. The Huggins constant for PVA containing Cu (II) ions is the same as for PVA without Cu (II) ions. The value of the Huggins constant for Cu (II)–PVA on adding propionic acid is slightly increased. This suggests that the configuration of PVA in the solution did not change even if the Cu (II) ion coexisted. Thus, the interaction between PVA and the Cu (II) ion in solution at pH $\leqq 5.8$ is very small.

Interaction betweeen PVA and the Cu (II) ion in the solid state

The film made from an aqueous solution containing PVA and Cu (II) acetate was greenish and insoluble in water, but the film cast from a solution of Cu (II) acetate coexisting with propionic acid became bluish and was soluble in water. U.v./vis. spectra of these films were measured and the absorption spectra are shown in *Figure 2*. A maximum absorption band shifted from 770 to 670 nm, and there was another shoulder-like band at 370 nm. The blue-shift in the visible region suggests some interaction between PVA and Cu (II) acetate. The interaction between PVA and Cu (II) acetate in the solid state is considered to be due to an environmental effect attributed to a domain of polymer matrix, in contrast to the aqueous results. The addition of propionic acid to PVA–Cu (II) acetate results in a decrease in the absorption at 370 nm and an increase in the absorption at 670 nm. This shows the addition of propionic acid could result in a change in the type of interaction between PVA and the Cu (II) ion. X-ray diffraction patterns of these films were measured. *Figures 3* and *4* show the patterns for the film cast from solution without and with propionic acid, respectively. The PVA film has a sharp peak at $2\theta = 20°$ as shown in *Figures 3a* and *4a*. As the concentration of Cu (II) acetate increases, the peak at $2\theta = 20°$ decreases and becomes broader, and a new

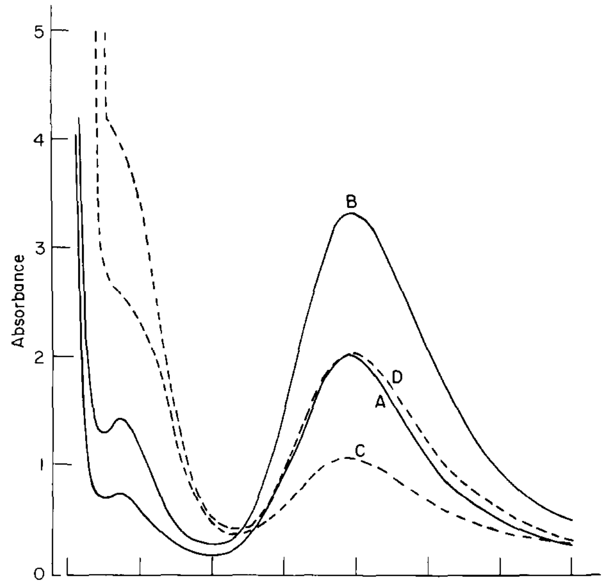


Figure 2 U.v./vis. spectra of the film cast from an aqueous solution of PVA and Cu (II) acetate: (A) [Cu]/[OH] = 0.054 with propionic acid; (B) [Cu]/[OH] = 0.11 with propionic acid; (C) [Cu]/[OH] = 0.054 without propionic acid; (D) [Cu]/[OH] = 0.11 without propionic acid

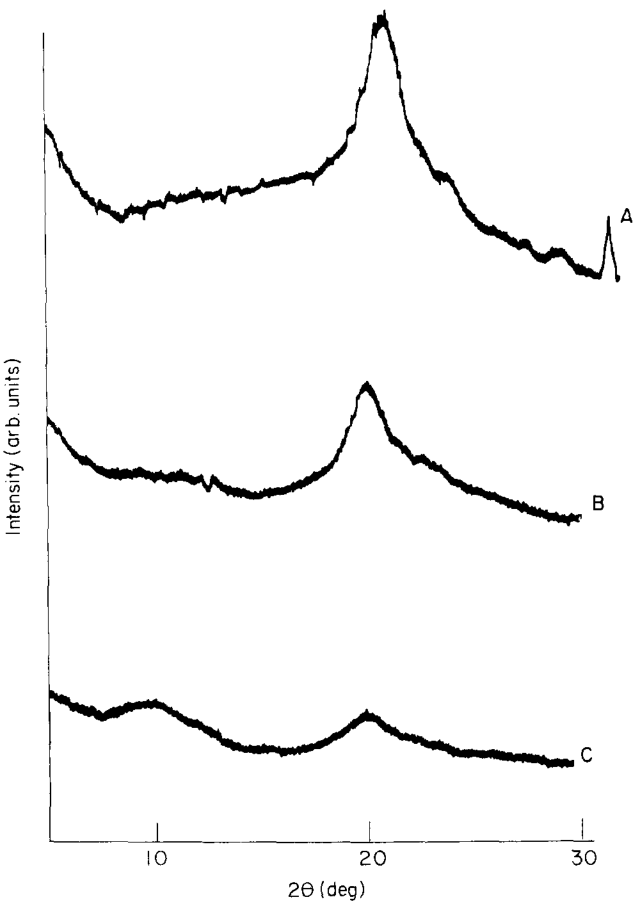
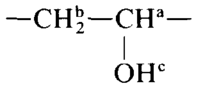


