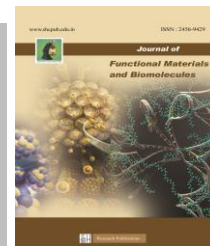




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Characterisation of unplasticised PVP – (H₂N-C₆H₄-CO₂H) based polymer electrolyte

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Abstract

Polymer electrolytes has been prepared with different concentrations of poly vinyl pyrrolidone (PVP) doped with organic salt 3- and 4- amino benzoic acid (3ABA & 4ABA) by solution casting technique using water and DMF (N, N-dimethyl formamide) as a solvent. The polymer electrolyte film has been investigated by various experimental techniques. UV and vibrational analysis reveals that the PVP – ABA in water / DMF (solvent) system forms a charge transfer complex. AC impedance analysis infers that among all the PVP – ABA based polymer electrolyte system, PVP – 15 mol% of 3ABA in DMF system possesses highest conductivity (8.01 X10⁻⁸ S/cm). Also the DMF (solvent) system possesses low activation energy and relaxation time. Wagner's polarization study has confirmed the conduction in the polymer electrolytes is predominantly due to ions. The observed values of ionic transport number for all the polymer electrolyte samples have been found to be in the range of 0.98 - 0.99. Linear sweep voltammetry study has confirmed that DMF (solvent) polymer electrolytes having well electrochemical stability window (range of 2V – 2.5V).

Keywords: Poly vinyl pyrrolidone, Linear sweep voltammetry, amino benzoic acid, relaxation time.

1 Introduction

Polymer electrolytes are currently of interest owing to their advantageous and special mechanical properties, ease of fabrication of thin films of desirable sizes and suitability for electrode–electrolyte contacts in different electrochemical devices such as solid state proton battery¹ [Daries Bella et.al 2014], electrochromic devices² [Elif Sahin et.al 2006], fuel cells³ [Lakshminarayana 2010] etc. Materials needed for this are proton conducting polymer electrolytes with ion conductivities in the range of mS cm⁻¹. Among the polymer host, PVP is an amorphous and vinyl polymer possessing planar and highly polar side groups due to the peptide bond in the lactam ring. In order to develop high ion conducting polymer electrolyte, polyvinyl pyrrolidone (PVP) has been suggested as host polymer, because of it being an amorphous polymer which can permit faster ionic mobility compared to other semi-crystalline polymers. Carbonyl group present in PVP act as a proton acceptor. Due to the presence of carbonyl group (C=O) in

the side chains of PVP, it complexes with various inorganic salts and provides free mobile ions in the system.

The conductivity of pure PVP is ~10⁻¹³ S/cm at room temperature⁴ [Jaipal Reddy et.al 2000] and its value increases sharply to ~10⁻⁹ - 10⁻⁴ by complexing with inorganic⁵ [Ramya et.al 2008] and organic salts⁶ [Hiromori et.al 1997]. PVP deserves a special attention among the conjugated polymers because of its good environmental stability, easy processability and moderate electrical conductivity and also the proton conducting polymer electrolytes based on PVP with organic salts are scarce.

Amino benzoic acid isomers are capable of forming a conducting polymer^{7,8} [Ida Mav-Golez et.al 2011, Belmokhtar et.al 2012]. Coating of the electrodes with polymer of amino benzoic acid isomers films has been used frequently to improve their properties for a wide variety of applications⁹ [Palle Swapna Rao et.al 2003] because of its high conductivity and thermal stability.

DMF makes an effective solvent for salts, gases, and compounds with high molecular weight. It has several characteristics which aid in its versatility as a solvent. DMF act as polar solvent for few polymer electrolytes to enhance the ionic conductivity¹⁰⁻¹⁴ [Patra et.al 2005, Baskaran et.al 2004, Watanabe et al 1982, Choi et al 2004, Shmukler et al 2012].

In the present work, the proton conducting polymer electrolytes, PVP-ABA isomers have been studied as a function of the ionic dopant, ABA isomers. The polymer electrolytes have been prepared with water and DMF as solvent and studied by various characterization techniques such as Fourier Transform Infrared spectroscopy, UV – Visible spectroscopy and AC Impedance spectroscopy.

