**International Journal of ChemTech Research**
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.12 No.04, pp 150-157, 2019

# Low cost and facile preparation of $Al(NO_3)_3$ doped PVA-PEG polymer electrolyte films for electrochemical applications

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**Abstract :** Polymer electrolyte films based on PVA-PEG with $Al(NO_3)_3$ as the dopant at different concentrations were prepared using solution casting technique. The structural properties of the samples were examined by optical microscope and FTIR studies. FTIR spectra confirm the complexation of the dopant with the polymer blend. AC conductivity and complex impedance of the samples were performed in the frequency range of 100 Hz to 1 MHz at different temperatures. The ionic conductivity increases with the $Al(NO_3)_3$ content and the maximum value at room temperature is found to be 1.0706 $10^{-5}$ S/cm for 5 mol% $Al(NO_3)_3$ doped PVA-PEG film. This value is three or four orders of magnitude greater than those obtained in the certain representative polymer-salt complexes as reported earlier. The results suggest that the $Al(NO_3)_3$ doped PVA-PEG polymer blend electrolytes are good candidates for future electrochemical devices.

**Keywords :** amorphous phase, ionic conductivity, optical properties, polymer blend, Solid polymer electrolyte.

## 1. Introduction

Polymer electrolytes have been extensively studied due to their potential applications in various electrochemical devices such as sensors, solid state batteries, fuel cells, electro chromic display devices, super capacitors, etc. On the other hand, the low cost and facile preparation of electrolytes make them as a promising candidate for wide variety of applications. However, the low ionic conductivity of polymer electrolytes at ambient temperature has limited their potential applications. Recently, the polymer blends often exhibit special properties that are superior compared to the properties of each individual component polymer. The main advantages of the blending of polymers is that they are able to dissociate the ion-pairs into free cations and anions and leads to overall conductivity enhancement, simplicity of preparation and ease of control of physical properties by compositional change. Polymer electrolytes usually contain both crystalline and amorphous phases but conductivity occurs only in the amorphous phase. In order to increase the conductivity at ambient temperature, polymer blending helps to reduce the crystalline content and enhance the amorphous content. Also the film formability with desirable mechanical, thermal and electrochemical stability makes polymer blend electrolytes more attractive than the conventional electrolyte materials [1-9].

**G.Shanmugam *et al* /International Journal of ChemTech Research, 2019,12(4): 150-157.**

**DOI= http://dx.doi.org/10.20902/IJCTR.2019.120418**

Among the polymers, poly vinyl alcohol (PVA) is most interesting polymer because of its high dielectric strength and thermal stability, good charge storage capacity and dopant-dependent electrical and optical properties. PVA is a semi-crystalline polymer, possessing both amorphous and crystalline phases at room temperature. Moreover it has a carbon chain backbone with hydroxyl groups attached to methane carbons. These -OH groups can be a source of hydrogen bonding and hence of assistance in the formation of polymer blends [3-9]. For preparing polymer blend with PVA, Poly ethylene glycol (PEG) was chosen as second polymer. PEG is an amorphous polymer and it forms a variety of complexes with various salts, due to the presence of -OH group in the chain of PEG, which can permit faster ionic mobility. It also deserves a special attention because of its good environmental stability, easy processability, moderate electrical conductivity and rich physics in ionic transport mechanism [3, 4, 9]. Both PVA and PEG are industrially most important water soluble polymers which are miscible in all proportions and their blends have potential applications in the fabrication of electrochemical devices.

