Spectroscopic investigations of Mn^{2+} ions doped polyvinylalcohol films

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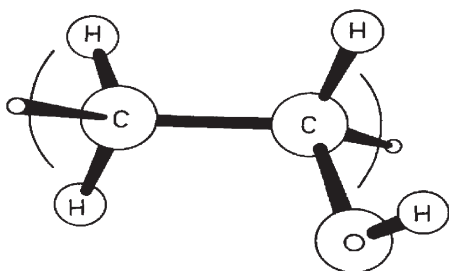[d]*Department of Polymer Science, S.K. University, Anantapur 515 003, India*

Abstract

Electron paramagnetic resonance (EPR), luminescence and infrared spectral studies have been carried out on Mn^{2+} ions doped in polyvinylalcohol (PVA) films. The EPR spectra at room temperature exhibit sextet hyperfine structure (HFS), centered at $g_{eff} \approx 2.0$ characteristic of Mn^{2+} ions in octahedral symmetry. The zero-field splitting parameter (D) at room temperature has been evaluated from the intensities of allowed hyperfine lines. The EPR spectra exhibit a marked concentration dependence. The EPR spectra have also been recorded at various temperatures. The number of spins participating in the resonance is measured as a function of temperature and the activation energy (E_a) is calculated. The paramagnetic susceptibility (χ) is calculated from the EPR data at various temperatures. From the plot of $1/\chi$ versus T, the Curie constant and Curie temperature have been evaluated. The emission spectrum of Mn^{2+} ions doped PVA film exhibits three bands centered at 390, 448 and 465 nm. The band at 448 nm is attributed to $^4T_{1g} \rightarrow {}^6A_{1g}$ transition of Mn^{2+} ions. The bands at 390 and 465 nm are attributed to the recombination of free charge carriers. The excitation spectrum exhibits two bands at 250 and 216 nm, which are attributed to host lattice absorption bands. 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.

Keywords: Polyvinylalcohol; Mn^{2+} ions; Electron paramagnetic resonance

1. Introduction

Polyvinylalcohol is well known for its wide range of potential applications in industrial, pharmaceutical, medical fields and continues to draw much attention of the researchers [1–5]. It is a semicrystalline, water soluble polymer with 1,3 glycol structure, as shown below.

Electron paramagnetic resonance (EPR) spectroscopy provides a sensitive method for detecting unpaired electrons (radicals) in polymeric materials [6]. Recently, Zainuddin et al. [7] used EPR technique to study the transformations of the radicals formed in PVA when subjected to γ-irradiation.

The transition metal ion complexes have often been used to elaborate or modify polymers in the domain of photography [8]. More recently, dichromated PVA and dichromated acrylic acid have been used to realize various applications in holography [9]. There are few reports on Cr (VI) and Fe (III) doped films as real time holographic recording materials [10,11]. Wang [12,13] studied extensively the optical absorption in PVA films when doped with CuCl nanoclusters and also studied the electric field dependence of optical absorption in PVA films. Mithlesh Kumar et al. [14,15] studied in detail the EPR and photo acoustic spectral (PAS) properties of PVA films doped with some 3d-transition metal ions (Cr^{3+}, VO^{2+}).

AC conductivity and dielectric constant measurements of PVA doped with Mn^{2+} ions were studied by Mohammed

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[16] and reported the hopping distance, activation energy and polaron binding energy, which were found to be composition dependent. However, no work was reported so far on EPR spectral studies of Mn^{2+} ions doped PVA film. Hence, the authors have taken up the present investigations.

The Mn^{2+} paramagnetic ion with partially filled d-electrons is a convenient impurity to monitor its charge state and environment, and it exhibits a characteristic EPR spectrum. In the present work, the authors studied the EPR spectra of Mn^{2+} ions doped in PVA matrix. The authors are also interested to know, how the intensity of the resonance lines varies with temperature and concentration of manganese ions in PVA film.

2. Experimental technique

PVA film doped with manganese sulphate monohydrate was prepared at room temperature by casting method. Both the polymer and dopant were dissolved separately in distilled water as they exhibit high solubility in the solvent. The desired concentrations of $MnSO_4 \cdot H_2O$ (1, 2, 3, 4, 6, 8 and 10 mol%) solutions were mixed with known amounts of PVA stock solution of 5 mol%, stirred thoroughly with a magnetic stirrer and the solution was casted to an 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 off from the glass surface after 24 h.

A JEOL FE1X ESR spectrometer operating in X-band frequency of 9.205 GHz with a field modulation of 100 kHz was used for the acquisition of EPR spectra, which were obtained as first derivative. The magnetic field was scanned from 0 to 5000 G and the field was swept at a rate of 1250 G/min.

