

## Effects of Dmf on Pva Based Proton Conducting Polymer Electrolytes



### Physics

**KEYWORDS :** XRD, FTIR, impedance analysis, Dielectric analysis

**K.P.Radha**

Department of Physics, S.F.R. College for Women, Sivakasi-626 123, Tamil Nadu, India.

**J.Rajeswari**

Department of Physics, S.F.R. College for Women, Sivakasi-626 123, Tamil Nadu, India.

### ABSTRACT

Plasticized polymer electrolytes composed of Poly (vinyl alcohol) polymer; ammonium fluoride salt and DMF as plasticizer have been prepared using Solution Casting Technique. The amorphous nature of the electrolytes has been confirmed by XRD analysis. FTIR analysis confirms the complex formation among the components of the polymer electrolytes. The maximum ionic conductivity has been found to be  $8.29 \times 10^{-5} \text{ Scm}^{-1}$  for 85PVA:15NH4F:20 DMF polymer electrolytes at ambient temperature. The complex permittivity indicates the presence of dipoles in the bulk material. The  $M''$  representation shows a peak due to dielectric relaxation.

### Introduction:

Polymers with enhanced ionic conductivities at ambient temperatures are being investigated for their use in electrochemical devices as solid polymeric electrolytes. Several methods have been adopted to modify the ionic conductivity of the polymer electrolytes. Plasticization is one of the most significant contemporary ways to enhance the ionic conductivity of the polymer electrolytes. Kelly et al [1] reported already that the addition of plasticizer enhances the amorphous phases present in the polymeric electrolytes and thus the ionic conductivity. Among the plasticizers Propylene carbonate PC [2], Ethylene carbonate (EC) [3],  $\gamma$  - butyrolactone [4], polyethylene glycol (PEG), the high dielectric constant, low viscosity and co-ordinating ability of N,N-Dimethyl formamide [5] plays a vital role to select as plasticizer in the present work.

Vargas et.al [6] has investigated Poly (vinyl alcohol) for the phase behavior. Ionically conducting poly electrolytes based on PVA has been developed by Fritz and Breitosomer [7]. PVA is a potential material having a very high dielectric strength, good film forming ability, mechanical strength etc. The present work is attempted to develop PVA based polymer electrolyte by incorporating ammonium fluoride salt (NH4F) and N, N- Dimethyl Formamide (DMF) having molecular weight 73.09 g/mol, dielectric constant 36.1 at 250C, viscosity 0.8 at 250C, donor number 26.6 and melting point -61 as plasticizer.

### Experimental Technique

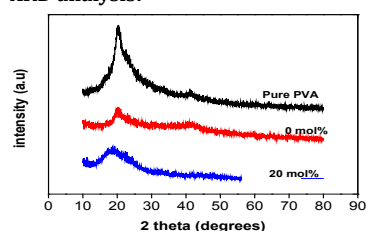
In the present work, electrolytes have been prepared using Poly (vinyl alcohol) PVA with average molecular weight 1,25,000 (AR grade, Sd fine CHEM-limited make), ammonium fluoride NH4F (AR grade, Merck), the plasticizer N,N - Dimethylformamide (AR grade, Merck) and the solvent Dimethyl Sulphoxide (DMSO) by Solution casting technique. From our earlier work on PVA:NH4F, it has been observed that the 85PVA:15NH4F polymer electrolyte has the highest ionic conductivity as  $6.9 \times 10^{-6} \text{ Scm}^{-1}$  at ambient temperature. 15 mol%, 20mol%, 25 mol% of the plasticiser have been added to 85PVA:15NH4F polymer electrolyte to prepare plasticised polymer electrolytes. The free standing nature and dryness of the prepared plasticised polymer electrolyte has been visually examined.

### Characterisation

Characterization of a material plays a vital role in the field of solid electrolytes. Hence the prepared polymer electrolytes have been subjected to structural, vibrational and electrical analysis.

### Results & Discussion

#### XRD analysis:

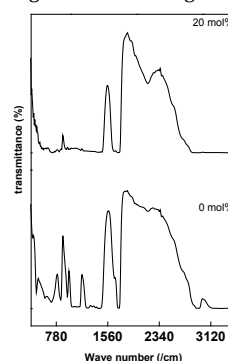


**Figure 1 XRD Spectra**

Figure 1 shows X-ray diffraction spectra of Pure PVA, 85PVA:15NH4F, 85PVA:15NH4F:20DMF polymer electrolytes. The Characteristic peak at  $2\theta=200$  of pure PVA get shifted slightly in the complexes. From the figure, it has been observed that the relative intensity of the peak decreases with increase in broadness. Hodge et. al [8] reported that there is a correlation between the height of the peak and the degree of crystallinity. It indicates the increase in the amorphous nature of the polymer.

#### FTIR analysis:

Figure 2 shows FTIR transmittance spectra of 85PVA: 15 NH4F: xDMF (x=0, 20 mol %). The vibrational peaks at 2925,1729,1663,1037,949 841  $\text{cm}^{-1}$  are corresponding to C-H asymmetric stretching, C=O, C-C, C-OC C-O symmetric stretching and CH<sub>2</sub> rocking vibrations of pure



**Figure 2 FTIR Spectra**

**Table -1 Vibrational peaks of the plasticized Polymer electrolytes**

Pure PVA	Vibrational Peaks of 85PVA:15NH <sub>4</sub> F with addition of DMF		Attributions
	0 mol%	20 mol%	
2925	2924	broad	C-H (asy. S)
2174	2165	2168	$\nu$ (S=O) overtone of DMSO
1729	1722	1713	C=O(S)
1663	1655	1659	C-C (S)
1037	1026	1065	C-OC (S)
949	951	949	CO (sym. S)
841	848	849	CH <sub>2</sub> (r)

PVA get shifted in the complexes as shown in the Table-1 [9-11]. The peak at 2174  $\text{cm}^{-1}$  is attributed to C-S stretching vibration of the solvent DMSO [12]. It indicates the presence of trace of the solvent in the polymer electrolytes. The addition of DMF increases the amorphous nature of the polymer. The change in the frequency is due to the attachment of NH<sub>4</sub><sup>+</sup> (ammonium ion) to hydroxyl (O-H) group and carbonyl group (C=O) of the polymer. The increase of amorphous nature, the presence of new peaks, the shift and changes in the intensity of the peak position of

FTIR spectra of doped samples confirm the complex formation among the polymer, salt and plasticizer.