2 Experimental

Poly vinyl Pyrrolidone K₉₀ (Sd fine – chem. Limited, India.), 3- amino benzoic acid (Himedia) - 97% pure, 4-amino benzoic acid (Avra) – 98% pure, DMF (Merck) – 99.8% pure were used as received. The polymer PVP and the salt

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amino benzoic acid isomers were dissolved in double distilled water or DMF (solvent) separately. All the solutions were mixed together and stirred continuously using magnetic stirrer in order to obtain a homogeneous mixture. Thus the obtained homogenous slurry was degassed to remove air bubbles for about five minutes and the slurry was poured on a well cleaned poly propylene dish. The casted slurry was allowed to evaporate at room temperature. Finally, the polymer electrolyte films were stored in highly evacuated desiccators to avoid the moisture absorption. The dried film (free standing film) has been subjected for various experimental characterizations.

The complex impedance measurement was carried out using a computer-controlled electrochemical work station (Biologic Science Instrument Model – SP 300) in the frequency range of 100 Hz - 5MHz with an applied voltage of 100 mV at different temperatures. The FT-IR spectra of the samples were recorded by using JASCO FT/IR-4100. The UV-Visible spectra were recorded in the wave length range of 200-800 nm using SHIMADZU (UV-2600) UV-Visible spectrophotometer.

Nomenclature of the Systems

Table 1. Nomenclature of PVP – ABA (solvent - water) polymer electrolyte system

PVP-3ABA	PVP:3ABA (mol%) ratio	PVP- 4ABA	PVP:4ABA (mol%) ratio
P3A1	99:01	P4A1	99:01
P3A3	97:03	P4A3	97:03
P3A5	95:05	P4A5	95:05
P3A7	93:07	P4A7	93:07
P3A10	90 :10	P4A10	90 :10

Table 2. Nomenclature of PVP – ABA (solvent - DMF) polymer electrolyte system

PVP-3ABA	PVP:3ABA (mol%) ratio	PVP- 4ABA	PVP:4ABA (mol%) ratio
(P3A5)D	95:05	(P4A5)D	95:05
(P3A10)D	90:10	(P4A10)D	90:10
(P3A15)D	85:15	(P4A15)D	85:15
(P3A20)D	80:20	(P4A20)D	80:20
(P3A25)D	75:25	(P4A25)D	75:25

3 Results and Discussion

3.1. FTIR Spectral Studies:

FT – IR spectra were recorded for PVP complexed with ABA isomers and analysed on the basis of literature data [15-19] [Stalin et.al 2006, Swisłocka et.al 2005, Benyoucef et.al 2005, Palle Swapna Rao et.al 2002 & 2003, Rajeswari et.al 2011].

3.1.1. PVP – ABA in water system

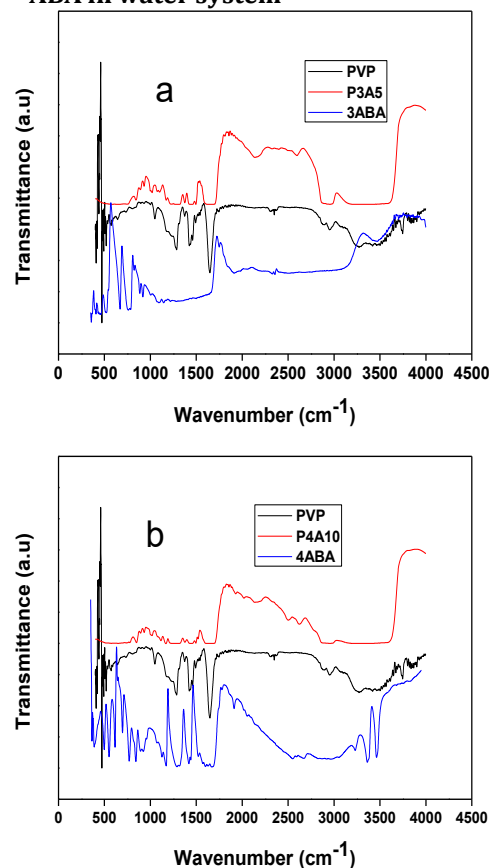


Fig.1. IR spectra of polymer electrolyte (a) PVP – 3ABA (b) PVP – 4ABA in water system

From the Figure 1(a) and (b), the presence of cyclic amide group and the C=O stretching frequency of pure PVP 1649 cm⁻¹ is red shifted to 1666 cm⁻¹ in the polymer electrolyte system. In pure 3ABA, the peaks at 1152 cm⁻¹ & 1500 cm⁻¹ are attributed to asymmetric in plane bending of NH₂ and asymmetric stretching mode of COO⁻. The former peaks shifted to higher wave number (red shift) and later shifted to lower wave number (blue shift) in the PVP – 3ABA polymer electrolyte system. The peaks found at 551 cm⁻¹ and 618 cm⁻¹ were responsible for out of plane bending of NH₂ and the stretching vibrational mode of C=O of pure 4ABA had been found blue shifted to 526 cm⁻¹ and red shifted to 648 cm⁻¹ in the P4A10 polymer electrolyte system. The characteristics peaks of CH₂ wagging (1425 cm⁻¹) and ring C-N stretching coupled with ring CH₂ wagging (1283 cm⁻¹) of pure PVP has been shifted to higher wave number side i.e. 1433 cm⁻¹ and 1261 cm⁻¹ respectively in the P4A10 polymer electrolyte system.

