

# EPR, Optical and IR Studies of VO<sup>2+</sup> Ions Doped Polyvinylalcohol Films

I. Omkaram, R.P. Sreekanth Chakradhar<sup>1</sup> and J. Lakshmana Rao

Department of Physics, Sri Venkateswara University, Tirupati 517 502, India

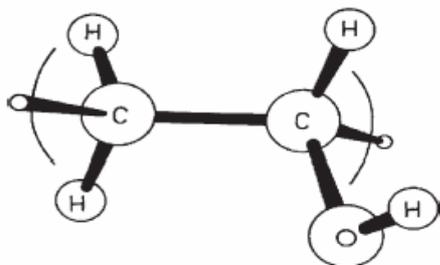
<sup>1</sup>Department of Physics, Indian Institute of Science, Bangalore 560 012, India

## Abstract

Electron paramagnetic resonance (EPR), optical and infrared spectral studies have been carried out on vanadyl ions doped in polyvinylalcohol (PVA) films. The spin-Hamiltonian parameters ( $g$  and  $A$ ), bonding parameter ( $\beta_2^{*2}$ ), Fermi contact interaction parameter ( $k$ ) have been evaluated. The values of spin-Hamiltonian parameters confirm that the vanadyl ions are present in PVA films as VO<sup>2+</sup> molecular ions in an octahedral site with a tetragonal compression. The temperature variation EPR studies reveal that the variation of number of spins with temperature is in accordance with Boltzmann law. It is interesting to observe that the variation of susceptibility with temperature obeys Curie-Weiss law. The FT-IR spectrum exhibits few bands, which are attributed to O-H, C-H, C=C and C-O groups of stretching and bending vibrations. The optical absorption spectrum exhibits two bands  ${}^2B_{2g} \rightarrow {}^2B_{1g}$  and  ${}^2B_{2g} \rightarrow {}^2E_g$  in the decreasing order of energy. The optical band gap ( $E_{opt}$ ) and the Urbach energies ( $\Delta E$ ) have also been determined from the ultraviolet absorption edges.

## INTRODUCTION

Polyvinylalcohol (PVA) is well known for its wide range of potential applications in industrial, pharmaceutical, medical fields and continues to draw much attention of the researchers [1,2]. It is a semicrystalline, water soluble polymer with 1,3 glycol structure, as shown below.



The transition metal ion complexes have often been used to elaborate or modify polymers in the domain of photography [3]. In the present study the authors are interested to study the VO(II) doped PVA films by using EPR and optical spectroscopies. We are also interested to know, how the intensity of the resonance lines varies with temperature and concentration of vanadyl ions in PVA film.

## EXPERIMENTAL

PVA film doped with vanadyl sulphate was prepared at room temperature by casting method. The desired concentrations of VOSO<sub>4</sub>·H<sub>2</sub>O (2 - 9 mol %) solutions were mixed with known amounts PVA stock solution of 5 mol %, stirred thoroughly with magnetic stirrer and the solution was casted to approximate thickness of 1 mm on a plain glass surface using a thin layer chromatography (TLC) spreader. The film was grown

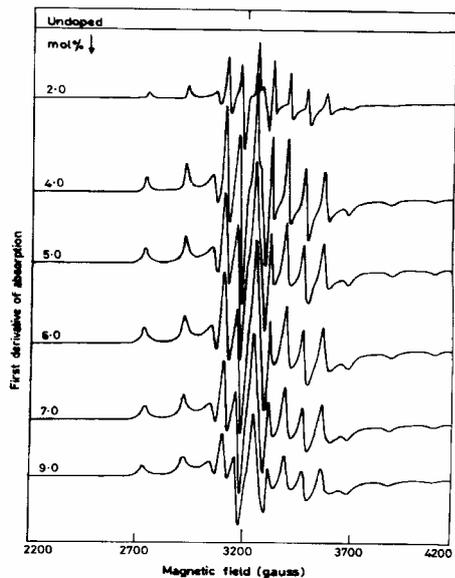
by slow evaporation in dry air and peeled from the glass surface after 48 h.

The EPR spectra were recorded on a JEOL FE1X ESR spectrometer operating in X-band frequency of 9.205 GHz. Optical absorption spectra of pure PVA and PVA samples doped with vanadyl ions were recorded at room temperature on a JASCO UV-VIS-NIR spectrophotometer (model V-570). A Perkin-Elmer FT-IR Spectrophotometer was used for recording the IR spectra of pure PVA and PVA:VO<sup>2+</sup> (4 mol %) samples in the region 400-4000 cm<sup>-1</sup>, with KBr pellet as IR transmitting material.

