

Ftir And Conductivity Studies of Pva-ZnCl₂ Based Solid Polymer Electrolytes

S. Jayanthi

Assistant Professor, Dept Of Physics
The Standard Fireworks Rajaratnam College For Women, Sivakasi.

Abstract- Solid Polymer electrolytes (SPEs) comprising of poly(vinyl alcohol) (PVA) added Zinc chloride (ZnCl₂) systems have been prepared via solvent casting technique. The prepared samples have been subjected to AC impedance spectroscopic analysis and Fourier Transform Infrared Spectroscopy (FTIR) studies. Maximum ionic conductivity of $3.91949 \times 10^{-7} \text{ Scm}^{-1}$ was achieved for 60 wt% of PVA and 40wt% of ZnCl₂ system at room temperature. The structural changes and hence the complex formation between the constituents used in the present study has been confirmed through FTIR analysis.

Keywords- Complexation, FTIR, Ionic conductivity, Polymer electrolytes.

I. INTRODUCTION

The potential application of polymer electrolytes in a variety of electrochemical devices arises from their advantages such as high energy density, electrochemical stability and easy handling. Solid polymer electrolytes are more convenient because they have better shape, easy to handle, and possibilities for electrolytes leaking are none. Poly(vinyl alcohol) (PVA) has excellent film forming nature, high tensile strength and flexibility. It is a crystalline, synthetic water-soluble polymer and has very important application due to the role of hydroxyl groups and hydrogen bonds assist in the formation of polymer blends. It has some technological advantages in electrochemical devices, fuel cells, etc [1]. The present work deals with the preparation and characterization of polymer electrolytes based on PVA with ZnCl₂ by solution casting technique using distilled water as solvent.

In order to characterize the prepared polymer electrolytes, various experimental techniques such as, Fourier-transform infrared spectroscopy (FTIR), AC impedance spectroscopy have been used.

II. MATERIALS AND METHODS

Polymer films of PVA : ZnCl₂ of different composition have been prepared using solution casting

technique. Suitable amount of PVA is dissolved in distilled water and it was stirred well. After complete dissolution of PVA suitable amount of ZnCl₂ is added in the same solution and this mixture was stirred well until a homogenous solution was obtained. Then, the homogenous solution have been poured in the propylene petri dishes and allowed to evaporate in hot air oven at 60°C. This procedure yields mechanically stable free standing films.

III. CHARACTERIZATION TECHNIQUES

A. AC impedance analysis

Impedance values of the SPEs were determined with the help of PSM 1735 impedance analyzer in the frequency range of 1 Hz – 5 MHz with a signal amplitude of 2mV using stainless steel blocking electrodes.

B. FTIR Analysis

The complexation between the PVA and ZnCl₂ was investigated via FTIR study. The FTIR spectra were recorded using SHIMADZU FTIR spectrophotometer in the wave number region 4000 – 400 cm⁻¹.

IV. RESULTS AND DISCUSSION

A. AC impedance analysis

AC impedance analysis is a powerful technique for determining the electrical properties of interfaces between electronically and ionically conducting phases. It may be used to investigate the dynamics of bound or mobile charges in the bulk or interfacial regions of a variety of solid and liquid materials ionic semi conducting, mixed electronic and even insulators [2].

AC impedance plot of PVA & ZnCl₂ system is given in Fig. 1. It consists of two well defined regions, a depressed semicircle in the high frequency region and an inclined spike in the low frequency region. The semicircular portion is due to the parallel combination of bulk resistance and capacitance.

Further the depressed semicircle reveals the non-Debye nature of the sample due to the potential well for each site, through which ion transport takes place [2].

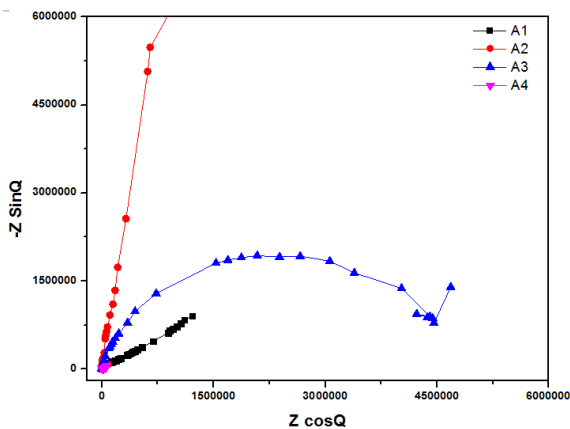


Fig. 1 AC impedance plot of PVA - ZnCl₂ system

The presence of an inclined spike at low frequency region at angle less than 90° is due to the roughness of the electrode-electrolyte interface.

Ionic conductivity of the prepared samples can be calculated using the following relation.

$$\sigma = \frac{l}{AR_B} \rightarrow (1)$$

where *l* is the thickness of the sample, 'A' is the area of the electrode and *R_B* is the bulk resistance. The intercept of the low-frequency spike at the real axis of the complex impedance plot gives the value of *R_B*. The calculated values of ionic conductivity for PVA-ZnCl₂ system are given in Table 1.

It is observed from the Table 1, that the value of ionic conductivity (σ) decreases against the increase of the concentration of ZnCl₂ from 10wt% to 30wt% in steps of 10wt%. The lesser value of ionic conductivity for 10, 20 and 30 wt% ZnCl₂ added system may be related to the re-association of the ions which leads to the formation of ion cluster of ZnCl₂ in the PVA matrix [2].