3.1.2. PVP –ABA in DMF system

The band at 1649 cm⁻¹ is attributed to C=O stretching of cyclic amide group present in pure PVP which is displaced to higher wave number 1653 cm⁻¹ in polymer electrolyte system. Aliphatic C-H stretching band at 2948 cm⁻¹ for pure PVP is shifted to higher wave number in the (P3A15)D system shown in Figure 2(a). The vibrational

modes observed at 761 cm^{-1} and 1500 cm^{-1} is ascribed for out of plane bending COO^- and asymmetric stretching of COO^- of pure 3ABA respectively, which are displaced to blue shift 754 cm^{-1} and 1492 cm^{-1} respectively in the salt doped polymer matrix. The above results confirm the complex formation between the polymer matrix (PVP) and the 3ABA salt.

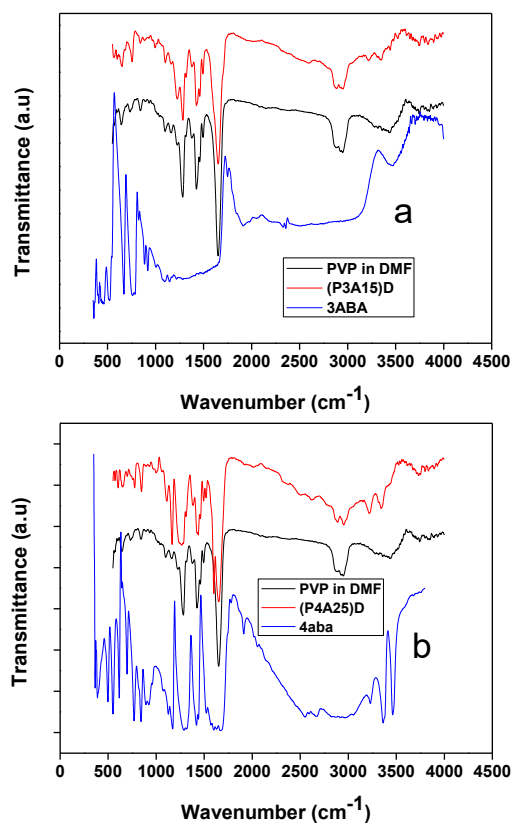


Fig. 2. IR spectra of polymer electrolyte (a) PVP – 3ABA (b) PVP – 4ABA in DMF system

From the Fig. 2(b), the bands observed at 839 cm^{-1} , 1376 cm^{-1} , 1649 cm^{-1} , 2948 cm^{-1} and 3430 cm^{-1} , are responsible for CH_2 Bending, C-H bending, cyclic amide group C=O Stretching, aliphatic C-H stretching and O-H Stretching and NH^+ Stretching of pure PVP respectively, which have been shifted to 846 cm^{-1} , 1383 cm^{-1} , 1651 cm^{-1} , 2952 cm^{-1} and 3341 cm^{-1} respectively in the 4ABA salt doped PVP polymer in DMF solvent system. The characteristic peaks for the out of plane bending mode of NH_2 , stretching mode of C=O and in plane bending mode of N-H in pure 4ABA have been observed at 551 cm^{-1} , 618 cm^{-1} and 1624 cm^{-1} shifted to 571 cm^{-1} , 652 cm^{-1} and 1600 cm^{-1} respectively in (P4A25)D polymer electrolyte system.

3.2. UV – Visible Analysis

The band observed at 270 nm is attributed to $\pi - \pi^*$ transition of PVP, which comes from unsaturated bonds, mainly C=O and/or C=C. The absorption spectrum of ABA exhibits a band at 320 nm and a more intense band at 270 nm ($\pi - \pi^*$) reported¹⁸ [Palle et.al 2002]. From the Fig. 3, it is observed that the PVP – ABA in water system, the ($\pi - \pi^*$) transition band are shifted like in P3A5 system to

352nm and P4A10 system to 316 nm, which are responsible for n - π^* transition of C=O bond. Hence it is concluded that the PVP – ABA complexed through the charge transfer.