EPR spectra of manganese doped PVA were recorded at different temperatures in 123–393 K range. The temperature was varied using a JES-UCT-2AX variable temperature controller. A temperature stability of ± 1 K was obtained by waiting for about 30 min at the set temperature before recording the spectrum. EPR spectra for different concentrations of Mn^{2+} ions doped in PVA films were also recorded at room temperature. The EPR spectra of $CuSO_4 \cdot 5H_2O$ powdered sample were recoded at different temperatures as a reference to calculate number of spins. Approximately 100 mg of sample was used for all EPR measurements.

The luminescence emission and excitation spectra of pure PVA and PVA: Mn^{2+} (10 mol%) were recorded at room temperature using Shimadzu Spectrofluorophotometer (model RF 510) and a 150 W Xenon lamp. The wavelength accuracy of emission and excitation was ± 1 nm.

Optical absorption spectra of pure PVA and PVA samples doped with manganese ions were recorded at room temperature on a JASCO UV–VIS–NIR Spectrophotometer (model V-570). PVA:Mn^{2+} samples of thick-

ness 0.6–1.0 mm were used for recording optical absorption spectra.

A Perkin–Elmer FT-IR Spectrophotometer was used for recording the IR spectra of pure PVA and PVA:Mn^{2+} (4 mol%) samples in the region 4000–500 cm^{-1} with KBr pellet as IR transmitting material.

3. Results and analysis

3.1. EPR studies

In pure PVA, no EPR signal is observed, confirming that the starting materials used in the present work were free from transition metal impurities or other paramagnetic centers (defects). When Mn^{2+} ions are introduced into the polymer, EPR spectra of all the polymer samples under investigation exhibit resonance signals.

Fig. 1 shows the typical EPR spectrum of 4 mol% of Mn^{2+} doped in PVA recorded at room temperature. The spectrum exhibits a sixline HFS characteristic of Mn^{2+} ion with $g \approx 2.0$.

The EPR spectra of Mn^{2+} ions doped in PVA film have been studied systematically as a function of $MnSO_4 \cdot H_2O$ content varying from 1 to 10 mol% and are shown in Fig. 2. Absolute concentrations of the centres were determined by numerical double integration of the experimental first derivative spectra and the number of spins per 100 mg was calculated with the help of a reference $CuSO_4 \cdot 5H_2O$ by using the formula [17]

$$N = \frac{A_x(\text{Scan}_x)^2 G_{\text{std}}(B_m)_{\text{std}}(g_{\text{std}})^2[S(S+1)]_{\text{std}}(P_{\text{std}})^{1/2}}{A_{\text{std}}(\text{Scan}_{\text{std}})^2 G_x(B_m)_x(g_x)^2[S(S+1)]_x(P_x)^{1/2}} [\text{std}]$$

(1)

where A is the area under the absorption curve; 'Scan' is the magnetic field corresponding to unit length of the chart; G is the gain; B_m is the modulation field width; g is the g factor; S is the spin of the system in the ground state, P is the power
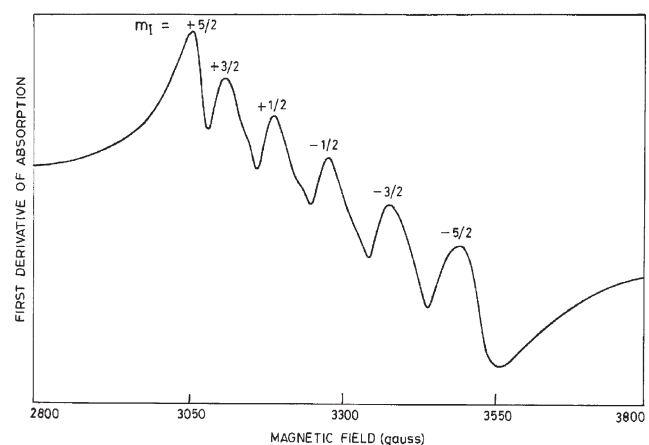

Fig. 1. EPR spectrum of PVA: Mn^{2+} (4 mol%) film recorded at room temperature.
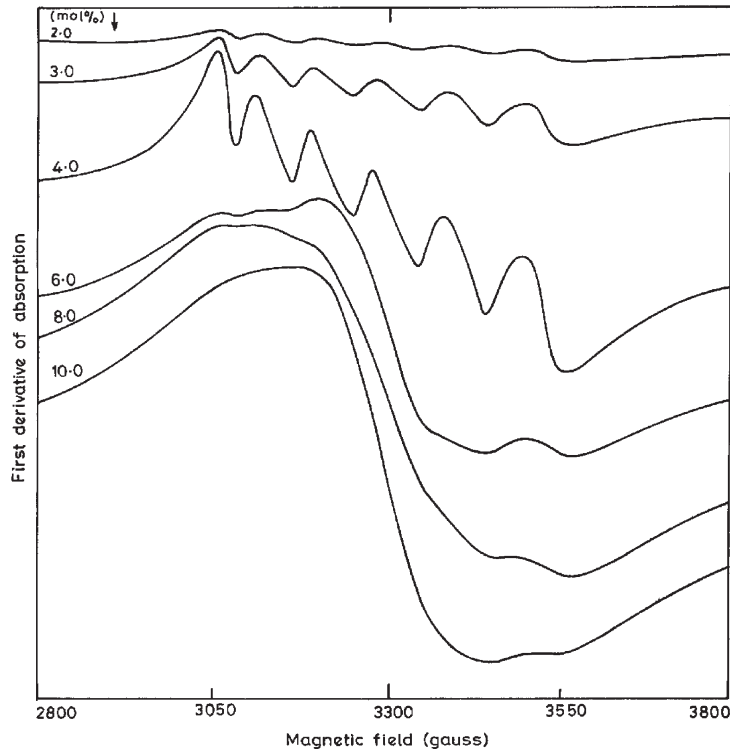
Fig. 2. EPR spectra for various concentrations of Mn^{2+} ions in PVA film at room temperature.