Figure 3 X-ray diffraction patterns of the film cast from an aqueous solution of PVA and Cu (II) acetate by using Cu Kα radiation: (A) [Cu]/[OH] = 0; (B) [Cu]/[OH] = 0.054; (C) [Cu]/[OH] = 0.11

broad peak at $2\theta = 10^\circ$ appears. Moreover, two peaks at $2\theta = 14$ and 7° are observed for the case of coexisting propionic acid. It is well known that PVA is easily crystallized by casting because of the formation of hydrogen bonds by the hydroxy groups, and the peak at $2\theta = 20^\circ$ is due to a reflection [1 0 1] of the crystal structure of PVA[10]. The addition of Cu (II) acetate broke the hydrogen bonding of PVA and made the structure amorphous. The broad peak at $2\theta = 10^\circ$ suggests the appearance of a new structure due to the interaction between PVA and the Cu (II) ion. The new peaks at $2\theta = 14$ and 7° for the film cast with propionic acid could indicate the formation of a different structure because of other interactions between PVA and the Cu (II) ion. The acetate complex of the Cu (II) ion is usually a binuclear complex of two Cu (II) ions, four acetate ions and two co-ordinating water molecules. The complex[11] is a monoclinic system with $a = 13.10$ Å, $b = 8.56$ Å, $c = 13.88$ Å and $\beta = 116^\circ 26'$. The peaks at $2\theta = 7$, 10 and 14° for the present films did not agree with the structure for the acetate complex of the Cu (II) ion. I.r. spectra of these films are shown in *Figure 5*. The spectra for PVA with and without the Cu (II) ion are almost the same except for the disappearance of the small absorption at 1140 cm^{-1} for the PVA–Cu (II) film. For the film cast from an aqueous solution of PVA and Cu (II) acetate, the absorption band due to the acetic group was not detected, as shown in *Figure 5b*. The acetic acid could vaporize on the film cast at 80°C. The absorption at 1140 cm^{-1} is caused by the crystallization sensitive band of PVA film, and the crystal structure of the PVA film disappeared by adding Cu (II), as discussed for the X-ray diffraction measurements. For the film cast from a solution where propionic acid coexisted, absorption bands of a strong peak at 1610 cm^{-1} and peaks at 1420 and 680 cm^{-1} appeared. These absorptions are characteristic bands of the caboxylate ion. This indicates that propionic acid could lead to the formation of a different complex between PVA and Cu (II) containing the carboxylate ion. A ^{1}H n.m.r. study of PVA–Cu (II) film with propionic acid was carried out in order to clarify whether the carboxylate group was acetic acid or propionic acid. The ^{1}H n.m.r. spectrum of the D_2O solution of the film cast from a mixed aqueous solution of PVA, Cu (II) acetate and propionic acid is shown in *Figure 6*. There are four clear peaks at 4.85, 4.04, 2.10 and 1.66 ppm. The structure of PVA is:



$$-\mathrm{CH}_2^{b}-\underset{\displaystyle \mathrm{OH}^{c}}{\underset{|}{\mathrm{CH}^{a}}}-$$