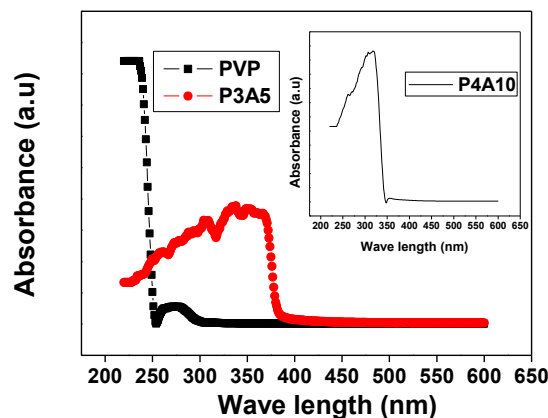


Fig. 3. Absorbance spectra of PVP – ABA in water system

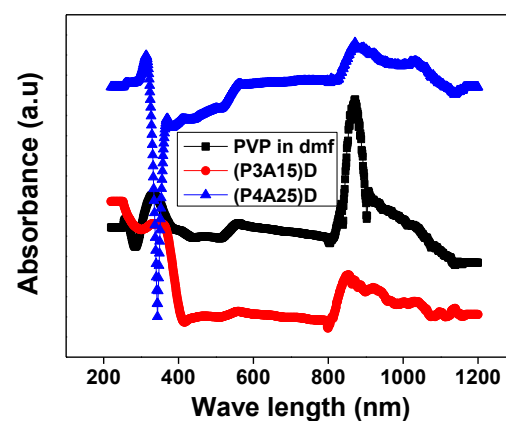


Fig. 4. Absorbance spectra of PVP – ABA in water system

In PVP – ABA in DMF system, the observed bands shown in Fig. 4 are

1. (P3A15)D – 253 nm, 358 nm, 559 nm, 855 nm
2. (P4A25)D – 258 nm, 317 nm, 559 nm, 872 nm

The band around at 250 nm is responsible for conjugated double bonds of PVP. In PVP – 3ABA, (P3A15)D, the peak at 358 nm has been attributed to ($\pi - \pi^*$) band gap absorption. In PVP – 4ABA, (P4A25)D the absorption around 317 nm has been ascribed to n - π^* transition of C=O bond. A strong absorption band at around 550 nm has been attributed to a charge transfer between a quinoid ring and the adjacent imine – phenyl amine unit [Ekarat et.al 2009]. The band at around 850 is due to the high wave length polaron transition. The intensity of the absorbance is depends on the effect of isomers of ABA and salt concentration.

The UV analysis infers that the charge transfer complex formation takes place between PVP and ABA salt in both water and DMF solvent system. In both the systems, the band observed depended on the position of the car-

boxylic acid group in the salt. In 3ABA doped polymer system the bands observed around 350 nm was found to be responsible for $\pi - \pi^*$ transition of C=O bond, whereas in 4ABA doped polymer system $n - \pi^*$ transition of C=O bond observed. Solvent interaction was also confirmed by this analysis. In DMF system charge transfer takes place very effectively compared to water system.

3.3. AC Impedance Analysis

3.3.1. Impedance Spectra Analysis

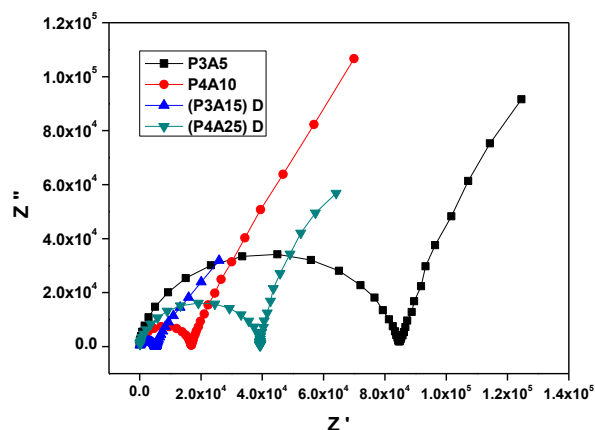


Fig. 5. Impedance plot of PVP – ABA based polymer electrolytes at 318K

The impedance response of all PVP – ABA system in the present study shows a semicircle in the higher frequency region followed by spike in the lower frequency region as shown in Fig. 5. This spike indicates the capacitive character of all the PVP – ABA system at lower frequency range, whereas the high frequency semicircle shows the bulk properties of the electrolytes and interfacial charge transfer processes [Tripathi et.al 2006].