of the microwave. The subscripts x and 'std' represent the corresponding quantities for PVA:Mn^{2+} sample and the reference sample, respectively.

Fig. 3 shows a plot of mol% of Mn^{2+} in the sample and the number of spins participating in the resonance at $g \approx$ 2.0. The EPR spectra for PVA doped with 4 mol% of Mn^{2+} ions were recorded at different temperatures in 123–393 K range and are shown in Fig. 4. The number of spins (N) participating in the resonance at $g \approx 2.0$ has been calculated at various temperatures. Fig. 5 shows a plot of Log N against $1/T$.

3.2. Calculation of paramagnetic susceptibility from EPR data

The paramagnetic susceptibility (χ) of the sample can be calculated from the EPR data using the formula;

$$\chi = \frac{Ng^2\beta^2 J(J+1)}{3k_B T} \tag{2}$$

where N is the number of spins per kg; the rest of the symbols have their usual meaning. Using Eq. (2), the paramagnetic susceptibilities have been calculated for various temperatures. Fig. 6 shows a plot of reciprocal of susceptibility ($1/\chi$) as a function of temperature (T).

3.3. Luminescence studies

The emission spectra of pure PVA and PVA:Mn^{2+}

(10 mol%) samples have been studied at room temperature, and are shown in Fig. 7(a). The emission spectrum of pure PVA exhibits two bands centered at 390 and 465 nm. The emission spectrum of PVA:Mn^{2+} (10 mol%) sample exhibits bands at 390, 448 and 465 nm.

The excitation spectra of pure PVA and PVA:Mn^{2+} (10 mol%) samples recorded at room temperature, monitored
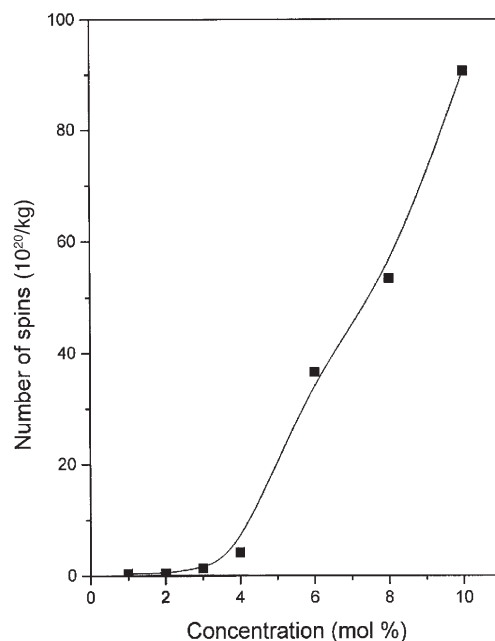

