

Optical Properties of Polyvinyl Alcohol doped with CoCl_2

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Optical absorption measurements in the spectral range 4000–50000 cm^{-1} were performed on cast thin films of polyvinyl alcohol (PVA) and its composites with cobalt chloride (CoCl_2). Identification of the structure and assignments of energy bands have been derived in terms of the ligand field theory. A mechanism based on the equilibrium between six-coordinated and four-coordinated symmetry is proposed to account for the obtained spectra. Such equilibrium is attributed to a small difference between the stabilization energies, and the symmetry is found to be altered with cobalt chloride concentrations.

INTRODUCTION

The addition of transition metal to polymeric network is of considerable interest for both scientific and technological purposes¹⁻⁴. The nature of the interaction between the metal ions and polymer molecules is usually approached using different techniques. The optical absorption is a direct and powerful tool for studying the transition metal environment and the feature of the metal-ligand bond. In the present work the author wishes to report the optical absorption spectra is cast thin films of polyvinyl alcohol- CoCl_2 composites. Such a study is likely to provide more information about the nature of intermolecular interactions as a result of the subsequent addition of CoCl_2 in the PVA matrix.

EXPERIMENTAL

The polyvinyl alcohol (PVA) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ used in this investigation were BDH chemicals. Weighed amounts of PVA were dissolved in distilled water. A solution of 20, 30, 50 and 80% of CoCl_2 by weight was added to the polymer. The mixture was stirred thoroughly and then poured on to dishes 12.5 cm in diameter; the homogeneous films free from bubbles were slowly dried in an air oven at 40°C for 24 hrs in order to minimize gelatin effects.

The optical absorption spectra of the sample under investigation were measured using Carl Zeiss PMQ 11 in the region 4000–50000 cm^{-1} at room temperature, with pure PVA films as a common reference.

RESULTS AND DISCUSSION

The optical absorption spectra of the investigated samples are shown in Fig. 1. The samples with CoCl_2 -content lower than 30% by weight do not show any detectable bands. The obtained spectra for samples containing 30% and 50% by weight of CoCl_2 show two absorption bands at about 14280 and 6000 cm^{-1} . The first band in the visible region has a shoulder in the high energy side at about 19000 cm^{-1} . On the other hand, the composite sample containing 80% CoCl_2 exhibits a high energy broad band around 14000 cm^{-1} with another band at about 6000 cm^{-1} .

In order to account for these results, it may be emphasized that the addition of CoCl_2 will cause structural variations in the polymeric network. These variations are most probably related to the interaction between the negatively charged hydroxyl groups and positive ions of cobalt. At the same time such interaction forms the ligand field affecting the Co ions. In such situation d-d transitions will reflect the effective ligand field in question. Co ions have the electronic configuration (A) ($3d^7$) which has a ground term of 4F in high spin state and 2G in the low spin state. Bearing this in mind, one can conclude that with respect to samples 30% and 50% CoCl_2 , cobalt ions exist in the divalent state and are acted upon by an octahedral symmetrical field. The asymmetric visible band ν_3 at 14000 cm^{-1} , which is typical of the spectra of octahedral Co^{2+} , can be assigned as due to the transition $^4T_{1g}(\text{P}) \leftarrow ^4T_{1g}$. The shoulder on the high energy side (19000 cm^{-1}) is most likely due to spin forbidden transitions. The band at low energy side (6000 cm^{-1}) is assigned as ν_1 due to $^4T_{2g} \leftarrow ^4T_{1g}$ transition. Careful analysis of the spectra also show a weak band at 11500 cm^{-1} which could be assigned as ν_2 due to $^4A_{2g} \leftarrow ^4T_{1g}$ transition. The equations governing such transitions are (5).

$$\nu_1 = 8D_q \quad (1)$$

$$\nu_2 = 18D_q \quad (2)$$

$$\nu_3 = 16D_q(\text{av}) + 15\beta \quad (3)$$

where β is Racah constant, D_q ligand field strength, $D_q(\text{av})$ is the average of the D_q values obtained from equations (1) and (2).