3.3.2. Concentration dependent conductivity

The ionic conductivity as a function of ABA salt concentration has been shown in Fig.6. The dependence of ionic conductivity on the salt concentration gives the information on the specific interaction between the salt and the polymer matrix. The conductivity varies with the wide range of factors, such as cation and anion types, salt concentration, temperature, etc.

The magnitude of the ionic conductivity is given as,

$$\sigma = n_i q_i \mu_i$$

The conductivity mainly depends on number of charge carriers (n_i), charge of the mobile species (q_i) and mobility of the charge carriers (μ_i). In PVP – 3ABA in water and DMF system, the ionic conductivity increases with increase in salt concentration due to the availability of free ions and then decreases at higher salt concentration. The decrease in conductivity at higher salt concentration is due to formation of ion aggregates that are electrically neutral [Kumudu Perera et.al 2006].

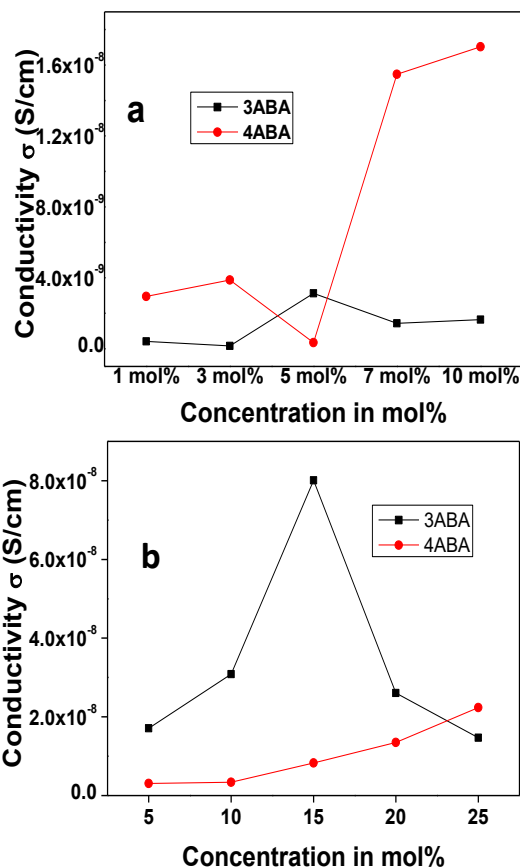


Fig. 6. Variation of conductivity with salt concentration at a temperature of 308K for PVP – ABA in a) water and b) DMF system.

In PVP – 4ABA in water system, the initial increase in conductivity is due to the availability of free mobile ions and then decrease in conductivity due to the formation of ion pairs which do not take part in conduction and then again increases. In PVP – 4ABA in DMF system, the ionic conductivity increases with increase in salt concentration and the decreases. The higher the number of charge carriers and higher the mobility, higher will be the conductivity.

Table 3. Highest ionic conductivity of PVP – ABA based polymer electrolytes

Sample code	Conductivity (σ) ($S\ cm^{-1}$) at 308K	Conductivity (σ) ($S\ cm^{-1}$) at 338K
Pure PVP in water	6.03×10^{-10}	1.56×10^{-8}
Pure PVP in DMF	7.32×10^{-9}	1.60×10^{-6}
P3A5	3.13×10^{-9}	1.63×10^{-6}
P4A10	1.7×10^{-8}	9.13×10^{-6}
(P3A15)D	8.01×10^{-8}	4.1×10^{-5}
(P4A25)D	2.24×10^{-8}	2.56×10^{-5}

3.3.3. Temperature Dependent Ionic Conductivity

Temperature dependent conductivity of the polymer complexes PVP – ABA in water and DMF systems for different salt concentrations have been shown in Fig. 7. The activation energy has been tabulated in Table 4. The experimental data have been fitted with Arrhenius equation by using least squares analysis; a good straight line fit (Regression > 0.9) has been obtained for few polymer electrolytes whereas remaining sample shows bad fit. The good straight line fit indicates that the sample obeys Arrhenius behaviour and bad fit indicates that the sample may follow free volume theory.

The activation energy, was calculated from the fitting parameter according to the Arrhenius model,

$$\sigma = (\sigma_0 / T) \exp (-E_a/kT)$$

where E_a is the activation energy for hopping and T is the absolute temperature.