Fig. 3. A plot of concentration of Mn^{2+} ions in PVA film versus number of spins at room temperature. The line is drawn as a guide for the eye.
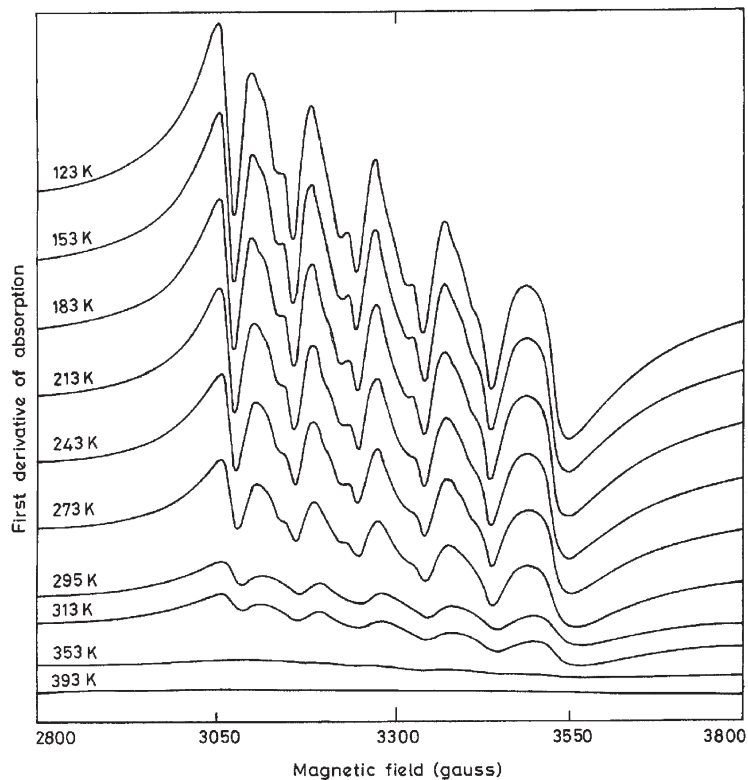
Fig. 4. EPR spectra of PVA: Mn^{2+} (4 mol%) film recorded at different temperatures.
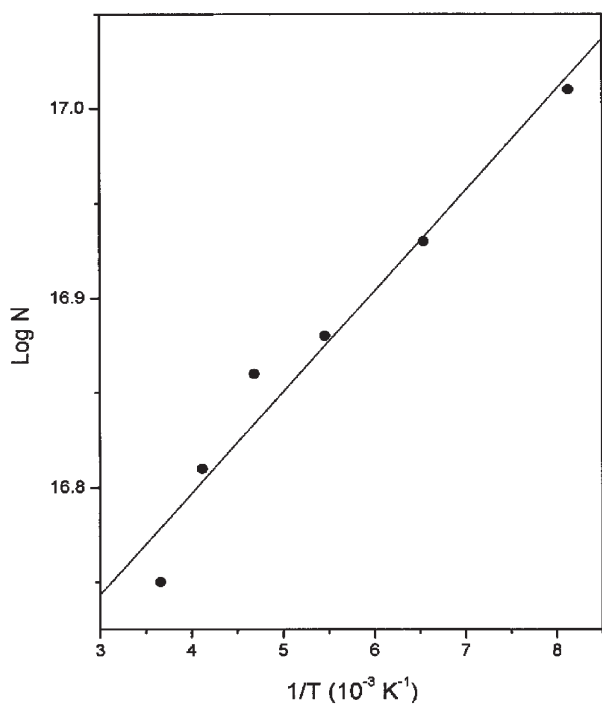

Fig. 5. A plot of Log N versus $1/T$ for PVA: Mn^{2+} (4 mol%) film.
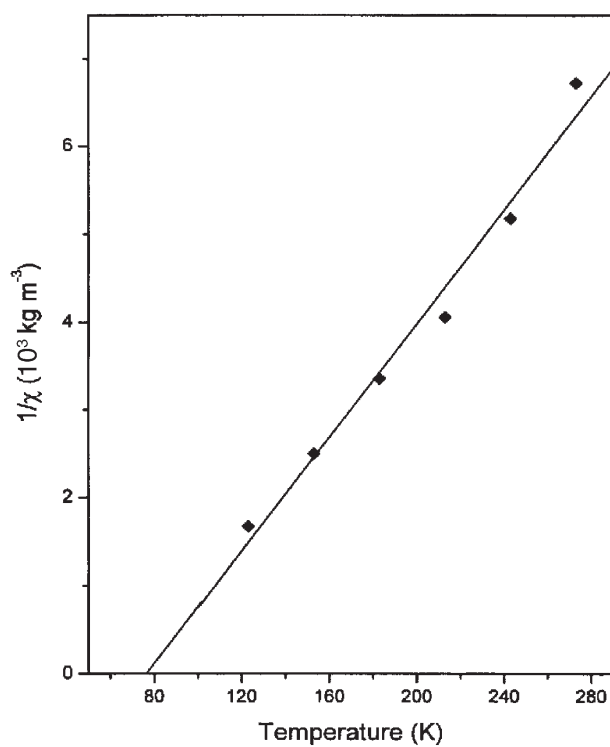

Fig. 6. A plot of reciprocal of susceptibility $(1/\chi)$ as a function of temperature for PVA: Mn^{2+} (4 mol%) film.

at 393 nm are shown in Fig. 7(b). The excitation spectra of pure PVA and also PVA:Mn^{2+} (10 mol%) film exhibits two bands centered at 216 and 250 nm.

3.4. Optical absorption studies

Fig. 8 shows the ultraviolet optical absorption spectra of pure PVA and PVA doped with different concentrations of Mn^{2+} ions recorded at room temperature. The spectra exhibit a weak band centered at 275 nm.

The study of the fundamental absorption edge in the UV region is a useful method for the investigation of optical transitions and electronic band structure in crystalline and non-crystalline materials. The main feature of the absorption edge is an exponential increase of the absorption coefficient α with photon energy $h\nu$ [18]. The absorption coefficient α can be determined as a function of frequency using the formula

$$\alpha(\nu) = \frac{A}{d} \times 2.303 \tag{3}$$

where A is the absorbance at frequency ω and d is the thickness of the sample.

