Structural and electrical characterisation of polymeric electrolytes: PVA-NH₄SCN system

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Received 10 September 1999; accepted 14 December 1999

The structural and ion transport studies on PVA₂₆·NH₄SCN solid polymer electrolytes (SPEs) with the aim of developing suitable proton conducting electrolyte for solid state ionic devices have been reported. DSC, XRD and IR analysis of as synthesised films have been carried out to study morphology and complexation behaviour of PVA with NH₄SCN. A possible structure of PVA complex has been proposed on the basis of IR spectroscopy. The electrical characterisation which comprises of I-t, coulometry, TIC measurements and impedance spectroscopy has been carried out to assess ion transport behaviour of these complexes. The electrical measurements evidenced cationic transport with a maximum in electrical conductivity of \(7.0 \times 10^{-5}\) S cm⁻¹ for \(x = 0.15\) in the system. The compositional variation of ionic conductivity has been correlated to morphology and concentration of charge carrier.

1 Introduction

Solid polymer electrolytes - a class of ionic conductors, have shown immense application potentiality as prominent electrolyte material for various electrochemical devices in the past two decades. A variety of polymers have been investigated in the past with emphasis on polyether based systems, essentially due to their ability to form stable complexes with variety of salts. However, most of these complexes simultaneously conduct via both anions and cations while electrochemical devices such as solid state batteries and electrochromic devices (ECDs) are designed around diffusion of either cations or anions for their proper operation. In wake of this, attempts have been made in the recent past to develop suitable single ion conducting polymer electrolytes.

Polyvinyl alcohol (PVA) is one of the few extensively studied polymer as a host material which possesses good dielectric properties and wide temperature application window. Due to high cohesive energy density, PVA does not seem to form real complexes with alkali metal salts. However, its solvent swollen characteristics have made it a potential candidate for the development of proton conducting polymer electrolytes. A few acid doped PVA complexes have been studied in the past to explore this possibility. In acid doped PVA complexes, Maruyama et al. have reported the formation of ester salts. Weeks et al. have pointed out that complexation occurs via protonation of OH linkage in the PVA host. These polymeric complexes behave as a solid polymer electrolyte in which protons are mainly available as mobile ions. However, due to dehydration of PVA and electrode corrosion these acid doped complexes have not shown much promise in the device applications.

In view of the above problems associated with acid doped PVA complexes, Bao et al. have studied PVA-Li salt complexes and found that despite exhibiting single ion conduction these complexes suffer from poor ionic conductivity in the absence of suitable plasticizer. In a recent investigation a new proton conducting electrolyte viz. PVA-NH₄SCN system have been studied by us. These electrolytes have exhibited considerable room temperature conductivity besides good stability for application in electrochemical devices such as ECDs. In the present work, emphasis has been laid on the study of chemical structure and morphology and their correlation with ion transport parameter in PVA-NH₄SCN system. The experimental investigation comprise of XRD, IR, DSC coulometry, mobility and conductivity measurements.
2 Experimental Details

The PVA·NH₄SCN polymer electrolyte films were synthesised using well known solution cast technique. Weighted amounts of PVA available in granular form (Rolex make, MW 78000; 86% hydrolyzed) and NH₄SCN (M/S Rd. Finer Chem.; AR grade) were separately dissolved in dimethyl sulfoxide (M/S Rd. Finer Chem.; spectroscopy grade) and subsequently mixed together. The mixture was stirred for eight hours at 80°C to form viscous homogeneous solution. The final solution was then poured in teflon moulds and placed in a dry box to allow slow solvent evaporation. The final traces of solvent and other volatile contaminants were eliminated by vacuum drying of the samples at 10⁻³−10⁻⁵ torr. The electrolyte films in different stoichiometry (0 ≤ x ≤ 0.25; where x represents weight fraction of the salt in the complex) were cast and kept in a vacuum desiccator to avoid atmospheric contamination. Prior to each measurement samples were repeatedly dried under vacuum for more than 12 hours to avoid effect of humidity. The relative humidity was maintained at 30% during the measurements.