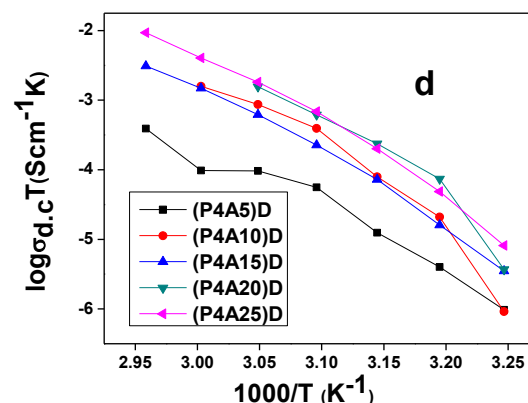
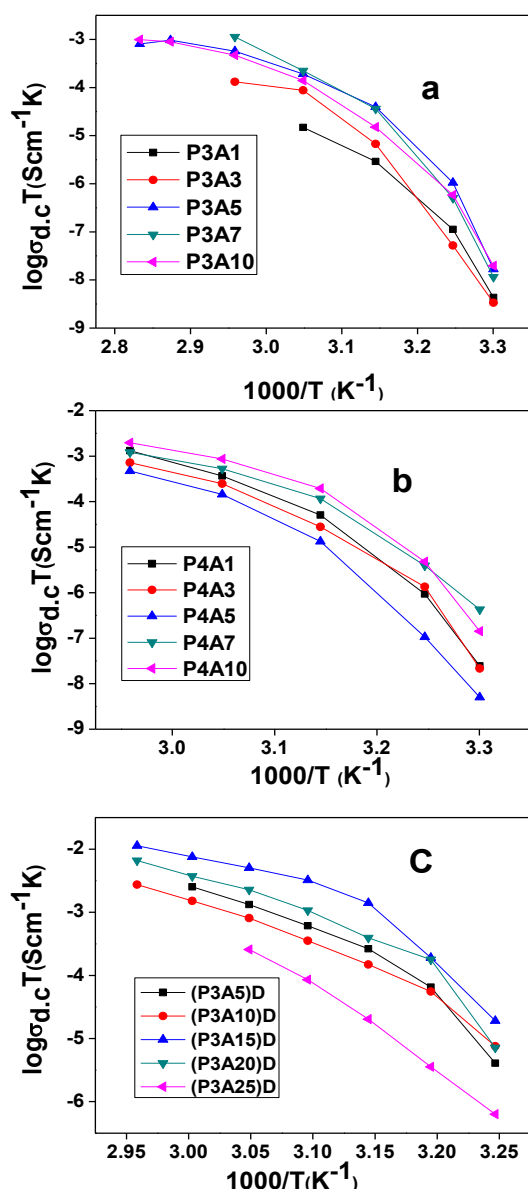


Fig 7. a, b, c and d shows the variation of dc conductivity (σ_{dc}) with inverse of temperatures for PVP - ABA in water and DMF based polymer electrolytes respectively.

The ionic conductivity is enhanced with increasing temperature, when the temperature is increased, the mobility of polymer chain and the fraction of free volume in the polymer electrolyte system increases. This facilitates the transitional motion of ions. The segmental motion either allows the ions to hop from one site to other site, or it provide pathway for ions to move, which leads to an increase in ionic conductivity of the polymer electrolyte.

Table 4. Activation energy of PVP – ABA based polymer electrolyte

System	E_a	Regression
P3A5	0.79	0.81
P4A10	1.01	0.86
(P3A15)	0.78	0.86
(P4A25)	0.90	0.98

3.3.4. Dissipation Factor Analysis

The relaxation parameters of the complexes can be obtained from the study of $\tan \delta$ as a function of frequency. Figure 8 shows the variation of $\tan \delta$ as a function of frequency for highest conductivity of PVP – ABA polymer electrolytes at different temperature.

For maximum dielectric loss at a particular temperature, the absorption peak can be described by the relation,

$$\omega\tau = 1 \quad \text{-----} \quad 5.4$$

where τ is the relaxation time and ω is the angular frequency of the applied signal.

The calculated relaxation parameters for all highest conductivity PVP - ABA systems in water and DMF have been tabulated in Table 5 and 6. The low relaxation time has been obtained for (P4A25)D polymeric system, the relaxation time increases and hence the conductivity decreases.