The optical band gap for an indirect transition can be determined by using the relation [19]

$$E_{opt} = h\nu - (\alpha h\nu/B)^{1/2} \tag{4}$$

Fig. 8. Ultraviolet absorption edge for pure PVA and PVA: Mn^{2+} (2, 4, 6, 8 and 10 mol%) films.

where B is a constant. Fig. 9 shows the plots between $(\alpha h\nu)^{1/2}$ and $h\nu$ for pure PVA and PVA doped with different concentrations of Mn^{2+} ions. From the figure, the optical band gap energies (E_{opt}) have been evaluated by extrapolating the linear region of the curve to the $h\nu -$ axis. The band gap energies obtained in the present work are given in Table 1.

3.5. FT-IR spectra

Fig. 10(a) and (b) shows the FT-IR spectra of pure PVA and PVA:Mn^{2+} (4 mol%) films, respectively, recorded at room temperature in the region $4000-500 \text{ cm}^{-1}$. The spectra exhibit bands characteristic of stretching and bending vibrations of O–H, C–H, C=C and C–O groups.
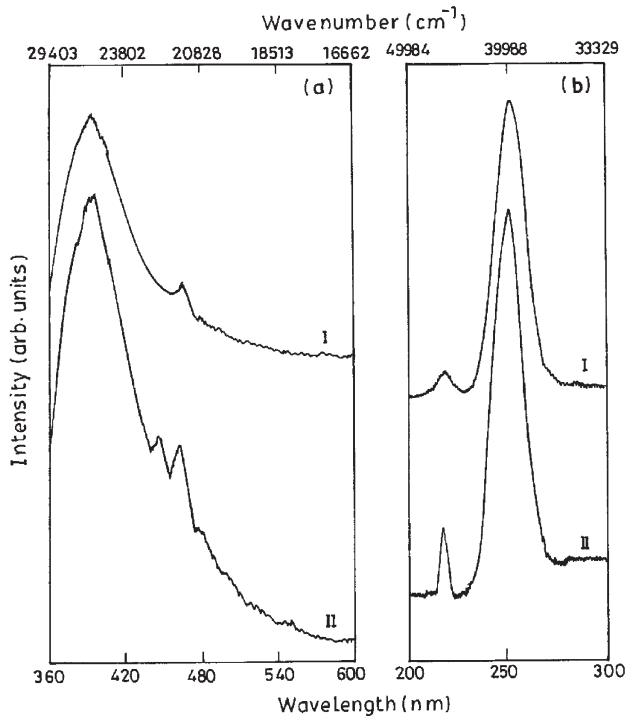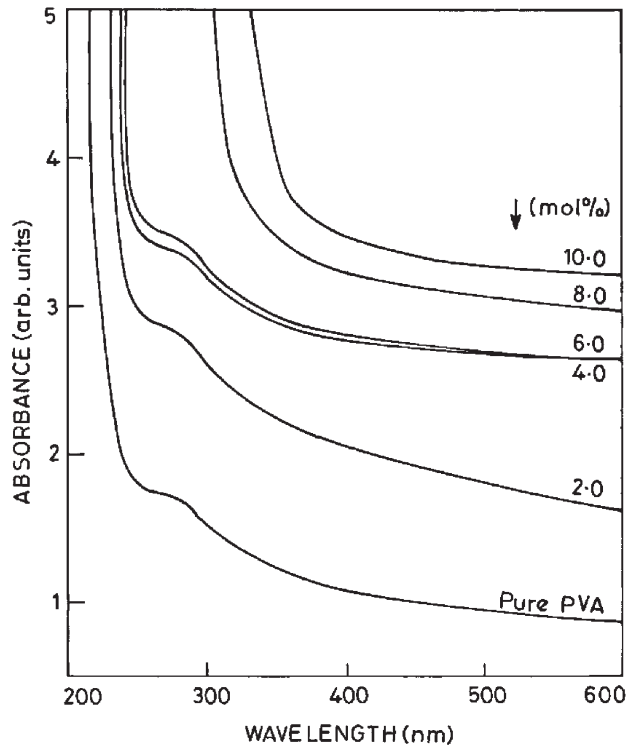
Fig. 7. (a) The emission spectra of (I) pure PVA and (II) PVA:Mn^{2+} (10 mol%) film recorded at room temperature, excited at 250 nm. (b) The excitation spectra of (I) pure PVA and (II) PVA:Mn^{2+} (10 mol%) films recorded at room temperature, monitored at 393 nm.