Table 1: Values of ionic conductivity PVA-ZnCl₂ system

Sample	PVA : ZnCl ₂ (wt%)	Ionic conductivity (Scm ⁻¹)
A1	90:10	2.5037*10 ⁻⁸
A2	80:20	1.0079*10 ⁻⁷
A3	70:30	1.0890*10 ⁻⁷
A4	60:40	3.9194*10 ⁻⁷

When the concentration of ZnCl₂ increased from 30wt% to 40%, an increase in the ionic conductivity is observed. At 40wt%, the ionic conductivity reaches a maximum value of 3.9194*10⁻⁷ Scm⁻¹ which is greater by two orders of magnitude when compared with the value 2.5037*10⁻⁸ Scm⁻¹ of PVA-ZnCl₂ (90:10) system at room temperature. This enhancement in ionic conductivity can be related to the increase in the number of mobile charge carriers. The film was fragile in nature when the concentration of ZnCl₂ was beyond 40%.

B. FTIR Analysis:

FTIR spectroscopy is an important technique for the investigation of polymer structure, since it provides information about the complexation and interactions among the various constituents in the complex polymer electrolyte film. The FTIR spectra of pure PVA, ZnCl₂ salt and PVA complexed with ZnCl₂ salt are shown in Fig. 2. The following spectral changes were observed on comparing the spectra of complexed polymer electrolyte films with those of pure PVA and ZnCl₂ salt.

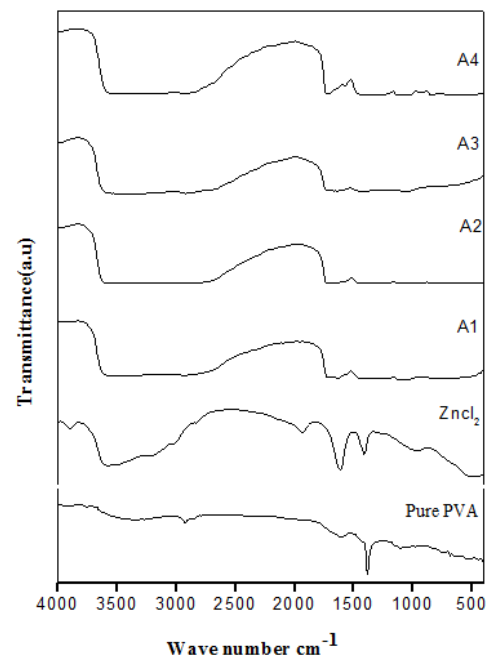


Fig. 2 FTIR spectra of PVA with ZnCl₂ system

The pure PVA has broad peak in the range 3757–3078cm⁻¹ pertains to O-H stretching. The broadness of the peak is attributed to the intra and/or intermolecular hydrogen bonding, and the same is found to be present for ZnCl₂ added PVA systems [3].

- 1) C-H stretching of CH₂ showed a peak 2924 cm⁻¹ for pure PVA and is slightly shifted to 2916 cm⁻¹ in 20% and 30% weight percentage of ZnCl₂ added systems respectively, whereas there is no shift for another weight percentage system.
- 2) The characteristic vibrational band at 1257 cm⁻¹ corresponds to C=O stretching of secondary alcohols and is shifted to 1242 cm⁻¹ in the complexed polymer electrolyte film.
- 3) C = C stretching occurring at 1111cm⁻¹ in pure PVA is shifted to 1121cm⁻¹ for ZnCl₂ added systems. All these changes in the FTIR spectra confirm the complexation between PVA and ZnCl₂.

Force constant:

The shift in frequency of the C=O group in polymer PVA is correlated with force constant values can be calculated using the following formula [4].

$$v = \frac{1}{2\pi c} \sqrt{k/\mu} \rightarrow (2)$$

where,

v is wave number (cm⁻¹),

C is the velocity of light (3*10¹⁰) cm/s,

K is force constant (N/cm) and

$$\mu = \frac{M_1 M_2}{M_1 + M_2}$$

Here, μ is the reduced mass and M₁ & M₂ are the atomic weight of two atoms respectively. The force constant values are calculated for pure PVA & PVA added with different concentrations of salt ZnCl₂ and they are tabulated in Table 2.

Table 2: Force constant for PVA & ZnCl₂ system (C = O stretching)

Sample	K (× 10 ⁵) Ncm ⁻¹
Pure PVA	10.366
A1	10.057
A2	10.185
A3	10.366
A4	9.587

The value of the force constant is found to be low for 40wt% of ZnCl₂ added PVA system when compared to the pure PVA. This decrease in value suggests that there is an interaction of Cl₂⁻ ion in salt (ZnCl₂) and oxygen atom in the polymer (PVA), which weakens the C = O bond by the

removal of electron density from it [4]. This result also confirms the complexation between the polymer (PVA) and the salt (ZnCl₂).

IV. CONCLUSIONS

In this work the structural and electrical properties of the solid polymer electrolytes based on the polymer PVA and ZnCl₂ via solution casting technique have been studied. Maximum ionic conductivity of 3.91949*10⁻⁷ Scm⁻¹ was observed for (60:40) PVA:ZnCl₂ system at room temperature. FTIR analysis reveals the possible bondings present in the polymer - salt complex and confirms the complex formation between the polymer and the salt. The force constants have also been calculated from FTIR spectrum for all the prepared samples.

REFERENCES

- [1] S. Chandra, “Super Ionic Solids”, vol.1, pp. 19-30, 1981.
- [2] S. Jayanthi, A. Arulsankar, B. Sundaresan, Applied Physics vol. 122, pp. 109, February 2016.
- [3] P. Balaji Bhargav, V. Madhu Mohan, A.K. Sharma, V.V.R.N. Rao, Journal of Korean Physical society, vol-9, (2008), page no 165-171.
- [4] Colin N. Banwell, and Elanie M. Mccash, “Fundamentals of Molecular spectroscopy”, Fourth Edition, 28th Reprint 2007, Page no 84-88.