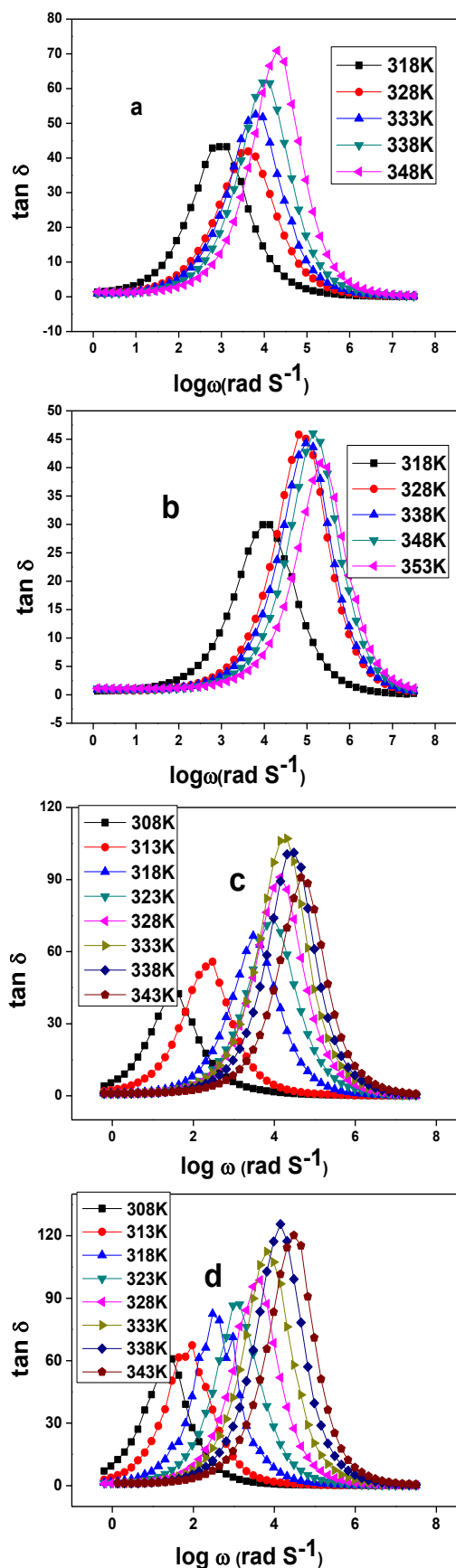


Fig 8. Log ω vs $\tan \delta$ of (a) P3A5 (b) P4A10 (c) (P3A15)D (d) (P4A25)D

At each temperature, $\tan \delta$ has been found to increase with increasing frequency and attained a maximum value ($\tan \delta_{\max}$) then decrease with further increase of frequency. At low frequencies, the dipoles have been able to keep in phase with the change of electric field and hence the power losses were low.

Table 5. Relaxation time for PVP – ABA based polymer electrolytes in water with various temperatures

Temperature in K	Relaxation time (τ) (sec)	
	P3A5	P4A10
318	1.13 X	9.70×10^{-5}
328	2.67 X	1.35×10^{-5}
338	1.02 X	1.09×10^{-5}
348	5.37 X	7.09×10^{-6}
353		4.71×10^{-6}

As the frequency was increased the dipole reorientation could not be completed in the time available and the dipole became out of phase with the electric field and hence, the power loss is maximum. The internal friction leads to the generation of heat. Furthermore, the increase of frequency resulted in no time for substantial dipole movement, so the power losses were reduced. It also been observed that the maximum of $\tan \delta$ decreased with increase of temperature. This is attributed to increase in mobility of the chains at higher temperature, resulting in low power loss. The position of loss tangent peak shifts to higher frequencies with increasing temperature.

Table 6. Relaxation time for PVP – ABA based polymer electrolytes in DMF with various temperatures

Temperature in K	Relaxation time (τ) (sec) $\times 10^{-3}$	
	(P3A15)D	(P4A25)D
308	4.66	13.6
313	0.31	2.73
318	0.12	0.82
323	0.077	0.29
328	0.062	0.15
333	0.039	0.77

3.4. Transference Number Measurements

From the transport number analysis reveals that the predominantly the ionic conduction takes place in liquid electrolyte. Among the eight polymer electrolyte systems, PVP – ABA in DMF solvent system the ionic transport number are 0.86 and 0.74 for PVP – 3ABA and PVP – 4ABA respectively. This may be due to the small amount of electronic conduction. But PVP – ABA in water based polymer electrolyte, the transference number is 0.99. This shows the proof for the majority charge carriers in the prepared

PVP – ABA based proton conducting polymer electrolyte are ions.