Table 1
The optical band gap energies for the polymer films studied in the present work

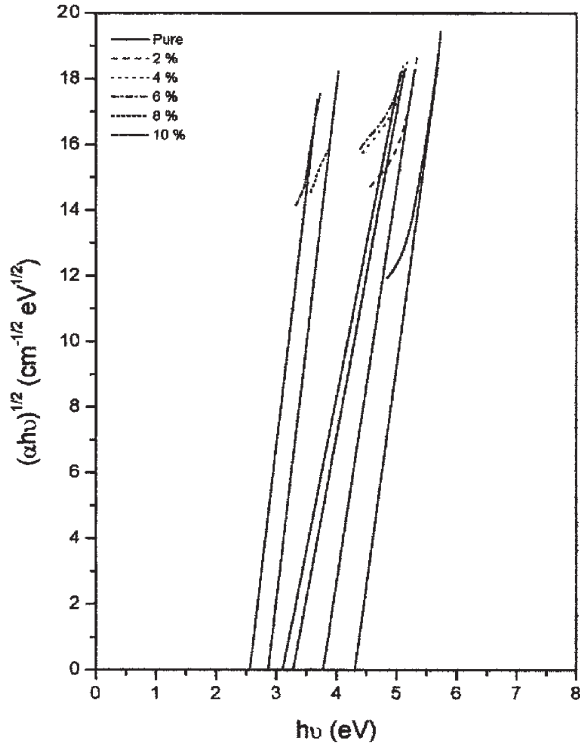| Concentration mol% Mn^{2+}:PVA	Optical band gap energy (E_{opt}) (eV)
Pure PVA	4.26
2.0	3.80
4.0	3.30
6.0	3.09
8.0	2.84
10.0	2.49

Fig. 9. A plot between $(\alpha h\nu)^{1/2}$ and $h\nu$ for pure PVA and PVA: Mn^{2+} (2, 4, 6, 8 and 10 mol%) films.

The IR band positions of both the samples and their assignments are presented in Table 2.

4. Discussion

4.1. EPR studies

Mn^{2+} ions belong to d^5 configuration. In the case of d^5 transition metal ions, it is known that axial distortion of

Table 2
The characteristic infrared absorption frequencies for pure PVA and PVA:Mn^{2+}(4 mol%) film

Vibrational frequency (cm^{-1})		Band assignment
Pure PVA	PVA:Mn^{2+}(4 mol%)	
3484	3325	OH (st)
2938	2945	CH$_2$ (st)
2163	2179	CH + CC
1653	1652	C=C (st)
1427	1423	CH$_2$ (b)
1375	1377	CH + OH
1331	1333	CH + OH
1236	1236	CH (st)
1097	1094	CO (st)
916	916	CC (st)
853	850	CH$_2$ (st)
632	610	OH (st)

st, stretching; b, bending.

octahedral symmetry gives rise to three Kramers doublets $|\pm 5/2>$, $|\pm 3/2>$ and $|\pm 1/2>$ [20]. Application of Zeeman field lifts the spin degeneracy of the Kramers doublets. As the crystal field splitting is normally much greater than the Zeeman field, the resonances observed are due to transitions within the Kramers doublets split by Zeeman field.

A well resolved sextet HFS observed for Mn^{2+} doped PVA film at room temperature (Fig. 1) at the resonance signal $g \approx 2.0$ is a characteristic of Mn^{2+} ions with a nuclear spin $I = 5/2$. The resonance observed at $g \approx 2.0$ is due to Mn^{2+} ions in an environment close to octahedral symmetry and is known to arise from the transition between the energy levels of the lower Kramers doublets. The presence of resolved HFS indicates that Mn^{2+} ions in octahedral sites are isolated or significantly distinct from each other so as to ignore the spin–spin interaction.

The ability to observe the ^{55}Mn HFS has the benefit of measuring the nature of bonding between metal ion and its surrounding ligands. The sextet observed at $g \approx 2.0$ has been analyzed using the following expression for resonance fields [21]

$$H_m = H_0 - Am - (35 - 4m^2)(A^2/8H_0) \tag{5}$$

where $H_0 = h\nu/g_0\beta$ and $m = +5/2, +3/2, --- -5/2$; g_0 is the isotropic g factor and A is the isotropic hyperfine interaction parameter. The hyperfine splitting constant A is found to be 9.5 mT. The magnitude of the hyperfine splitting constant A provides a qualitative measurement of the ionicity of bonding between the Mn^{2+} ion and its surrounding ligands. Van Wieringen [22] empirically determined a positive correlation between A and the ionicity of manganese–ligand bond. The magnitude of the hyperfine splitting value obtained in the present work reveals that the bonding between Mn^{2+} and the surrounding ligands is significantly ionic.

The EPR spectra of Mn^{2+} ions doped in PVA films show a remarkable concentration dependence as shown in Fig. 2. At low concentrations of Mn^{2+} ion (less than 4 mol%), the spectra show a sextet HFS. The six resolved hyperfine lines spread over a region of approximately 50 mT in width. When the concentration of Mn^{2+} ions is increased by more than 4 mol%, the sextet HFS disappears leaving behind a single broad Lorentzian signal. This has been attributed to the ligand field fluctuations in Mn^{2+} ion vicinity and also due to spin–spin interaction. Fig. 3 shows a plot of mol% of Mn^{2+} in the film and the number of spins participating in the resonance at $g \approx 2.0$. From the figure it is evident that the number of spins increases with the increase of Mn^{2+} concentration.