The structural, optical, and electrical properties of polymer blends can be suitably modified by the addition of the migrating ion species depending on their reactivity with the host matrix. Until recently most of the migrating ion species had been only limited to mono- and divalent ions, and some of them have been already brought to the market in many industrial fields. In this regard, a target for the next generation is to develop a trivalent ion doped electrolytes. Among the trivalent cations, $Al(NO_3)_3$ is a well known metal ion which is extremely attractive on the grounds of high specific energy, stemming from the low atomic mass and small ionic radius, three-free electron reaction, as well as its low cost. Although a series of $Al(NO_3)_3$ ion conducting solid electrolytes have been reported [10-14], a literature survey indicated that surprisingly no report on trivalent $Al(NO_3)_3$ ion doped polymer electrolyte films exists. Hence it is quite interesting and important to gain an understanding of ion transport mechanism of PVA-PEG blends with $Al(NO_3)_3$. In view of the above factors, for first time we report the PVA-PEG polymer blend electrolytes doped with the various concentrations of aluminium nitrate ($Al(NO_3)_3$) which have been prepared by solution casting technique. The influence of $Al(NO_3)_3$ ion on structural, optical and electrical properties of PVA-PEG polymer blend electrolyte films over a wide range of frequency and temperature have been studied in detail.

## 2. Experimental

We used PVA ($M_W$=14000, Kemphasol, India), PEG ($M_W$=40000, HiMedia Laboratories Pvt. Ltd, India) and $Al(NO_3)_3.9H_20$ (Nice Chemicals Pvt.Ltd, India) to prepare undoped and $Al(NO_3)_3$ doped PVA-PEG polymer blend electrolyte films. All chemicals were used as received. Polymer blending electrolyte films of PVA:PEG (70:30, wt%) doped with various concentrations (x) of aluminium nitrate (x = 0, 2 and 5 mol%) have been prepared by means of solution casting technique using distilled water as solvent. The appropriate weights of PVA, PEG and $Al(NO_3)_3$ were dissolved in distilled water and then solution was stirred continuously for 5 h until the homogeneous solution obtained. The resulting solution was poured onto cleaned petri dishes and then dried in hot air oven at 70°C for 2 h to ensure removal of solvent traces. After drying, the films were peeled off from the petri dishes and kept in vacuum desiccators until use. The surface morphology of the films was examined using Euromex trinocular stereo zoom optical microscope. The Fourier transform infrared (FTIR) spectra were recorded at room temperature using a Brucker Tensor 27 FTIR spectrophotometer with a resolution of 2 $cm^{-1}$ in the wave number range of 400-4000 $cm^{-1}$. The complex impedance and electrical conductivity measurements were performed using N4L Phase Sensitive Multimeter interfaced with Impedance Analyzer with a cell with stainless steel electrodes in the temperature range of 303-423 K over a frequency range of 100 Hz-1 MHz.

## 3. Results and discussions

### 3.1. Optical micrograph studies

Figure 1 (a-c) displays the optical micrograph of all the electrolyte films. In optical micrograph, the white region indicates the non-porous crystalline nature of polymers whereas dark region indicates the electrolyte-rich phases (amorphous) within the porous structures [15]. The area of the dark region increases (as can been seen from Figure 1(a) to Figure 1(c)) with $Al(NO_3)_3$ doping, as would be expected, which indicates the miscibility of dopant with polymer blend to increase content of carrier ion and enhanced the conductivity of the electrolyte, accordingly.

