

Preparation and Characterization of Poly(1-vinylpyrrolidone-co-vinyl acetate)/Poly(methyl methacrylate) Polymer Electrolyte based on TPAI and KI

M. K. Jawad^{1*}, S.R. Majid², E.A.Al-Ajaj¹, M. H. Suhail¹

1. Baghdad University, College of Science, Physics Department

2. University of Malaya, Faculty of Science, Department of Physics

* E-mail of the corresponding author: mohamedkadhom@yahoo.com

Abstract

Polymer electrolytes are promising materials for electrochemical device applications, such as, high energy density rechargeable batteries, supercapacitors, fuel cells, electrochromic displays, etc. Polymer blend electrolytes based on (PVP-co-VAc) and (PMMA) with different weight ratio of Tetra propyl ammonium iodide (TPAI) and Potassium iodide (KI), salts using DMSO as solvent. The gel electrolytes were prepared by solution cast technique. The ionic conductivity values increase with increasing KI salt weight ratio up to 30% beyond which the conductivity values decrease and the highest ambient temperature conductivity has been found to be 0.0035 S cm^{-1} , whereas for electrolyte with TPAI, the conductivity increase up to 50% with $0.00139 \text{ S cm}^{-1}$. FTIR data is used in order to study characterization of chemical bonds, polymer microstructure, chain conformation. Dielectric constant at lower frequency region, is observed to decrease with increasing frequency and level off at higher frequency region.

Keywords: Gel electrolyte, Electrochemical Impedance Spectroscopy, Poly(1-vinylpyrrolidone-co-vinyl acetate), poly(methyl methacrylate), FTIR.

1. Introduction

The term 'polymer gel electrolyte' includes three terms i.e. polymer, gel and electrolyte. Polymers are substances of high molecular weight formed by union of small molecular substances known as monomers held together by covalent bonds. Gels are substances which have jelly like structures. In the steady state it does not flow. They are formed from plasticizers, a polymer and a salt[1]. The quasi-solid state, or gel state, is a particular state of matter, neither liquid nor solid, or conversely including high ionic conductivity and excellent interfacial contact property. These unique characteristics of quasi-solid-state electrolytes have been actively developed as highly conductive electrolyte materials for Dye Sensitized Solar Cells(DSSCs), lithium secondary batteries, and fuel cells [2,3]. Polymer electrolytes have been developed in order to replace liquid electrolytes. Though they possess suitable mechanical strength and eliminate the problem of leakage, yet low ionic conductivity limits their applicability. Generally, a quasi-solid-state electrolyte is defined as a system which consists of a polymer network (polymer host) swollen with liquid electrolytes [4]. They are very attractive materials to be used in applications such as batteries, photo electrochemical (PEC) solar cells, electro-chromic devices, super capacitors and fuel cells [5]. The mechanism for ionic motion in polymer electrolytes results from a solvation– desolvation process along the chains that occurs predominantly in the amorphous polymer phase. Since the ionic motion is strictly correlated with the segmental motion of the polymer chains, the ionic conductivity increases with increasing chain mobility. The ionic conductivity is also a function of the number of charge carriers in the polymer matrix[6]. With respect to the specific application the electrolyte should comply with following requirements; (a) sufficient ion conductivity (between 10^{-4} and $10^{-7} \text{ S.cm}^{-1}$), (b) very low electron conductivity (preferably below $10^{-12} \text{ S.cm}^{-1}$), (c) high electrochemical and mechanical stability, (d) good optical properties (persistence against long-term UV irradiation, transparency/translucency). [7]. Polymer blend is one of the methods that have provided new desirable polymeric materials. Polymer-salt complexes are normally formed by dissolving an amount of salt with the host polymer in the appropriate solvent to influence the ionic conductivity based on the host polymer[8]. Several polymers have been used as polymer matrices for ionic liquid electrolytes such as poly(ethylene oxide), poly(acrylonitrile), poly-(methyl methacrylate), poly(vinylidene fluoride), poly(1-vinyl pyrrolidone), poly(N-methyl acrylamide)and poly(1-vinyl pyrrolidone-co-vinyl acetate), as well as ionogel. The ionic conductivities at ambient temperature for such gel polymer electrolytes reach values above $10^{-3} \text{ S cm}^{-1}$ [9]. In the present work, a new plasticized polymer electrolyte composed of the (PVP-co-VAc) with PMMA) blend as the host polymer containing TPAI and KI iodide salts has been synthesized and characterized. Salts concentration on conductivity. The variation of ionic conductivity of polymer gel electrolytes with temperature has also been studied. Fourier transform infrared (FTIR) studies have been carried out to check the interaction, formation, and dissociation of ion aggregates in the electrolytes.