**Impedance analysis:**

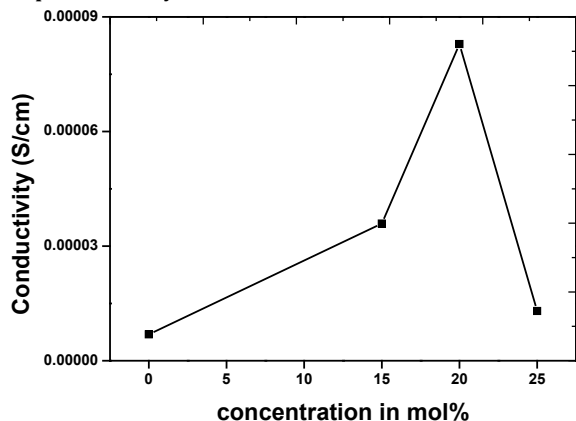


Figure 3 Conductivity vs Concentration of DMF

Table -2 Conductivity of PVA-NH<sub>4</sub>F-DMF polymer electrolytes

Composition	Conductivity at 303K (Scm <sup>-1</sup> )
85PVA:15NH <sub>4</sub> F	6.90 X 10 <sup>-06</sup>
85PVA:15NH <sub>4</sub> F:15DMF	3.59 X 10 <sup>-05</sup>
85PVA:15NH <sub>4</sub> F:20 DMF	8.29 X 10 <sup>-05</sup>
85PVA:15NH <sub>4</sub> F:25 DMF	1.3 X 10 <sup>-05</sup>

Figure 3 shows the room temperature conductivity as a function of concentration of DMF. The ionic conductivity of the polymer electrolytes increases up to 20mol% of DMF. The plasticizer dissociates the salt into ions thereby enhances the number of charge carriers. The ionic conductivity decreases for higher concentration (25mol %) of DMF. It is due to the formation of ionic clusters which impedes the ionic movement. The conductivity value of all electrolytes have shown in the Table-2. The maximum ionic conductivity has been found to be 8.29 x 10<sup>-5</sup> Scm<sup>-1</sup> for 20 mol% DMF added electrolytes.

**Dielectric analysis:**

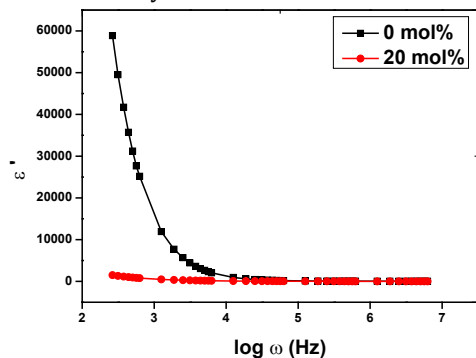


Figure 4 Dielectric Spectra

The frequency dependence of the dielectric constant spectra of 85PVA:15NH<sub>4</sub>F: X DMF (X=0, 20 mol %) electrolyte at 303K is depicted in Figure 4. Sharp rise in the dielectric constant towards low frequency is due to electrode polarization effects [13]. The dielectric constant of the plasticized polymer electrolyte is higher than the unplasticised polymer electrolyte. It owes to be the enhanced charge carrier density at spaced charge accumulation region. As a result there is an increase in the equivalent capacitance. In the high frequency region, the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. Hence the polarization due to the charge accumulation decreases, resulting to the decrease in the value of dielectric constant.

**Dielectric modulus analysis:**

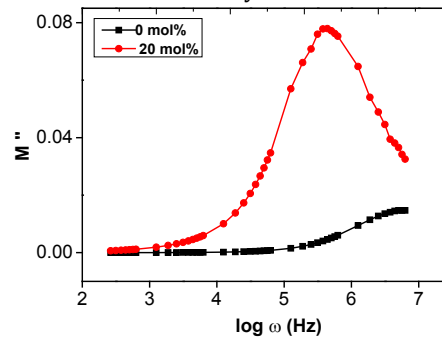


Figure 5 Dielectric Modulus Spectra

The plot between the imaginary part of the dielectric modulus and frequency is shown in

Figure 5. The peak in the high frequency range may be ascribed to the bulk effect. The height of the peak decreases in the plasticized system indicating the plurality of relaxation mechanisms [14]. The long tail in the low frequency region suggesting the contribution of electrode polarization is negligible.

**Conclusions:**

The new plasticized polymer electrolyte comprising of poly (vinyl alcohol), Ammonium fluoride and N, N-Dimethyl formamide have been prepared by solution costing technique. The conductivity, dielectric and modulus analysis of the samples have been studied as a function of frequencies. From XRD analysis, the amorphous nature of the investigated sample has been confirmed. The complex formation among the polymer, salt and plasticizer has been confirmed by FTIR analysis. The low frequency dispersion in the dielectric constant is due to space charge accumulation near the electrode/ electrolyte contact. Higher values of dielectric constant at high temperatures indicate that the sample is super ionic one. The dielectric permittivity decreases with increase in frequencies. It is verifying the fact that the dielectric permittivity is dependent on temperature and frequency for polar polymers [15].

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