Making use of these equations, average values of 695 cm^{-1} , 674 cm^{-1} and 1.92 were obtained for D_q , β and ν_2/ν_1 respectively. Such values agree well with that given for $\text{Co}(\text{H}_2\text{O})_6^{2+}$ in aqueous solutions⁶. It is worthy noticing that in both cases Co ions are ionically coordinated with hydroxyl groups. It is usually accepted in practice that the ratio ν_2/ν_1 is always lower than the theoretical value which is

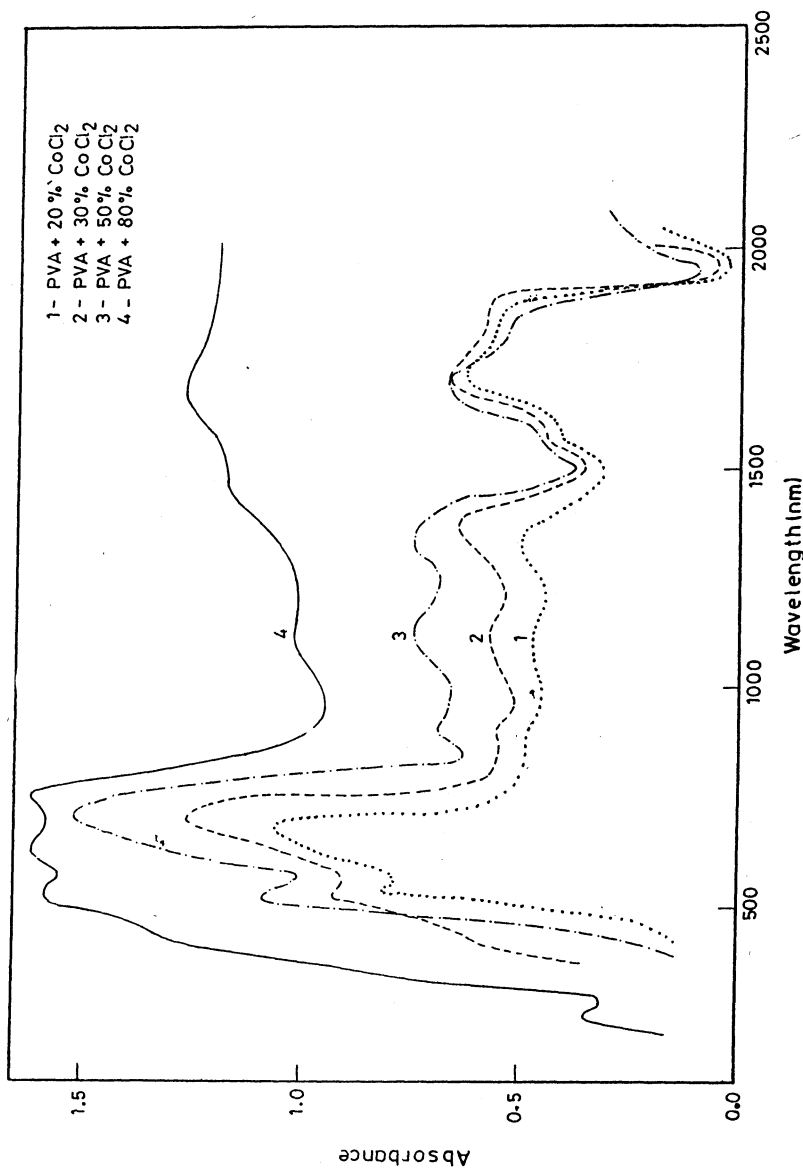


Fig. 1 Electronic absorption spectra of PVA-CoCl composites.

almost invariant at 2.1–2.2. During this, the more ionic the system the closer will the ratio be to the theoretical limits.

With respect to the sample containing 80% CoCl_2 , the spectrum exhibits a multiple absorption in the visible and near infrared regions. Such bands are too broad to be accounted for by spin-orbit coupling. This allows us to conclude that cobalt is in tetrahedral symmetric field. The observed band at about 14000 cm^{-1} is assigned as ν_3 which is due to ${}^4\text{T}_1(\text{P}) \leftarrow {}^4\text{A}_2$ transition, while the low energy band at 6000 cm^{-1} is most likely due to ${}^4\text{T}_{1g}(\text{F}) \leftarrow {}^4\text{A}_2$ transition. An average value of 780 cm^{-1} was calculated for Racah constant β .

The addition of CoCl_2 to the colourless PVA gives characteristic colours principally due to d-d transitions and basically depending on the symmetry of the ligand field affecting Co ions. Divalent cobalt ions in six-coordinated system usually give rise to pink colour, while as in tetragonal symmetry a blue colour is often observed.

Accordingly, the spectra of Co^{2+} ions could be interpreted in terms of an equilibrium between six and four coordinated Co^{2+} ions^{7,8}. The occurrence of Co^{2+} ions in both octahedral and tetrahedral symmetries finds plausible and tetrahedral fields of stabilization energies. This proposed mechanism was found in the present work to be sensitive to Co^{2+} concentration. One can then visualize that the Co^{2+} ions form almost ionic bands with the negative hydroxyl groups belonging to different chains of PVA in the composite PVA– CoCl_2 . At low cobalt content, the probability that Co^{2+} ions form six-coordinated symmetry is favourable. By increasing cobalt concentration to 80%, the number of OH-groups becomes insufficient to take up all cobalt ions and hence the tetragonal symmetry predominates.

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