2. Experimental Section

2.1 Raw Materials

Poly(1-vinylpyrrolidone-co-vinyl acetate) [PVP-co-VAc] with an average molecular weight of 5,0000 , poly(methyl meth acryl ate) (PMMA) with an average molecular weight of 996,000 , The solvent used was Dimethyl sulfoxide (DMSO) with molecular weight of 78.13, Tetra propyl ammonium iodide (TPAI) (Pr4NI) with molecular weight of 313.26, and Potassium iodide (KI) with molecular weight of 166, all materials purchased from Sigma Aldrich were used as received .

2.2 Preparation of electrolytes

Two kinds of polymer electrolytes were prepared with two types of salts at different weight ratio as follows. First we dissolve the salt (TPAI or KI) in 2 ml of DMSO solvent in a glass bottle by using stirrer and heat to (70 °C) ,and then added the two polymers; (PVP-co-VAc) and PMMA one by one with weight ratio 2:1 , the mixture was stirred for 1 h until became gel . The mixture was allowed to cool down to room temperature. The gel electrolytes were prepared and studied under controlled temperature and humidity conditions (25°C and RH~50%). The components and states of all electrolytes are listed in Table1.

Table 1: Two types of polymer electrolyte with different salt weight ratio .

Electrolyte type	Salt%0	Salt %7	Salt %15	Salt %22.5	Salt %30	Salt %37.5	Salt %50
Electrolyte A [(PVP-co-VAc)+PMMA] +TPAI	A0	A1	A2	A3	A4	A5	A6
Electrolyte B [(PVP-co-VAc) +PMMA]+ KI	B0	B1	B2	B3	B4	B5	B6

2.3 FTIR studies

The FTIR spectrum is a powerful tool in polymer composite chemistry in order to know the specific chemistries and orientation of the structure [10]. FTIR measurements were performed on a Nicolet-iS10-IR Thermo equipped with a diamond ATR crystal. FTIR spectra at a nominal resolution of 4 cm⁻¹ were recorded in the range of 400–4000cm⁻¹.

2.4 Ionic conductivity measurements

The electrochemical impedance spectroscopy (EIS) measurements were done by using a computer interfaced HIOKI 3532-50 LCR Hi TESTER BU CH1 Glass Oven B-585 , the frequency range between 50 Hz and 1MHz. The sample was placed in a poly(tetrafluoroethylene) spacer ring compressed between two stainless steel electrodes and sealed in a testing cell. The EIS measured at over temperatures range (273-373 K). The Fig. 1 show the Nyquist plot for polymer electrolyte, from the complex impedance plot, the bulk resistance (R_b) was determined and the conductivity was calculated by the following equation (1):

$$\sigma = t / AR_b \quad (1)$$

Where t is thickness for the sample , A is the area of the electrode and R_b is the bulk resistance of the gel electrolyte measured by impedance analyzer at 0.1MHz..After calculate the conductivity(σ) of the two electrolytes, and plotting (Log σ) vs T/1000, σ vs TPAI, and σ vs KI ,weight ratio . The dielectric constant (ε_r)values were calculated using the following equation (2) :

$$\epsilon_r = Z_i / \omega C_o [Z_r^2 + Z_i^2] \quad (2)$$

where ω is the angular frequency(ω=2πf) being the frequency in Hertz (Hz), C_o is vacuum capacitance and Z_r and Z_i are real and imaginary parts of impedance .