The peaks at 4.85, 4.04 and 1.66 ppm are based on the protons denoted by c, a and b in PVA, respectively[12], although the peak at 4.85 ppm contains the signal of HOD. The peak at 2.10 ppm shows methyl protons (d) from the acetate group ($\mathrm{CH}_3^d\mathrm{COO}-$) and the unsaponified vinyl acetate unit. Thus, the peak of methylene protons (e) in propionic acid ($\mathrm{CH_3CH_2^eCOOH}$) did not appear. Propionic acid may vaporize during film casting at 80°C. The ^{1}H n.m.r. spectrum of PVA alone indicated that the mole fraction of the unsaponified vinyl

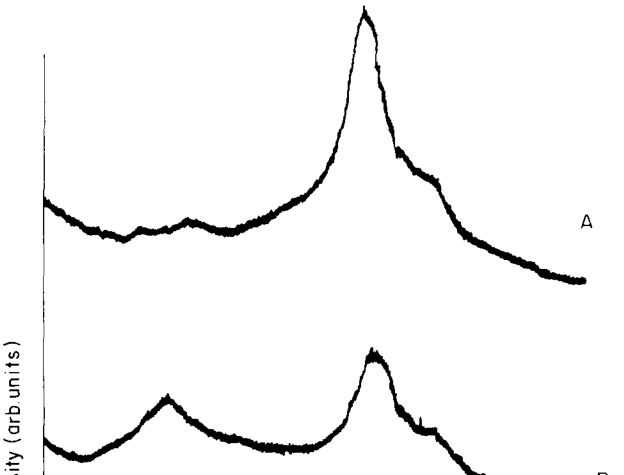


Figure 4 X-ray diffraction patterns of the film cast from a mixed aqueous solution of PVA, Cu (II) acetate and propionic acid by using Cu Kα radiation: (A) [Cu]/[OH] = 0; (B) [Cu]/[OH] = 0.054; (C) [Cu]/[OH] = 0.11

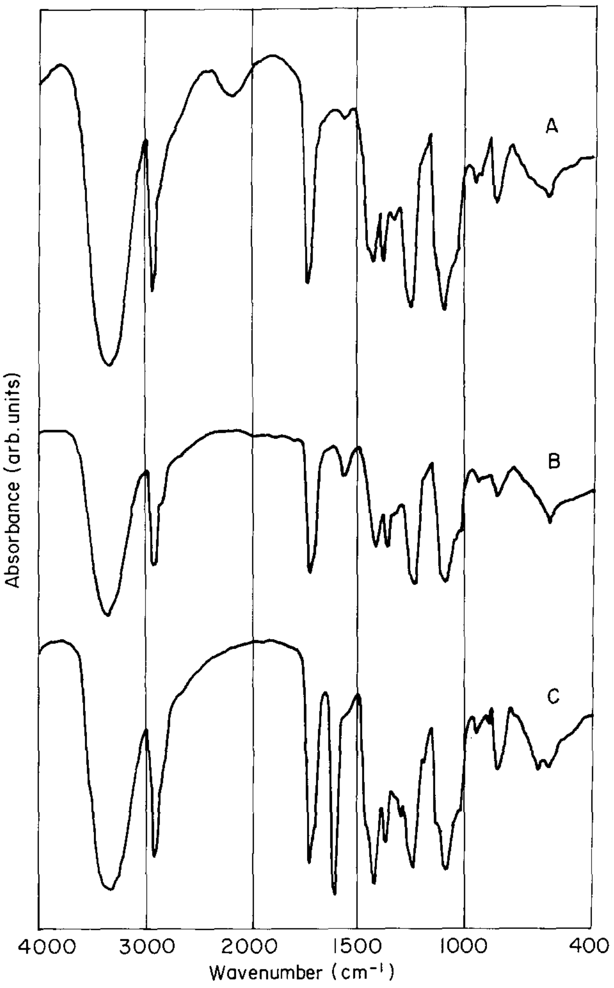


Figure 5 I.r. spectra of the film cast from various aqueous solutions of PVA: (A) PVA; (B) PVA + Cu (II) acetate, [Cu]/[OH] = 0.11; (C) PVA + Cu (II) acetate + propionic acid, [Cu]/[OH] = 0.11

