

## **Spectral changes of co-doped PVA films in relation to their structures**

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### **SUMMARY**

The optical absorption spectra of Co-doped PVA thick films (~1 mm) of different concentrations from 0.0 to 30%  $\text{CoCl}_2$  are obtained at room temperature in the range 190-900 nm. Cobalt (II) is found to exist only in octahedral coordination for concentrations up to 10% with an asymmetrical absorption band located at 511 nm and shifted to longer wave length with increasing  $\text{CoCl}_2$  content. For higher concentration (>10%) the coexistence of both octahedral and tetrahedral coordinations is indicated by the appearance of a new structured broad band centered at 665 nm. Variations in the obtained spectra suggest a tendency to higher degree of ordering in the amorphous regions of the polymer structure by  $\text{CoCl}_2$  addition.

### **I. INTRODUCTION**

PVA is a crystalline polymer which has a wide range of technological uses [1]. An important feature of crystalline polymers is that they consist not only of crystalline but amorphous regions as well. These two regions are separated by portions of an intermediate degree of ordering. There is no sharp borderline between the crystalline and amorphous regions so that one macromolecule may run through several crystallites and amorphous regions. The existence of such two-phase chains is a characteristic feature of crystalline polymers.

It is sometimes believed that a crystalline polymer may be regarded as an amorphous matrix in which small crystallites are randomly distributed. However, it is more natural to treat a crystalline polymer as a certain (sufficiently imperfect) crystalline lattice in which the voids are filled with amorphous matter [2]. The role of amorphous regions may be played by sites saturated with crystal defects, kinked and joggled chains which form chain-folded crystals, etc... .

The sensitivity of the optical properties of transition metal ions to the immediate environment has long been used to probe structural variations of the given composite. The optical spectra of Co (II) has been extensively studied in different complexes by different authors at room temperature [3-11], liquid nitrogen temperature [12] and elevated temperatures [13].

Co (II) is known to exist either in octahedral, tetrahedral or both coordinations. The coordination number and band position largely depend on the structure of the composite. The observed absorption bands for Co (II) were interpreted well in terms of ligand field theory.

The aim of this paper is to investigate the role played by cobalt chloride addition on the structure of a crystalline polymer such as PVA.

## II. EXPERIMENTAL

Commercial PVA Powder (Hayashi pure chemical industries Ltd.), with an average degree of polymerization 1700 was used as the starting material. PVA films were prepared by casting method. The powder was dissolved in distilled water and gently heated in a water bath until it was completely dissolved. cobalt (II) was introduced as  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  dissolved in absolute ethyl alcohol and added in concentrations varying from 5 to 30%. The solutions were left to attain a suitable viscosity after which they were cast to glass dishes and left to dry in a dry atmosphere at room temperature. Thick films of the order of 1.0 mm were obtained. The absorption spectra were measured in the range 190-900 nm, using a computerized Perkin-Elmer spectrophotometer model Lambda 4B, at room temperature.

## III. RESULTS AND DISCUSSION

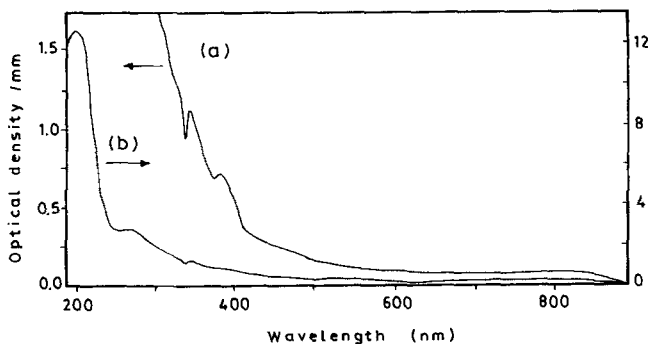
### III.1. PVA Spectrum

Figure 1 shows the absorption spectrum of undoped PVA film. As depicted from this figure two absorption bands appear at 340 and 373 nm in the region of wavelengths above 300 nm (curve a). The presence of two other absorption bands in the uv range at 200 and 273 nm is indicated for the same sample by increasing the scale of absorbance as shown by curve (b).