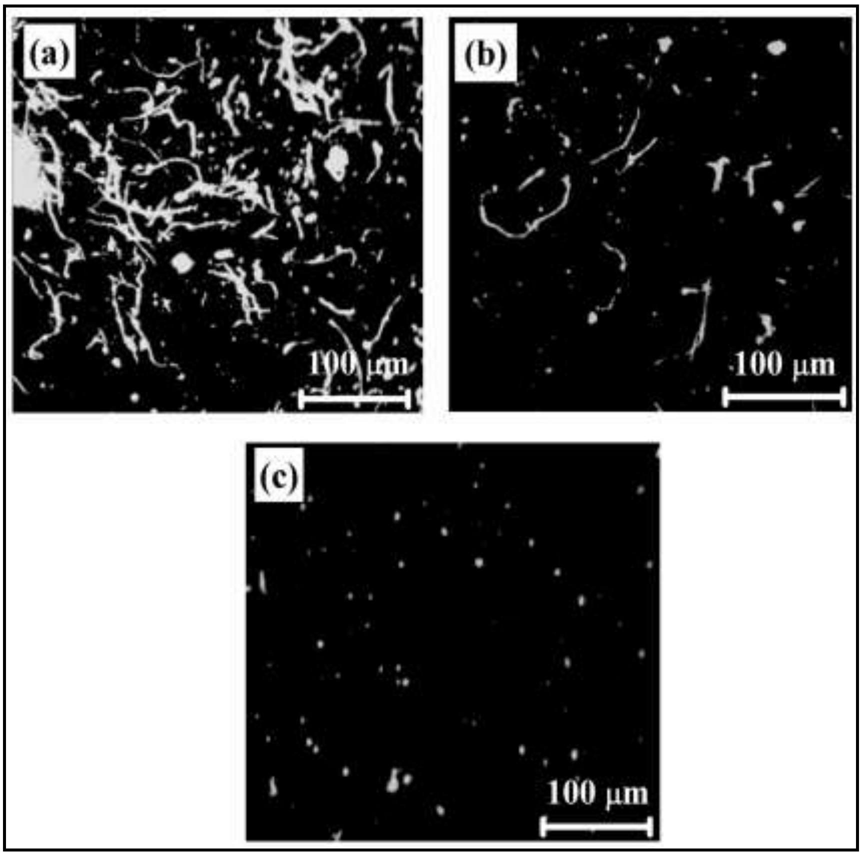

**Fig. 1. Optical micrograph of PVA-PEG polymer blend doped with different $Al(NO_3)_3$ concentrations (a) 0 mol%, (b) 2 mol% and (c) 5 mol%.**

### 3.2. FTIR studies

FTIR spectra of the samples are shown in Figures 2(a-c). The FTIR spectrum of pure PVA-PEG (Figure 2(a)) showed the peaks at 3442, 2927, 1716, 1663, 1435, 1366, 1085, 943 and 846 $cm^{-1}$ which could be assigned to O-H stretching, C-H asymmetric, C=O stretching, acetyl C=C group, wagging of $CH_2$, C-H wagging, C-O stretching, C-C stretching and $CH_2$ stretching respectively. These observed bands get shifted towards higher wavenumber in comparison with those previously reported in FTIR spectrum of pure PVA [3, 5-8]. The shift in the observed bands confirms a successful complex formation between PVA and PEG. This was expected to take place through intermolecular hydrogen bonding between the hydroxyl group of PVA and of PEG [3]. It can be observed that the FTIR spectrum (Figure 2(b)) of 2 mol% $Al(NO_3)_3$ doped film shows a small shift in wavenumber with that of pure PVA-PEG film which indicates weak interaction between polymer complex and salt concentration. However, in the Figure 2(c), the broadening of O-H stretching vibration with C-H asymmetric vibration and C=O stretching with acetyl C=C group vibration and disappearance of other bands can be observed in the spectrum of PVA-PEG doped with 5 mol% $Al(NO_3)_3$ which indicates the breaking of hydrogen bonding between the dopant and polymer complex by inducing charge transfer complexation between the polymer composite and dopant [15].