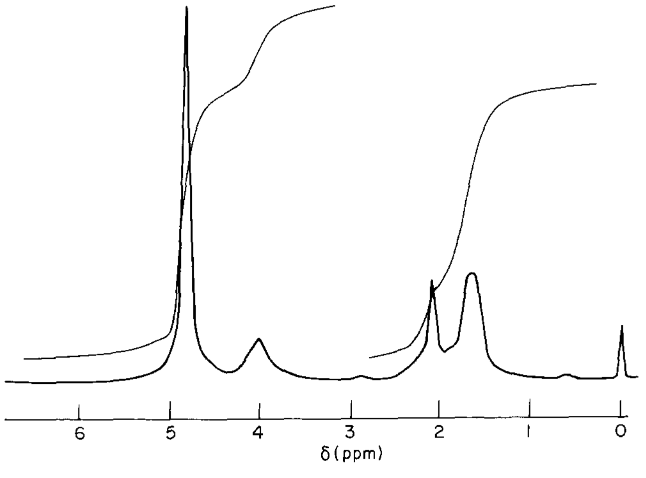


Figure 6 N.m.r. spectrum of the D_2O solution of the film cast from a mixed aqueous solution of PVA, Cu (II) acetate and propionic acid. [Cu]/[OH] = 0.11

acetate unit in PVA was 0.15. The peak area ratio of the methyl proton (2.10 ppm) in *Figure 6*, by considering the amount of residual vinyl acetate unit, suggested that two acetate groups and one Cu atom were linked together. D.s.c. measurements were performed and the curves are shown in *Figure 7*. For PVA film, an endothermic peak below 200°C and an exothermic peak above 300°C were observed, indicating the melting and decomposition of PVA, respectively. By adding Cu (II), the endothermic temperature of the peak decreased and a new exoethermic peak from 200 to 250°C appeared. The depression of melting point could be caused by the formation of a PVA–Cu (II) complex. It is considered that the new broad exothermic peak at 200 ~ 250°C was due to the decomposition of the polymer–metal complex and oxidation of the Cu (II) ion. The additional endothermic peak at 145°C and exothermic peak at 220°C are shown for the film cast from a solution with propionic acid. The endothermic peak at 145°C could arise from the melting of the new crystal structure formed by the complex containing the acetate group, and another exothermic peak at 220°C could show the thermal decomposition and elimination of the organic acetate group. D.t.a and t.g.a. of gel powders of Bi-Sr-Ca-Cu-O ceramics made from metal acetates were studied by Zhuang *et al.*, and an exothermic peak at 230°C due to thermal decomposition of the acetate ions co-ordinating Cu (II) ions was found[13].

A schematic diagram of the PVA–Cu (II) complex is shown in *Figure 8*. N.m.r. and e.s.r. measurements in solution and in the solid state would be required for a detailed structure of the complex. The hydroxy groups on PVA are co-ordinated to the Cu (II) ion and a network of polymers is formed for the film cast from an aqueous solution of PVA and Cu (II) acetate (*Figure 8a*). Two acetate ions and the hydroxy groups on PVA are co-ordinated to the Cu (II) ion for the film cast from an aqueous solution of PVA, Cu (II) acetate and propionic acid (*Figure 8b*).

On the solution spinning of a Ba–Y–Cu–O superconductor, the addition of propionic acid enhanced the solubility of the Ba, Y and Cu (II) acetates and enabled fibre formation to take place. It is generally accepted that the configuration of the polymer molecules in the crystalline or linear ordered regions of fibres can be linear or helical. The linear complexing shown in *Figure 8b* should be beneficial for the formation of the precursor filament.