Fig. 4 shows the EPR spectra of PVA:Mn^{2+} (4 mol%) sample recorded at various temperatures, which reveals that the peak-to-peak width of the $g \approx 2.0$ resonance line is independent of temperature in 123–393 K range. At 123 K, the intensity of the resonance signal is distinctly large. A
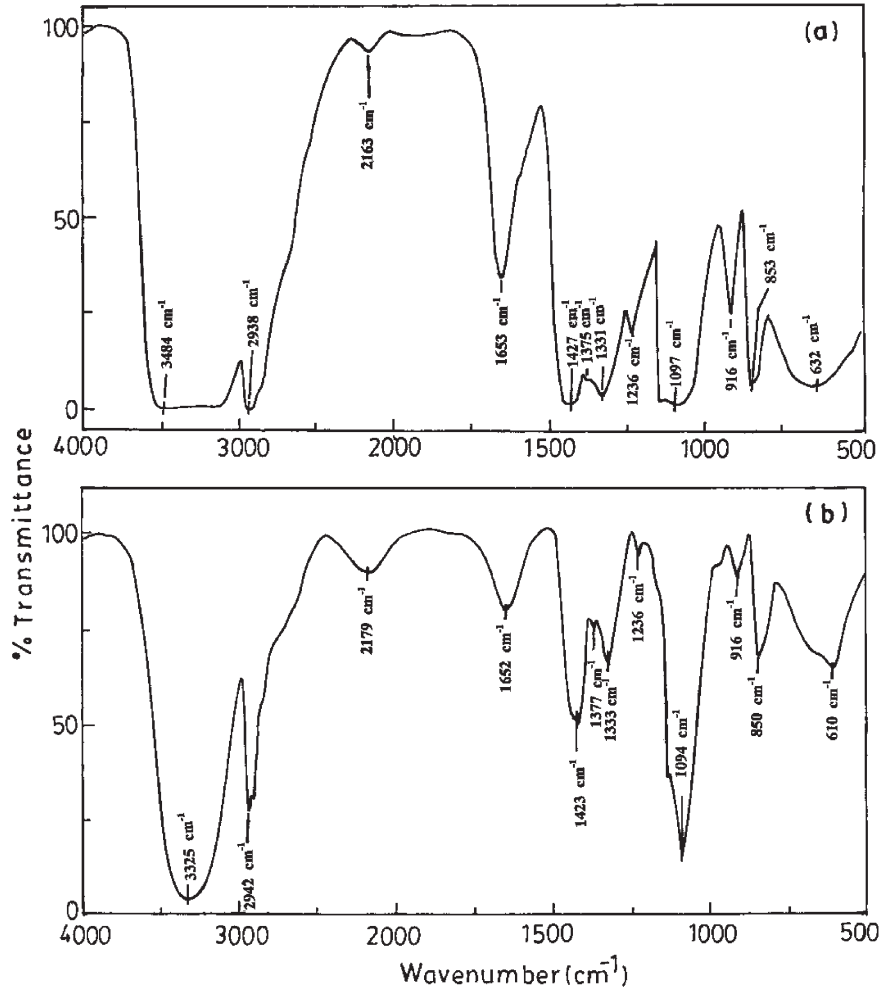
Fig. 10. FT-IR spectra of (a) Pure PVA and (b) PVA: Mn^{2+} (4 mol%) films recorded at room temperature.

plot of Log N versus $1/T$ is shown in Fig. 5. From the graph, it is evident that as temperature is lowered, the number of spins increases and a linear relationship between log N and $1/T$ is observed. This is the phenomenon that can be expected from the Boltzmann law. From the slope of the graph, the activation energy has been calculated. The activation energy thus obtained is found to be 0.0106 eV.

A graph of reciprocal of susceptibility $(1/\chi)$ against absolute temperature (T) for PVA doped with 4 mol% of Mn^{2+} ions is shown in Fig. 6. From the graph it is observed that the paramagnetic susceptibility goes on increasing with decreasing temperature, which in accordance with the Curie's law. The intercept on the X-axis of this graph gives the Curie temperature, which is found to be 77 K. From the slope of this graph, the Curie constant has been evaluated, which is 0.03089. The Curie constant and Curie temperature values obtained in the present work are in good agreement with the values reported in literature for paramagnetic ions [23].

The zero-field splitting (ZFS) parameter D has been calculated from the intensities of the allowed hyperfine lines

using the formula [24]

$$I_{\mathrm{m}} \propto 2 - \frac{A^2(35 - 4m^2)}{2(g\beta H)^2} - \frac{5.334D^2}{(g\beta H)^2}$$
$$- \frac{35.14D^2(35 - 4m^2)}{(g\beta H)^2} + \frac{208D^4(35 - 4m^2)^2}{(g\beta H)^4} - - - \quad (6)$$

where m is the nuclear spin quantum number; I_m is the intensity at the m th allowed hyperfine line, A is the hyperfine splitting constant, D is the ZFS parameter and the rest of the symbols have their usual meaning. Using Eq. (6), the value of D obtained for PVA doped with 4 mol% Mn^{2+} ions at room temperature is 21.4 mT. The D value is of the same order with that of Mn^{2+} complexes reported in literature [25].