The X-ray diffractograms were obtained using Phillips make X-ray diffractometer (model PW 1710) with the scan rate fixed at 4.8° min⁻¹. The Cu-Kα radiation was used for the analysis. Thermal analyses of the SPE films were performed on a DuPont series 2000 thermal analyzer with a scan rate of 10°C min⁻¹ in a nitrogen purged cell. For IR spectral analysis Perkin Elmer IR spectrophotometer (model 883) was used.

Total ionic transference number (tᵣₑₐₑ) was measured using dc polarisation technique in which a constant dc voltage (below the decomposition potential) was applied across the cell and resultant current was monitored as a function of time. Using the initial (i₀) and final (iₜ) values of current, tᵣₑₐₑ was calculated from the relation:

\[ t_{\text{ion}} = (i₀ - iₜ)/i₀ \]  

In order to separate out the cationic and anionic contribution to tᵣₑₐₑ, coulometric investigation was also carried out using a specially designed double arm coulometer. In this experiment, a constant current (≈ 30μA) was passed through the Hg/SPE film/Hg cell and the amount of the electrolysis product at respective electrodes (H₂ at cathode in the present case) was monitored as a function of total charge (q) passed through the cell. The values of tᵣₑₐₑ were calculated using the relation:

\[ t_{\text{ion}} \text{coul} = 2(v \text{H₂ NTP} \text{Nel}/22400 q) \]  

where (v)H₂ is the volume (ml) of the gas at NTP, evolved on cathode/anode side, N the Avogadro’s number, e the electronic charge and q is the total charge passed through the cell during electrolysis. Gas chromatographic analysis of the gas collected during coulometry was performed to ascertain protonic conduction.

Transient ionic current (TIC) measurements were performed for direct evaluation of bulk mobility of mobile ionic species in the sample. The sample was first polarised by applying a fixed dc potential (below the decomposition potential) across the cell to enable mobile ionic species to collect at their respective electrodes. Then the polarity of electric field was reversed and current versus time plot was recorded. The plot thus obtained exhibited distinct peaks corresponding to different ion species present in the sample. By measuring the time of flight (τ; the total time taken by an ion to reach from one electrode to another), bulk mobility (μ) of the mobile ion was evaluated using the relation:

\[ \mu = \delta/\tau V \]  

where \( \delta \) is the thickness of the sample and \( V \) is the applied dc potential.

Complex impedance data were recorded in the frequency range 40 Hz-100 kHz with the help of LCR meter (Hioki make; model 3520) to evaluate the ionic conductivity of as synthesized samples. For all the electrical measurements, thermally evaporated Al electrodes (thickness = 800-1000Å) were used in a spring loaded cell assembly: Al/SPE film/Al.

3 Results and Discussion

3.1 X-ray analysis

Fig. 1 shows the X-ray diffraction pattern of as synthesized PVA complexes alongwith that of pure PVA and NH₄SCN. It has been noted that besides the background modulation (characteristic of semicrystalline/amorphous polymers), XRD pattern for pure PVA exhibit a relatively sharp peak around 2θ = 15.2°. This peak shifts when salt is admixed to form solid polymer electrolyte. Initially the peak shifts towards lower 2θ value and retraces back after a critical salt concentration (x = 0.15) in the complex. Furthermore, no distinguishable peak of NH₄SCN (2θ values 30.7, 33.6, 34.3, 37.8 and 38.7) has been observed up to a value of x = 0.20 in the system. At still higher concentration (x > 0.25), some of the characteristic reflections of NH₄SCN start appearing. The predicted 2θ values for the main reflections alongwith associated d spacing for these complexes are shown in Table 1. These observations lead to the following conclusions:
(i) The increase in $d$ value up to critical concentration of salt ($x = 0.15$) suggests enhancement in amorphousness due to loose packing of macromolecular chains in the complex; (ii) after a critical concentration (i.e. for $x > 0.15$), unlike components start agglomerating and hence on one hand, $d$ spacing related to primary reflection approach its original value in pure PVA while on the other hand the uncomplexed salt start giving its own reflection.

To account for the morphology of these electrolytes, other relevant parameters, namely, degree of crystallinity ($X_{\text{Cryst}}$) and crystallite size ($L$) have also been calculated and the values are listed in Table 1. The crystallite size has been calculated using well known Scherrer equation while $X_{\text{Cryst}}$ has been evaluated following the technique of Tada et al.\textsuperscript{19}. It is important to stress here that though XRD patterns are not much convincing, the above observations show that complexation has been taking place and solubility of NH$_4$SCN in PVA is limited up to $x = 0.15$.