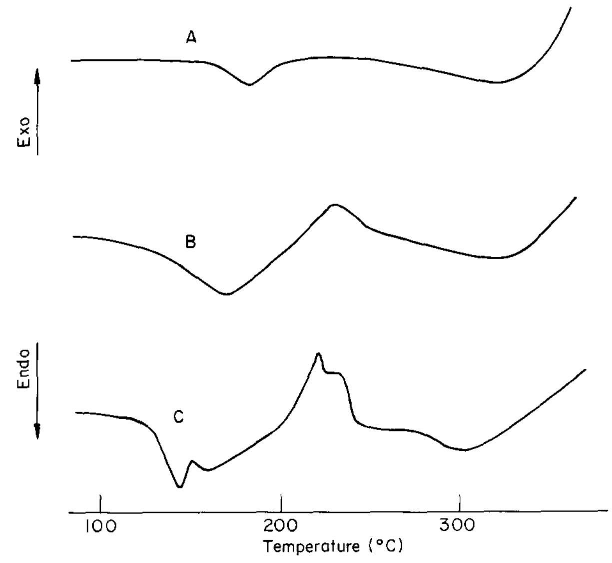


Figure 7 D.s.c. curves of the film cast from an aqueous solution of PVA at a heating rate of 20°C min^{-1}: (A) PVA; (B) PVA + Cu (II) acetate, [Cu]/[OH] = 0.11; (C) PVA + Cu (II) acetate + propionic acid, [Cu]/[OH] = 0.11

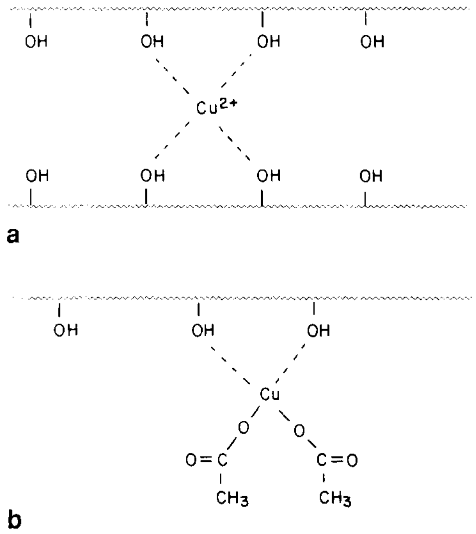


Figure 8 Schematic diagram of the PVA–Cu (II) complex: (a) for the film cast from an aqueous solution of PVA and Cu (II) acetate at 80°C; (b) for the film cast from an aqueous solution of PVA, Cu (II) acetate and propionic acid at 80°C

CONCLUSIONS

As basic research for the solution spinning of an oxide superconductor, the effect of propionic acid on the interaction between PVA and Cu (II) acetate in aqueous solution and in the solid state was studied using u.v./vis. and i.r. spectroscopy, solution viscometry, X-ray diffraction, d.s.c. and ^{1}H n.m.r. The interaction between PVA and the Cu (II) ion with and without propionic acid in aqueous solution was extremely weak or non-existent. The complex formation of PVA–Cu (II) was observed by casting the film from solution. The PVA film including only the Cu (II) ion was greenish and insoluble in water, and the Cu (II) ion co-ordinated to the hydroxy groups on PVA and a network of polymers was formed. Addition of propionic acid varied the structure of the complex. The film cast from a mixed aqueous solution of PVA, Cu (II) acetate and propionic acid was bluish and soluble in water and formed a Cu (II) complex with two acetate ions and the hydroxy groups on PVA.

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REFERENCES

1 Saito, S. and Okuyama, H. *Kolloid. Z.* 1954, **139**, 150
2 Hojo, N., Shirai, H. and Hayashi, S. *J. Polym. Sci. Symp. Ser.* 1986, **47**, 299
3 Yokoi, H., Kawata, S. and Iwaizumi, M. *J. Am. Chem. Soc.* 1986, **108**, 3358
4 Ku, C. L. and Chen, J. H. *Polymer* 1991, **32**, 3177
5 Kida, S., Nishida, Y. and Sakamoto, M. *Bull. Chem. Soc. Jpn* 1973, **46**, 2428
6 Klech, C. M., Cate, A. E. and Suttle, A. B. *Colloid Polym. Sci.* 1991, **269**, 643
7 Goto, T. and Sugishita, T. *Jpn J. Appl. Phys.* 1991, **30**, L997
8 Goto, T., Sugishita, T. and Kojima, K. *Physica C* 1990, **171**, 441
9 Goto, T. and Yamada, K. *J. Appl. Polym. Sci.* 1992, **44**, 361
10 Mooney, R. C. L. *J. Am. Chem. Soc.* 1941, **63**, 2828
11 Kawamori, A. *J. Phys. Soc. Jpn* 1966, **21**, 1096
12 Kenney, J. F. and Willcockson, G. W. *J. Polym. Sci. A1* 1966, **4**, 679
13 Zhuang, H. R., Kozuka, H. and Sakka, S. *J. Mater. Sci.* 1990, **25**, 4762