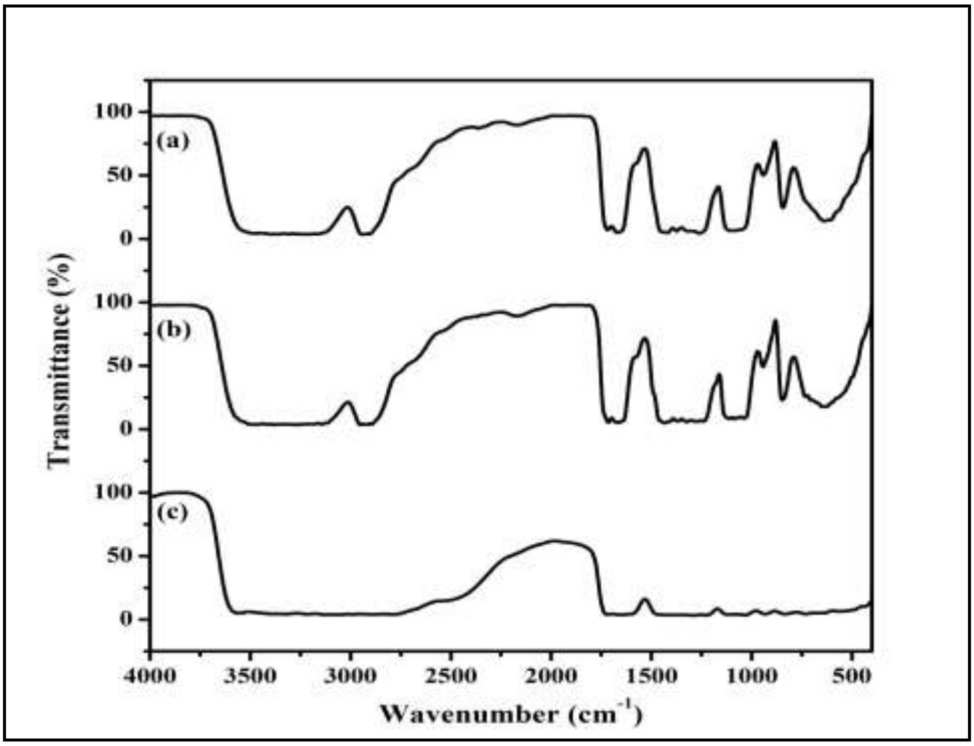

**Fig. 2. FTIR spectra of (a) PVA-PEG, (b) 2 mol% and (c) 5 mol% $Al(NO_3)_3$ doped PVA-PEG polymer blend films**

### 3.3. ac conductivity studies

The frequency dependent ac conductivity of pure and $Al(NO_3)_3$ doped PVA-PEG polymer blend electrolyte films at room temperature is shown in Figure 3(a). The ac conductivity increases with increasing salt concentration, as shown in Figure 3(a), which is due to an increase in the number of mobile charge carriers by the addition of $Al(NO_3)_3$. Hence, it confirms that the mobility of anions has been restricted and the conductivity is enhanced by mobility of aluminium trivalent cations. It is also noticed that the ac conductivity of $Al(NO_3)_3$ doped PVA-PEG polymer blend electrolyte films is higher than those obtained in undoped PVA-PEG film. The maximum conductivity is found to be $1.4833\times10^{-4}$ S/cm at 1 MHz for 5 mol% $Al(NO_3)_3$ doped PVA-PEG film. The ac conductivity plots show a plateau at low frequency, which corresponds to the dc conductivity of bulk material and exhibit dispersion at high frequency, which corresponds to the ac conductivity. The conductivity increases as the frequency increases towards higher frequency side. This behavior obeys Jonchers's power law as follow: [16]

$$\sigma(\omega) = \sigma_0 + A\omega^n$$

where $\sigma_0$ is the dc conductivity of bulk material, $A$ is the pre-exponential factor and $n$ is the power law exponent. The values of $\sigma_0$, A and $n$ can be obtained by fitting the above equation and they are given in Table 1.