## RESULTS AND DISCUSSION

The EPR spectra of vanadyl ions doped PVA films are shown in Fig.2. The observed resonance signals are due to the hyperfine interaction of an unpaired electron ( $S = 1/2$ ) from VO<sup>2+</sup> with its nuclear spin ( $I = 7/2$ ). The spin-Hamiltonian parameters  $g$  and  $A$  obtained in the present work reveals that the vanadyl ions in PVA polymers exist as VO<sup>2+</sup> ions in octahedral coordination with a tetragonal compression and have a C<sub>4v</sub> symmetry.

Absolute number of spins participating in resonance were determined by numerical double integration of the experimental first derivative spectra with the help of a reference CuSO<sub>4</sub>·5H<sub>2</sub>O using the formula [4]. It is observed that the value of  $N$  increases with vanadyl content up to 6 mol % and there after it decreases. The decrease is due to the dipolar interactions between the vanadyl ions. From the temperature variation spectra, it is observed that the intensity of the spectral lines decreases with increasing temperature following the Boltzmann law.



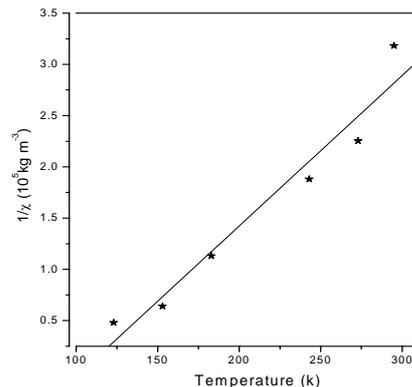
**Fig. 1.** EPR spectrum of  $\text{VO}^{2+}$  ions in PVA film as a function of vanadyl content

The magnetic susceptibilities were calculated for  $\text{VO}^{2+}$  ions at room and various temperatures from the EPR data using the formula

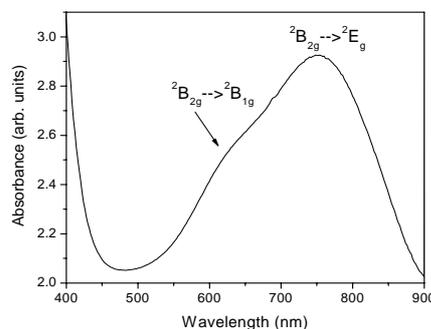
$$\chi = \frac{N g^2 \beta^2 J(J+1)}{3k_B T} \quad \dots (1)$$

where the symbols have their usual meaning. Fig. 2 shows a plot of  $1/\chi$  as a function of absolute temperature (T). It is interesting to observe that it obeys Curie-Weiss law. From the slope of the graph, the Curie constant is evaluated and it is found to be  $68.2 \times 10^{-3}$ .

The values of spin-Hamiltonian parameters  $g$  and  $A$  were used to calculate the molecular orbital coefficient ( $\beta_2^{*2}$ ) and  $k$  values, where  $\beta_2^{*2}$  is a measure of the degree of  $\pi$  bonding with the equatorial ligands and  $k$  is the Fermi contact interaction parameter. The values of  $\beta_2^{*2}$  show that the electrons in the inplane vanadium ligand  $\pi$  bonding orbitals are almost localized on the ligand atoms and the bonding is ionic character. The optical absorption spectrum (Fig. 3) exhibits two bands corresponding to d-d transitions, characteristic of  $\text{VO}^{2+}$  ions in tetragonal symmetry. The two bands have been assigned to the transitions  ${}^2B_{2g} \rightarrow {}^2B_{1g}$  and  ${}^2B_{2g} \rightarrow {}^2E_g$  in the decreasing order of energy respectively. The optical band gap and Urbach energies for vanadyl doped PVA films were obtained from their ultraviolet absorption edges. The optical bandgap energies calculated for the films were found to lie in the range 2.66 – 3.20 eV.



**Fig. 2.** A plot of  $1/\chi$  as a function of absolute temperature (T) for PVA: $\text{VO}^{2+}$  sample.



**Fig. 3.** Optical absorption spectrum of 8 mol % of vanadyl ions doped PVA film.

The observed strong and weak bands in the FT-IR spectrum indicates the presence of stretching and bending vibrational modes of O–H, C–H, C=C and C–O groups.

## REFERENCES

1. J.G.Pritchard, Polyvinylalcohol (London MacDonald Technical and Scientific); 1970.
2. T.Takeda, K. Nakagawa, H.Fujiwara, Nonlinear Opt 7 (1994) 295.
3. C. Pizzocaro, C. Lafond, M. Bolte., J Photochem. Photobiol A: Chem **151** (2002) 221.
4. J. A. Weil, J R. Bolton and J. E. Wertz, "Electron Paramagnetic Resonance – Elementary Theory and Practical Applications (NY :Wiley ) 1994 p. 498.