3.2 DSC analysis

It is well established that variable amounts of crystalline and amorphous phases in general co-exist in polymeric materials\textsuperscript{20}. Also the distribution of dopant salt amongst these phases considerably affect the thermal behaviour of polymeric complexes. Henceforth, a number of endothermic transitions are likely to be present in the system under investigation. Fig. 2 depicts the DSC thermograms of as synthesized casted PVA-NH$_4$SCN complexes alongwith that of constituent materials. Vari-
ous thermal transitions noticed from these thermograms have been listed in Table 1. The observed glass transition temperature ($T_g$) and melting temperature ($T_m$) for pure PVA are in close proximity with the results of Gupta et al.$^{12}$ and Gong and Cai.$^{15}$ The shift in glass transition and melting temperature of polymer electrolytes upon complexation (Table 1) has been correlated to flexibility of the polymeric back bone$^8$ which affects the ionic conductivity of the complex (to be discussed later on). Multiple thermodynamic transitions observed above $200^\circ C$ ($T_m$) in the DSC thermograms of the complexed material have been correlated to heterogeneous distribution of crystalline complex phases formed during complexation. To understand the morphology of films, degree of crystallinity ($X_c$) has been calculated from the ratio of enthalpy change associated with crystalline part of the complex to that of paradi bromobenzene ($\Delta H_m = 112.9 \text{ J g}^{-1}$) taken as standard material. These results show enhancement in amorphous nature of PVA complexes up to $x = 0.15$ and crystalline nature retrieved there after. The large difference in magnitude of the two $X_c$ data ($X_c \text{X-ray}$ and $X_c \text{DSC}$) is on account of the difference in the method of calculation. However, the variations with composition are in consonance. Furthermore, for higher salt concentrations ($x \geq 0.25$) an additional endothermic peak around $148^\circ C$ starts to appear. This peak corresponds to the melting temperature of NH$_4$SCN and hence suggests the presence of uncomplexed salt in the complex at such concentrations. Similar results were also observed during X-ray analysis. The broad endothermic transitions observed around 127.2$^\circ C$ and 114$^\circ C$ for the ratios $x = 0.05$ and $x = 0.25$ might be related to evaporation of pseudo-absorbed water in the sample or commencement of crystallization in the amorphous part of the complex above $T_g$ or both.$^{10}$ It is worth mentioning here that as the complex for $x = 0.10$ did not reveal any endothermic transition till $300^\circ C$. DSC scan was carried beyond this temperature. This particular complex did show a broad endothermic transition in the temperature range 292-330$^\circ C$ which is a region where degradation of pure PVA occurs$^{15}$. Few endothermic kinks were also noticed in the lower temperature zone of this broad endothermic peak. These kinks could be associated to melting transition in the crystalline part of the complex suppressed by the onset of degradation of PVA present in the complex, therefore $X_c \text{DSC}$ data for this complex was not evaluated.

### 3.3 IR analysis

IR spectral analysis of PVA complexes were carried out to understand their complexation behaviour. Fig. 3 depicts the IR spectra of pure PVA, and one of its complex with NH$_4$SCN (viz. for $x = 0.10$) for comparison of characteristic spectral bands. A few new absorption bands in the IR spectra of the complex were observed along with certain bands of the pristine material. The new features observed in the complexed film are:

1. Peak at 1895 cm$^{-1}$ corresponding to combination band of C=O stretch and C-O-C bending vibrations;
2. peak at 1725 cm$^{-1}$ related to C=O stretch vibrations;  
3. a peak at 1495 cm$^{-1}$ lying in C-O-C bending region;  
4. a shoulder peak at 1950 cm$^{-1}$ associated to combination band of CH$_2$ rocking and O-H bending vibrations.

The existence of these peaks besides those of constituent material ascertains complex formation. All the important characteristic absorption bands along with their assignment are listed in Table 2.