These absorption bands could be related to carbonyl-

containing structures of the types  $\text{-(CH=CH)}_n\text{-C}\overset{\text{O}}{\parallel}$  where  $n = 1, 2, \dots$ . These carbonyl-containing structures arise predominantly from the presence of acetaldehyde and dissolved air in the vinyl acetate monomer during polymerization [14].

The concentration of  $\text{-CH=CHCO-}$  structures can be estimated from the absorbance at 200 nm while the concentration of  $\text{-(CH=CH)}_3\text{CO-}$  structures can be estimated from the absorbance at 340 nm. However, the absorption at 273 nm is the result of an intense band due to  $\text{-(CH=CH)}_2\text{CO-}$  and a probable weak band due to isolated carbonyl groups.

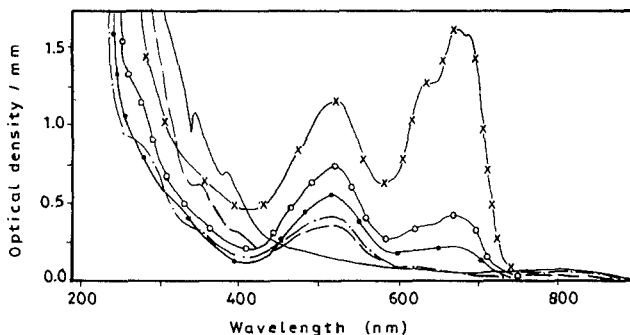


1. The optical absorption spectrum of undoped PVA film .

### III.2. Six- coordinated cobalt

The absorption spectra of Co-doped PVA with different concentrations are shown in Fig. (2). The spectrum of Co-free PVA is included for comparison. Addition of 5% cobalt

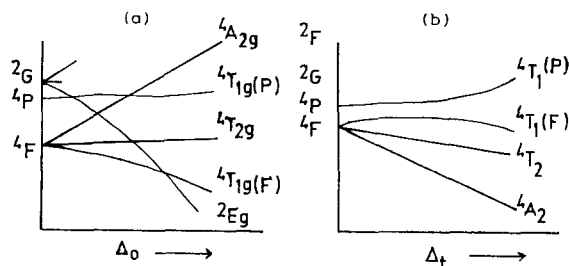
chloride caused the appearance of an asymmetrical absorption band located at 511 nm, and shifted to longer wave lengths for higher concentrations. The appearance of this band together with the faint pink colour of the sample indicate the presence of  $\text{Co}^{2+}$  ions in octahedral coordination. The presence of  $\text{Co}^{2+}$  ion entirely as six-coordinated cobalt has been reported in low-alkali borate glasses [3],  $(\text{Co}(\text{H}_2\text{O})_6)_2$  in solution and crystal [15],  $\text{Co}(\text{Pic})_2 \text{Cl}_2$  and  $\text{Co}(\text{Pic})_2 \text{Br}_2$  [10] and phosphate glasses [4].



2. The optical absorption spectra of PVA films doped with 0 (—), 5 (---), 10 (-.-), 15 (-.-.-), 20 (-.-.-) and 30 % (-x-) cobalt chloride .

From the energy level diagram of  $\text{Co}^{2+}$  ion ( $3d^7$ ) in octahedral coordination (Fig. 3 a), this band can be assigned to the  $4T_1(F) \Rightarrow 4T_1(P)$  allowed transition. On the other hand, the asymmetry of this band can be attributed to the removal of degeneracy of the  $4T_1(P)$  state probably by a small rhombic distortion of the octahedron of ligands arising from the Jahn-Teller effect. This rhombic distortion is found to gradually decrease with increasing the  $\text{CoCl}_2$  which may indicate a tendency to local ordering in the amorphous regions of the polymer structure by cobalt chloride addition.

This local ordering may be played by the role of intermolecular interactions in the polymer structure. It is suggested that addition of  $\text{CoCl}_2$  to PVA causes an increase in the intra- and intermolecular interactions between the polymer chains. Thus, the octahedron is expected to become more symmetric due to the contraction effect brought about by such interactions.