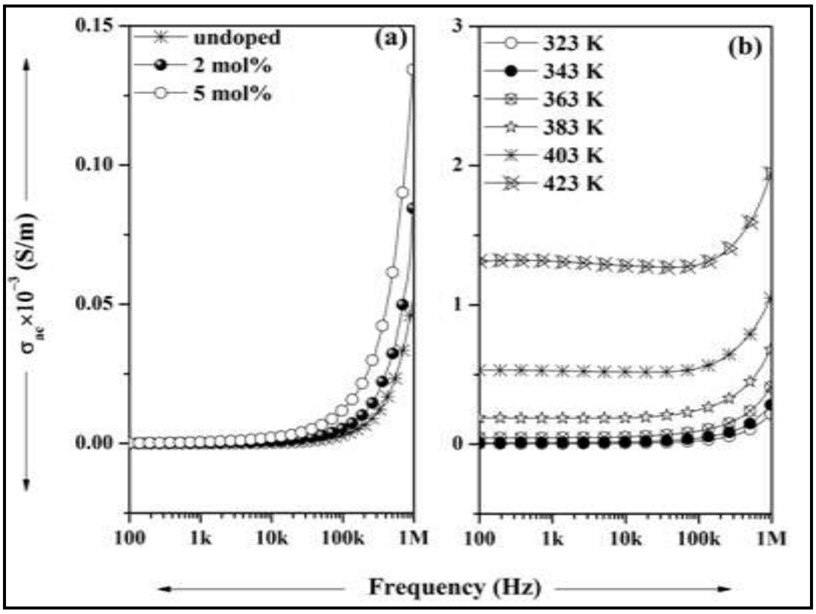

**Fig. 3. AC conductivity of (a) PVA-PEG polymer blend doped with different concentrations of $Al(NO_3)_3$ at room temperature and (b) 5 mol% $Al(NO_3)_3$ doped PVA-PEG polymer blend electrolyte film at different temperatures.**

For ideal ion conducting polymer electrolyte, *n* should be between 0 and 1 indicating the ideal long-range pathways and tortuous pathway. The values of *n* are in the range of 0.78-0.94. As given in Table 1, the increase in *n* with Al doping shows that the long range drift of ions may be one of the main reasons of ionic conduction. Figure 3(b) represents the frequency dependent ac conductivity of 5 mol% $Al(NO_3)_3$ doped PVA-PEG polymer blend electrolyte film at different temperatures. The conductivity increases with increasing temperature which is common in solid polymer electrolytes [9, 16]. In the present work, the increase in conductivity with increasing temperature can be related to the increase in the number of mobile charge carriers contributing to the transport of ions [16].

### 3.4. Complex impedance analysis

The room temperature complex impedance plots of undoped and $Al(NO_3)_3$ doped PVA-PEG polymer blend electrolyte films are shown in Figure 4. The plots obey the Cole-Cole type relaxation by exhibiting only one semicircular arc over the entire frequency range which corresponds to the bulk properties of grain (dc resistivity). The ionic conductivity ($\sigma_{dc}$) can be calculated using the standard relation, $\sigma_{dc} = d/R_bA$, where $d$ is the thickness of the sample, $A$ is area of the sample and $R_b$ is the bulk resistance derived from the intercept of the impedance plot on real axis.