### Table 1 — XRD and DSC data of PVA$_x$NH$_4$SCN complexes

<table>
<thead>
<tr>
<th>$x$ (weight fraction)</th>
<th>$d$ (Å)</th>
<th>$L_1$ (Å)</th>
<th>$X_c \text{X-ray}$ (%)</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$X_c \text{DSC}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.821</td>
<td>29.7</td>
<td>34.82</td>
<td>90.0</td>
<td>216.1</td>
<td>-</td>
<td>52.33</td>
</tr>
<tr>
<td>5</td>
<td>6.213</td>
<td>50.1</td>
<td>24.05</td>
<td>71.2</td>
<td>197.3</td>
<td>242-252</td>
<td>35.71</td>
</tr>
<tr>
<td>10</td>
<td>7.367</td>
<td>33.3</td>
<td>19.06</td>
<td>-</td>
<td>-</td>
<td>292-330</td>
<td>79.87</td>
</tr>
<tr>
<td>15</td>
<td>-</td>
<td>10.3</td>
<td>-</td>
<td>51.3</td>
<td>165.2</td>
<td>202-258</td>
<td>32.13</td>
</tr>
<tr>
<td>20</td>
<td>5.851</td>
<td>32.9</td>
<td>17.43</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>5.062</td>
<td>28.7</td>
<td>30.75</td>
<td>73.2</td>
<td>186.6</td>
<td>244-260</td>
<td>67.94</td>
</tr>
</tbody>
</table>

*$^*$NH$_4$SCN
The appearance of an intense and broad peak around 2080 cm\(^{-1}\) (related to C=N stretch) is due to partial complexation of salt with the polymer host. The increased intensity and broadening may be due to co-existence of combination band of C-O-C bending and C-H stretching vibrations and its coupling with C=N stretch vibrations. The presence of broad peak around 1640 cm\(^{-1}\) suggests the existence of pseudo absorbed water. Moreover, it can also be correlated to the presence of C=C group in the parent material (PVA) as conjugated end groups or non hydrolizable vinyl acetate groups in PVA\(^{25,26}\). Appearance of 1725 cm\(^{-1}\) peak can be linked to C=N stretch vibrations on account of interaction between SCN group of the salt with polar OH group of host polymer and formation of bridging network. Hence C=N stretch frequency (1640-1690 cm\(^{-1}\)) shifts towards higher frequencies\(^{25}\).

In view of the preceding discussion, the possible structure of PVA-NH\(_4\)SCN complex can be given as:

![Structure Diagram](image)

### Table 2 — Assignment of IR bands of PVA and PVA\(_{x}\)NH\(_4\)SCN complex

<table>
<thead>
<tr>
<th>PVA(_{x}) NH(_4)SCN (cm(^{-1}))</th>
<th>PVA (cm(^{-1}))</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3600-2620 O-H stretch, N-H stretch</td>
<td>3500-3260</td>
<td>C-H stretch, N-H stretch</td>
</tr>
<tr>
<td>2955-2890 -</td>
<td>-</td>
<td>C-H stretch (submethyl stretch)</td>
</tr>
<tr>
<td>- 2080-2040 C=N stretch, combination band of C-O-C bend and C-N stretch</td>
<td>- 1950</td>
<td>combination band of CH(_3) symmetric rocking and O-H bend</td>
</tr>
<tr>
<td>- 1895</td>
<td>- 1725</td>
<td>combination of C-O stretch and C-O-C bend</td>
</tr>
<tr>
<td>- 1640</td>
<td>- 1640</td>
<td>C=N stretch</td>
</tr>
<tr>
<td>- 1495</td>
<td>- 1495</td>
<td>presence of pseudo absorbed water and C=N stretch</td>
</tr>
<tr>
<td>- 1470</td>
<td>- 1470</td>
<td>O-H and CH bend</td>
</tr>
<tr>
<td>- 1450-1410</td>
<td>- 1450-1410</td>
<td>submethyl C-H stretch, CH(_2) bend</td>
</tr>
<tr>
<td>1377</td>
<td>- 1320</td>
<td>CH(_2) in-plane distortion</td>
</tr>
<tr>
<td>1225</td>
<td>- 1225</td>
<td>OH bend</td>
</tr>
<tr>
<td>- 1195</td>
<td>- 1195</td>
<td>CH wagging</td>
</tr>
<tr>
<td>1144</td>
<td>- 1144</td>
<td>C-O stretch, OH bend</td>
</tr>
<tr>
<td>1086</td>
<td>- 1086</td>
<td>C-C stretch, C-O stretch</td>
</tr>
<tr>
<td>916</td>
<td>- 916</td>
<td>C-O stretch and OH bend</td>
</tr>
<tr>
<td>850</td>
<td>- 850</td>
<td>skeletal (PVA amorphous)</td>
</tr>
<tr>
<td>- 765</td>
<td>- 765</td>
<td>CH(_2) asymmetric rocking</td>
</tr>
<tr>
<td>- 535</td>
<td>- 535</td>
<td>C-S stretch</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>NCS bend</td>
</tr>
</tbody>
</table>