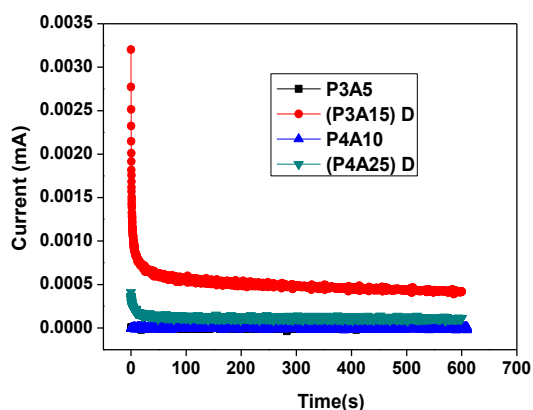


Fig. 9. Transference Number for PVP – ABA polymer electrolyte system

The dc polarization technique is utilized to determine the ionic transport number (t_{ion}) for the prepared proton conducting PVP – ABA based solid polymer electrolytes.

Table 7. Transference Number for PVP – ABA polymer electrolyte systems

S.No	System	Transference Number
1	P3A5	0.99
2	P4A10	0.99
3	(P3A15)D	0.86
4	(P4A25)D	0.74

3.5. Linear Sweep voltammetry:

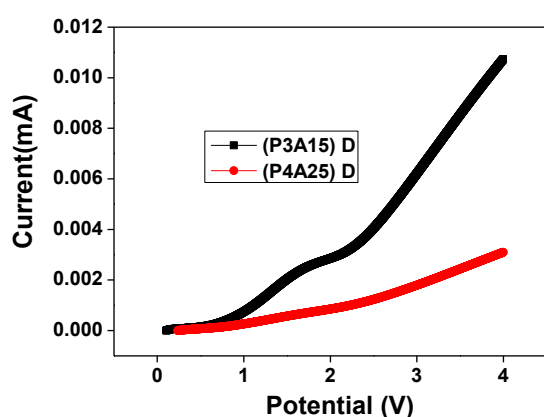


Fig. 10. Linear sweep voltammetry of PVP – ABA in DMF polymer electrolyte system.

4. Summary and Conclusion:

Solvent free unplasticised solid polymer electrolytes based on PVP complexed with different concentration of ionic dopant as 3- & 4 - amino benzoic acid in different solvent such as water and DMF has been prepared by solution casting technique. These polymer electrolytes have been characterized by different experimental techniques.

The complex formation between the polymer and the dissociated salt has been confirmed from FTIR and UV spectral analysis. The results obtained from the UV and FTIR analysis of polymer – salt complexes are given below.

The unplasticised PVP – ABA in water / DMF (solvent) system forms a charge transfer complex, which was confirmed by the shifting of ($\pi - \pi^*$) transition band of pure PVP (270nm) in the salt doped polymer system. In DMF system, the new bands were observed for n - π^* transition of C=O bond and high wave length polaron transition at around 350 nm and 550 nm respectively. The intensity of the absorbance is depending on the effect of isomers of ABA and salt concentration.

The characteristic vibrational modes of CH₂ bending (839 cm⁻¹), cyclic amide group C=O stretching (1649 cm⁻¹) and O-H stretching and NH⁺ stretching (3430 cm⁻¹) of polymer PVP have been shifted to higher and lower number side in the case of ABA doped PVP based unplasticised polymer electrolyte system. Also the various characteristic bands of amino benzoic acid isomers also shifted, which proves the complex formation. From the above analysis reveals that the proton accepting carbonyl group in the PVP involved the complex formation.

AC impedance studies have been used to investigate the conductivity and dielectric relaxation of the polymer electrolytes. Pure PVP in water and in DMF, the conductivity values are in the order of 10⁻¹⁰ S/cm and 10⁻⁹ S/cm respectively. By adding the ABA salt the conductivity increased in to 10⁻⁸ S/cm in unplasticised system. In DMF solvent possesses highest conductivity compared to water solvent system. Among all the PVP – ABA based polymer electrolyte system, PVP – 15 mol% of 3ABA in DMF ((P3A15)D) system possesses highest conductivity (8.01 X10⁻⁸ S/cm). Also the DMF (solvent) system possesses low activation energy and relaxation time.

The observed values of ionic transport number for all the unplasticised polymer electrolyte samples have been found to be in the range of 0.74 - 0.99. Linear sweep voltammetry study has confirmed that DMF (solvent) polymer electrolytes having well electrochemical stability window (range of 2V – 2.6V) and it is also suitable for electrochemical device fabrications.

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