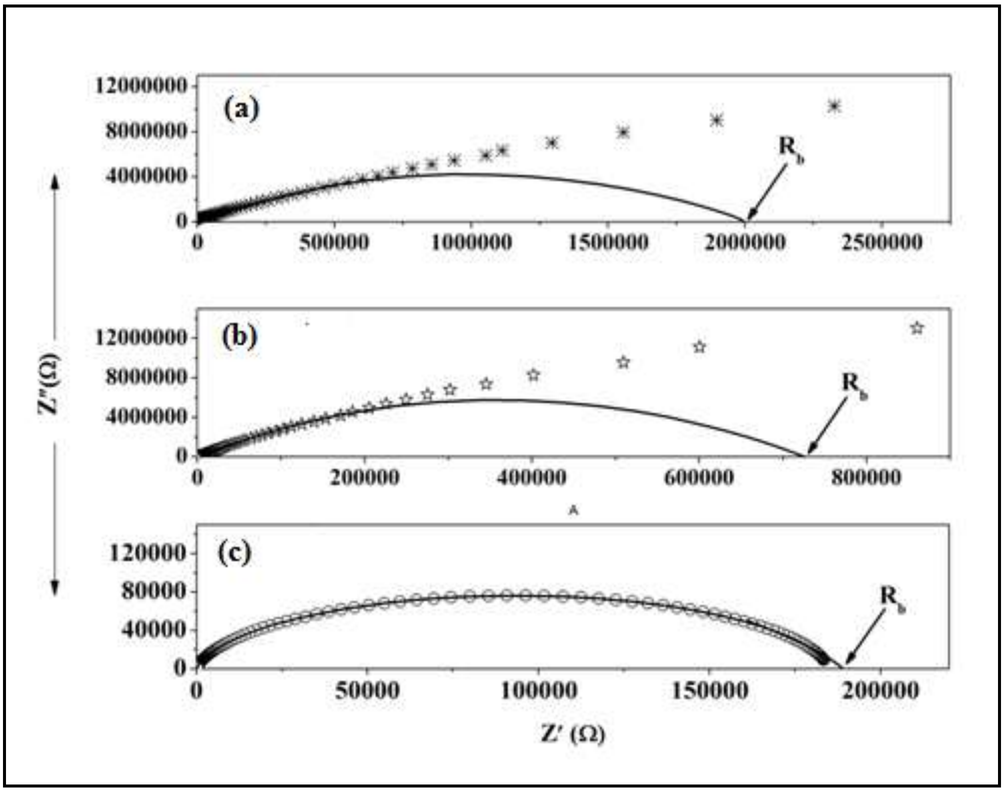

**Fig. 4. Room temperature complex impedance plots of pure and Al doped PVA-PEG polymer blend electrolyte films**

The ionic conductivity values of different complexes at room temperature are summarized in Table 1. As seen in the Table.1, the ionic conductivity increases with increase in dopant concentration and found to be high for 5 mol% $Al(NO_3)_3$ doped film. This might be attributed to increase in number of mobile charge carriers which results in a dominant amorphous phase in the film. This would happen when the interaction between polymer and salt takes place. It has been confirmed by FTIR spectra as discussed above. Also, the $\sigma_{dc}$ value of 5 mol% $Al(NO_3)_3$ doped film is three or four orders of magnitude larger than those previously reported in certain representative metal salts doped polymer electrolytes [5-9, 17-19]. Hence, it confirms that the interaction of trivalent $Al(NO_3)_3$ with polymer blend could also improve the ionic conductivity which leads them as a superior candidate against the other solid electrolytes.

**Table 1. Absorption edge, band gaps, $\sigma_{ac}$ and $\sigma_{dc}$ values of PVA-PEG polymer electrolyte doped with various concentrations (x mol%) of $Al(NO_3)_3$ films at room temperature.**

| x | $\sigma_{ac}\times10^{-4}$ (S/cm) | $\sigma_0\times10^{-5}$ (S/cm) | $A\times10^{-8}$ | n | $\sigma_{dc}\times10^{-5}$ (S/cm) |
|---|---|---|---|---|---|
| 0 | 0.5728 | 0.1364 | 0.0148 | 0.76 | 0.0533 |
| 2 | 0.9547 | 0.3435 | 0.2125 | 0.88 | 0.1360 |
| 5 | 1.4833 | 0.6041 | 0.9871 | 0.94 | 1.0706 |