Fig. 3 — IR spectra of pure NH\(_4\)SCN(a), PVA(b) and PVA\(_{x}\) NH\(_4\)SCN complex for x = 0.10(c)
Various other absorption bands supporting the said structure of the complex have also been listed along with their assignments in Table 2. Absence of characteristic peaks of DMSO reveals the absence of solvent in the electrolyte films under consideration.

3.4 Ionic transference number and mobility

The current versus time plots obtained for these complexes exhibited typical behaviour of ionic charge transport. Total ionic transference number for all the samples have been calculated from these plots and found to lie in the range 0.82-0.97. In order to identify the type of mobile ionic species and their relative contribution, coulometric investigations have been carried out. On passing a current of $= 30 \mu$A through the electrolysis cell, gas evolved only on the cathode side. Neither a chemical deposition nor variation in anode side mercury column was noticed during the experiment. These observations indicate only cationic charge transport through the sample with the mobile ionic species being such that when reduced on cathode liberates a gas. This gas when analysed through a gas chromatograph was found to be hydrogen which justifies that only protons are the ionic charge carriers in these electrolytes. The volume of gas evolved as a function of charge passed through the cell for one of the samples is shown in Fig. 4. Cationic transport number ($n_{H}^+$) for all the samples was calculated using relation 2 and the so obtained values have been depicted in Fig. 6. The $n_{H}^+$ values resemble $t_{\text{total}}$ data obtained through dc polarisation technique. A comparison of data from two experiments reveal that $t_{\text{total}}$ values are a bit smaller which is however not possible. The only possible reason behind such an observation can be the limitations of dc polarisation technique.$^{17}$

The participation of single type of mobile ionic species in the process of charge transport was also affirmed during mobility measurements using transient ionic current (TIC) technique$^{17}$. Fig. 5 depicts TIC curve obtained for one of the samples. From the measurement of time of flight ($\tau$), bulk mobility ($\mu$) of charge carrier was calculated using relation given in Eq. (3). The so obtained mobility data as a function of salt concentration in the complex has been shown in Fig. 6. To validate the credibility of mobility data, TIC measurements were performed at different voltages as well as on samples of different thicknesses for few compositions. In association with morphological predictions these ions transport parameters ($t$ and $\mu$) were subsequently used to understand the conductivity behaviour of system under consideration.
3.5 Ionic conductivity

In general the ionic conductivity (\(\sigma\)) is expressed as:

\[
\sigma = \sum n_i q_i \mu_i
\]  

...(4)

where \(n_i\) is the concentration of mobile charge carriers, \(q_i\) the charge and \(\mu_i\) the ionic mobility. According to this relation, conductivity of ionic solids is strongly influenced by \(n\) as well as \(\mu\). The effective number of mobile charge carriers depends not only on salt concentration but also on ionic interactions inside the bulk leading to ion association and charge multiplet formation processes. On the other hand, mobility depends on morphology of the system. Therefore, to understand the conductivity behaviour, mobility \(\mu\) and concentration \(n\) of charge carriers were also evaluated and plotted against salt concentration along with conductivity \(\sigma\) (Fig. 6). The concentration of charge carriers \(n\) was evaluated using \(\mu\), \(n_i\) and \(\sigma\) values obtained as described in the experimental section. Therefore, it seems imperative to understand the mobility data obtained through an independent experiment (TIC) before discussing the conductivity response of electrolytes under consideration.