4.2. Luminescence studies

The emission spectrum (Fig. 7(a)) of pure PVA sample exhibits a strong band at 390 nm and a weak band at 465 nm. These bands can be assigned to the recombination

of free charge carriers at the defects, possibly at the surface, in PVA [26]. Similar bands appear in the emission spectrum of PVA:Mn^{2+} (10 mol%) sample also, with an additional peak observed at 448 nm. This additional peak has been attributed to $^4T_{1g} \rightarrow {^6}A_{1g}$ transition of Mn^{2+} impurity.

Fig. 7(b) shows the excitation spectrum of the pure PVA sample observed at room temperature. The spectrum exhibits a moderate band at 216 nm and an intense band at 250 nm. These bands have been attributed to the host-lattice absorption bands [27]. Similar bands have also been observed in the excitation spectrum of PVA:Mn^{2+} (10 mol%) film, which indicates that Mn^{2+} ion impurity causes no significant change in the position of the excitation bands.

4.3. Optical absorption spectra

In the optical absorption spectrum (Fig. 8), a weak and broad band has been observed at 275 nm, which is characteristic of pure PVA. This band has also been observed for PVA doped with Mn^{2+} ions up to 6 mol%. Above 6 mol% of Mn^{2+} this band has been masked by the absorption edges.

The optical band gap energies of the PVA:Mn^{2+} samples observed in the present work indicates the semiconducting nature of these samples. From Table 1, it is evident that the optical band gap energy goes on decreasing with increasing Mn^{2+} content. This indicates that with increase in concentration of Mn^{2+} ions, PVA film become more semiconducting in nature. The E_{opt} values obtained in the present work are of the same order reported in literature [12].

4.4. IR spectra

The IR spectrum (Fig. 10(a)) of pure PVA exhibits several bands characteristic of stretching and bending vibrations of O–H, C–H, C=C and C–O groups. A broad, very strong band observed at 3484 cm^{-1}, together with the broad 632 cm^{-1} band, which arises from O–H stretching frequency, indicates the presence of hydroxyl groups [28,29]. Another strong band observed at 2938 cm^{-1} indicates an asymmetric stretching mode of CH_2 group [29]. A moderate absorption peak at 1653 cm^{-1} has been attributed to the C=C stretching mode [30]. A strong band observed at 1427 cm^{-1} has been assigned to bending mode of vibration corresponding to CH_2 group, while another strong band observed at 853 cm^{-1} has also been attributed to CH_2 in stretching mode. A moderate absorption peak at 1236 cm^{-1} has been attributed to C–H group, while a strong absorption peak observed at 1097 cm^{-1} has been assigned to C–O in stretching mode [31]. A C–C stretching mode of moderate absorption is observed at 916 cm^{-1}. A weak band observed at 2163 cm^{-1} has been attributed to combination frequency of (CH + CC). The bands observed at 1375 and 1331 cm^{-1} have been attributed to combination frequencies of (CH + OH) [29].

The IR spectrum (Fig. 10(b)) of PVA:Mn^{2+} (4 mol%) film exhibits bands, whose vibrational frequencies and bands assignments are found to be similar to several bands observed for undoped PVA. However, O–H stretching frequency observed at 3484 cm^{-1} for pure PVA shows a remarkable shift towards low frequency region on doping of Mn^{2+} ions and positioned at 3325 cm^{-1}. This change indicates the possibility of Mn^{2+} ion to be attached to O–H group in the side chain of PVA molecule.

5. Conclusions

1. The EPR spectra of PVA:Mn^{2+} films at room temperature exhibit a well resolved sextet hyperfine structure (HFS) characteristic of Mn^{2+} ions in octahedral symmetry. The EPR spectra exhibit marked concentration dependence. The HFS disappears for higher concentrations of Mn^{2+} ions due to spin–spin interactions.
2. The magnitude of the hyperfine splitting constant A indicates that the bonding between Mn^{2+} ions and its surrounding ligands is significantly ionic.
3. The temperature variation EPR studies reveal that the variation of number of spins with temperature is in accordance with Boltzmann law. The activation energy has been calculated from Log N versus $1/T$ graph and is found to be 0.0106 eV.
4. The variation of susceptibility with temperature is in accordance with the Curie's law. From the $1/\chi$ versus temperature graph, the Curie constant and Curie temperature have been evaluated and are found to be 0.03089 and 77 K, respectively.
5. The emission band observed at 448 nm for PVA:Mn^{2+} film is attributed to $^4T_{1g} \rightarrow {^6}A_{1g}$ transition of Mn^{2+} ions whereas the bands observed at 390 and 465 nm are attributed to the recombination of free charge carriers. The bands observed at 216 and 250 nm in the excitation spectra are attributed to the host-lattice absorption.
6. The optical band gap energy (E_{opt}) is found to be dependent upon Mn^{2+} content in PVA films.
7. 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.

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