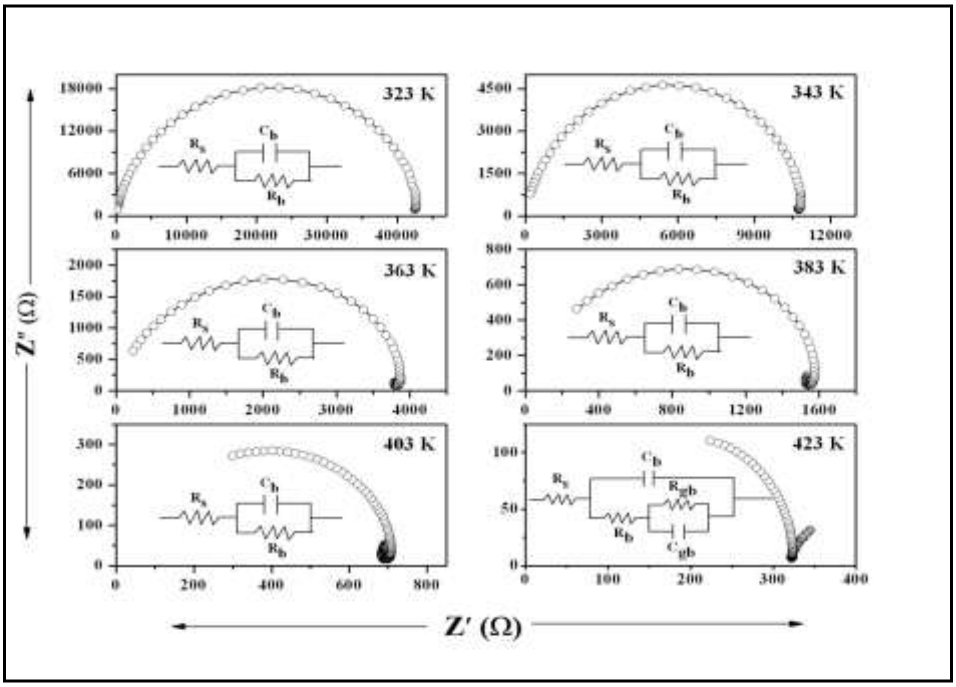

**Fig. 5. Complex impedance plots of 5 mol% Al(NO$_3$)$_3$ doped PVA-PEG polymer blend electrolyte films at different temperatures**

Figure 5 shows the complex impedance plots of PVA/PEG/5 mol% Al(NO$_3$)$_3$ electrolyte film at different temperatures. The extrapolation of intercept of semicircular arc on the real axis tends to lower values with increasing temperature which is attributed to the enhancement in ionic conductivity. This may be explained on the basis of free volume model. When the temperature increases the vibration energy of a segment of polymer chain becomes sufficient to push against the hydrostatic pressure imposed by its neighbouring atoms and create a small amount of space surrounding its own volume in which vibrational motion can occur. Therefore, the free volume around the polymer chain causes the mobility of the ions to increase and the segmental motion of polymer chain causes the conductivity to increase [5]. Moreover, the complex impedance plots demonstrate the pronounced temperature dependence of the device impedance in low frequency range. The electrical conduction of the films is represented using an equivalent circuit, as shown in the inset of Figure 6. The plots show a single semicircular arc over the temperature range of 323-403 K which suggests the presence of grain interior (bulk) property of the material. The equivalent circuit for this case is showed as the parallel combination of grain (bulk) resistance ($R_b$) and grain capacitance ($C_b$) with a series resistor ($R_s$) [19]. At high temperature (>403 K), impedance plot exhibits two semicircular arcs. The high frequency arc corresponds to the grain interior property whereas the low frequency arc indicates the grain boundary effect. Hence, the equivalent circuit is given by the series of parallel combination of $R_bC_b$ and $R_{gb}C_{gb}$ where $R_{gb}$ is the grain boundary resistance [1-2, 7].

## Conclusions

Pure and Al(NO$_3$)$_3$ doped PVA-PEG polymer electrolyte films were prepared by solution casting technique. FTIR spectra showed the certain changes in intensity and position of the peak with salt content which confirm the formation of polymer-salt complexes. Frequency dependent ac conductivity of films obeys Jonscher power law and its value is found to be increase with increasing dopant concentration. From the complex impedance plots, the ionic conductivity was calculated and is higher for 5 mol% Al(NO$_3$)$_3$ doped PVA-PEG polymer electrolyte film. The obtained ionic conductivity value is three or four orders of magnitude larger than those previously reported on certain representative polymer-salt complexes. Temperature dependence of ionic conductivity showed a single semicircular arc over the temperature range of 323-403 K while the two semicircular arcs appeared at above 403 K temperature. The electrical conduction of the sample was depicted using an equivalent circuit. These results suggest that the Al(NO$_3$)$_3$ doped PVA-PEG electrolyte films are potential candidate for electrochemical device applications.

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