It is well known that mobility of transporting species is dependent on the flexibility of polymeric backbone which is indicated by lowering of glass transition temperature and degree of crystallinity of the system. In the present system it has been observed that the degree of crystallinity lowers upon salt addition in the polymer host up to an optimum value \((x = 0.15)\) and thereafter it enhances (Table 1). Lowering of \(X_c\) \((X_{c\text{ray}}\) and/or \(X_{c\text{DTSC}}\)) leads to enhancement in amorphous phase of the complex which is believed to be the conducting phase in ion conducting polymers\(^{17}\). Also the segmental mobility increases with decrease of crystallinity and \(T_e\) of the system.

The \(X_c\) values shown in Table 1 broadly depicts a typical feature of polymer salt complexes\(^{19}\). The observed higher degree of crystallinity for \(x = 0.25\) can be attributed to the formation of aggregates of host polymer and salt as separate entities at such concentrations. Mobility results (Fig. 6) have been found to be in agreement with the corresponding changes in \(X_c\) and \(T_e\) values.
Maurya et al\textsuperscript{17}, have also observed similar features for PEO-(N\textsubscript{2}H\textsubscript{6})\textsubscript{2}SO\textsubscript{4} polymeric complexes.

From Fig. 6 it is also observed that \( n \) first shows an initial increase then decrease followed by an increase and subsequent decrease as the salt concentration enhances in the complex. The rapid increase in \( n \) for low salt concentrations \((x \leq 0.10)\) is simply due to effect of doping and the transient cross link density (leading to ionic association) will be low for such concentrations\textsuperscript{26}. Subsequently, the decrease in \( n \) can be attributed to formation of non conducting ion pairs and conducting triplets (ion association effect) as believed by several workers\textsuperscript{27,28}. For salt concentrations \( x \) such that \( 0.15 \leq x \leq 0.20 \), the increase in \( n \) value can be attributed to re-dissociation of non conducting ion pairs into conducting triplets and higher multiplets\textsuperscript{29}. This feature can be associated to the formation of quadrupoles (immobile entity where salt molecules are associated two by two. These quadrupoles being unstable entities, dissociate either into ion pairs or a triplet ion plus a free ion\textsuperscript{29}. Thus triplets are supposed to contribute to electrical conductivity at intermediate salt concentrations \((0.10 \leq x \leq 0.15)\) in the present case. At still higher concentrations \((x \geq 0.20)\), the number of mobile charge carriers decreases possibly due to enhanced ion association dominating re-dissociation as well as formation of higher order multiplets and/or salt segregation as evidenced by X-ray and DSC experiments.

The observed conductivity behaviour can now be described on the basis of the variation in \( \mu \) and \( n \). For the purpose of simplicity, the conductivity curve can be split into four different regions, namely, OA, AB, BC and CD. The initial rapid increase in \( \sigma \) (region OA) is due to increased availability of mobile charges as well as enhanced segmental mobility as revealed by \( \chi \) and \( T_c \) data. In region AB, the rate of increase in \( \sigma \) slows down which is due to distinct fall in \( \mu \) (as discussed in the previous paragraphs) in this region. The moderate rise in \( \sigma \) for region BC is again due to counter change in \( \mu \) and \( n \) values. Thus, according to Eq. (4), the corresponding change in conductivity is reflected in Fig. 6. The decrease in \( \sigma \) in region CD follows much steeper decrease in the mobility.

4 Conclusion

On the basis of structural, thermal and structural characterization following conclusions can be drawn in regard to PVA-NH\textsubscript{2}SCN system.

(1) X-ray analysis shows the formation of PVA-NH\textsubscript{2}SCN complex with enhanced amorphous nature; (2) DSC analysis confirmed the formation of complex with co-existence of variable degree of amorphous and crystalline phases; (3) on the basis of IR analysis a possible chemical structure of the complex has been proposed; (4) highest conductivity was observed for intermediate salt concentration; \( x = 0.15 \); (5) compositional dependence of conductivity has been explained in terms of sample morphology and its correlation with other electrical transport parameters namely \( \mu \) and \( n \).

Acknowledgments

Thanks are due to M/s Vindhya Telelinks Ltd., Rewa, India, and Prof. S Chandra, Physics Department, Banaras Hindu University, Varanasi, for providing DSC and IR facilities respectively. Authors are thankful to Dr K Sharma, Chemistry Department, Autonomous Model Science College, Rewa and Prof S Chandra for fruitful discussions regarding IR results. Financial support from CSIR, New Delhi in form of research project is also gratefully acknowledged.

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