3. The energy level diagram of  $\text{Co}(\text{II})$  in octahedral (a) and tetrahedral (b) coordinations .

Moreover, increasing the Co-content from 0 to 10% is accompanied by a decrease in the intensity of the absorption bands at 340 and 373 nm (Fig.2). The values of optical density per mm for the other two bands ( $n = 1$  and  $n = 2$ ) below 300 nm were obtained by increasing the scale of absorbance and are plotted versus  $\text{CoCl}_2$ -concentration (Fig.4). The drastic decrease (more than 80%) in the absorbance of the band related to  $n = 1$  by increasing  $\text{CoCl}_2$  % from 0 to 10 % indicates a sharp decrease in the concentration of carbonyl-containing

structures of shortest length. This decrease may be attributed to the formation of a chlorine bridge (16) inbetween them by  $\text{CoCl}_2$  addition. Such summation of separate groups, together with the role played by intermolecular interactions are possible factors for a higher degree of ordering to be expected in the amorphous regions of the polymer structure.

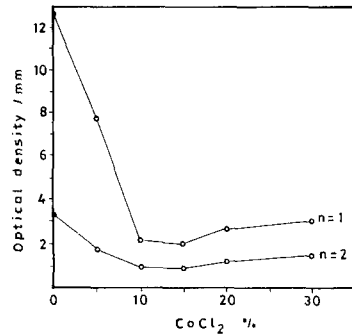
The observed shift in the 511 nm absorption band to longer wavelengths (Fig. 5) imply a lower value of field strength (i.e. lower B value) with increasing  $\text{CoCl}_2$  content. Regarding that covalency is expected to increase with increasing intermolecular interactions by  $\text{CoCl}_2$  addition, this shift has its explanation in the fact that increasing covalency should lead to lower B values (17).

### III.3. Four-coordinated cobalt

Increasing the cobalt concentration in PVA to 15% (Fig.2) caused the appearance of a new structured band centered at 665nm. The appearance of this band indicates the presence of Co (II) in tetrahedral coordination. It can be seen that the ratio of  $\text{Co}^{2+}$  ions which are present as  $(\text{CoCl}_4)^{2-}$  increases with increasing  $\text{CoCl}_2$ -concentration up to 30% (Fig.2). The variation in sample colour is consistent with this assignment. Sample colour gradually changes from faint pink to intense blue for samples containing 5 to 30% cobalt chloride respectively. The presence of Co (II) in both coordinations has been reported in borate [5,7] silicate [6] and phosphate glasses [3,9]. The intense blue colour of the 30% sample is due to the fact that the molar extinction coefficient of Co (II) in tetrahedron systems is very much higher than that of the octahedron systems.

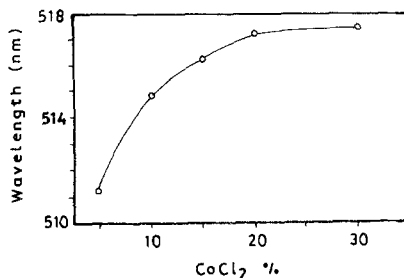
From the energy level diagram (Fig.3 b), this band can be assigned to the spin-allowed transition  $4A_2 \Rightarrow 4T_1$ . The two lower peaks at 626 and 682 nm could be assigned to spin forbidden transitions to doublet states allowed by spin-orbit coupling. However, it is preferable to consider the three peak system as due only to the spin allowed transition  $4A_2 \Rightarrow 4T_1$  split by LS interaction i.e. departure from Russell-Saunders coupling [12,15].

Again, inspecting Figure (4), it is noticed that formation of  $\text{CoCl}_4^{2-}$ , in samples containing more than 10% cobalt chloride, is accompanied by a slight increase in the intensity of the bands related to  $n = 1$  and  $n = 2$ . Therefore, it may be suggested that



4. Variations in the optical density /mm of the two bands at 200 and 273 nm with  $\text{CoCl}_2$  concentration .

increasing  $\text{CoCl}_2$  content beyond 15% causes a limited degradation in the polymer chains and consequently an increase in the concentration of carbonyl-containing structures with  $n = 1$  and  $n = 2$ . However, the slight increase in the intensity of these two bands may be attributed to an increase in the intensity of the tail of the 511 nm absorption band by subsequent  $\text{CoCl}_2$  additives as another explanation. The stabilized attained polymer structure as suggested by the stability of band position of six-coordinated cobalt at high concentrations (Fig.5) favours the second explanation.



5. Band position of six-coordinated cobalt for different  $\text{CoCl}_2$  concentrations.

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