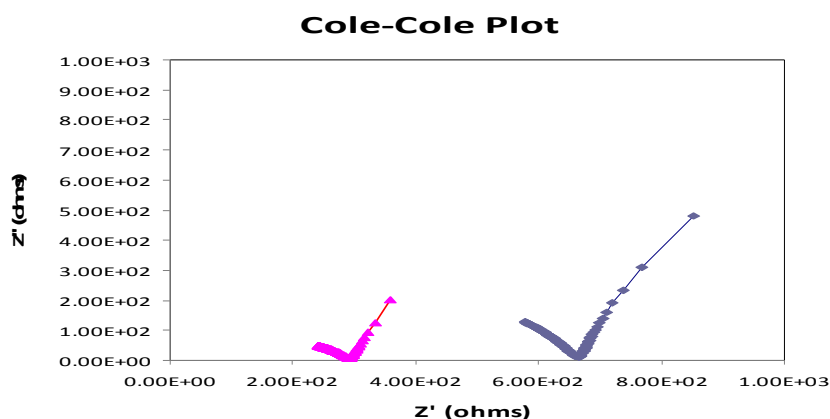


Fig.1: Cole–Cole plot for polymer electrolyte (PVP-co-VAc)+PMMA with TPAI and KI at 273K.

3. Results and discussions

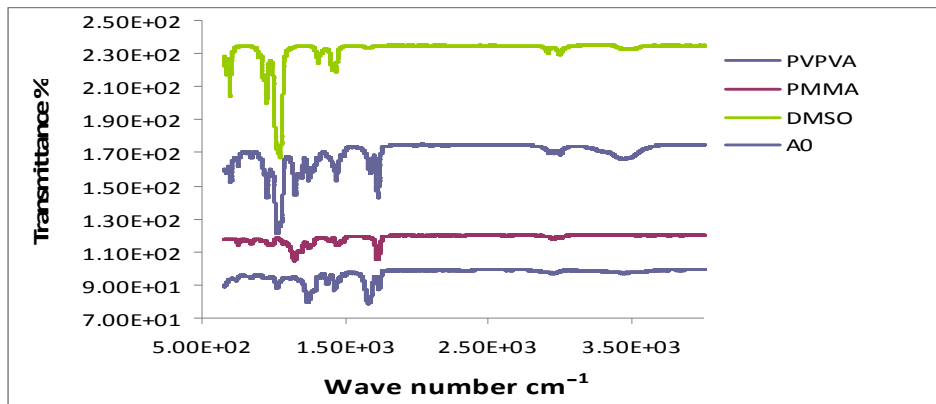
3.1 FTIR Results

FTIR spectroscopy is an important technique in the investigation of polymers electrolytes structure, the infrared of materials vary depending on their compositions and may be able to show the occurrence of complexation and interaction between the various constituents. FTIR for pure components and for the types of electrolytes listed in table 1, are shown in Figs.(2-4) ,FTIR spectra were obtained in the transmittance mode. The main absorption bands for (PVP-co-VAc) were associated with O-H stretching at $3600-3000\text{ cm}^{-1}$, C-H stretching at $3000-2800\text{ cm}^{-1}$ and at 1371.09 cm^{-1} , C=O carbonyl groups from (PVP-co-VAc) at 1731.83 cm^{-1} and PVP at 1662 cm^{-1} and C-O-C stretching at $1300-1000\text{ cm}^{-1}$. On the other hand, the plain PVP sample exhibits an absorption peak with its maximum at 1687 cm^{-1} , as shown in Fig.(2-a).The FTIR spectrum of PMMA in Fig. (2-a) indicates the details of functional groups present in the synthesized PMMA. Very strong and sharp intense peak appeared at 1722.85 cm^{-1} due to the presence of ester carbonyl group stretching vibration, C=O stretching [11]. The broad peak ranging from $1260-1000\text{ cm}^{-1}$ can be explained owing by the C-O (ester bond) stretching vibration and a peak at 1189.89 cm^{-1} is assigned to -O-CH₃ stretching vibrations. The broad peak ranging from $4000-2900\text{ cm}^{-1}$ is attributed to the presence of stretching vibration [12,13] , while peaks at 749.98 cm^{-1} and 841.74 cm^{-1} are attributed to the puckering vibration of PMMA chains and deformation vibrations of O-C-O of PMMA, respectively. Peak at 985 cm^{-1} represented C-H bending wagging vibration. It should be noted that there is no peak near $1680-1640\text{ cm}^{-1}$ range ,which confirms that all methyl methacrylate (MMA) monomer is converted into PMMA polymer .This data confirms that the polymerization of monomer has been accomplished successfully [14] .

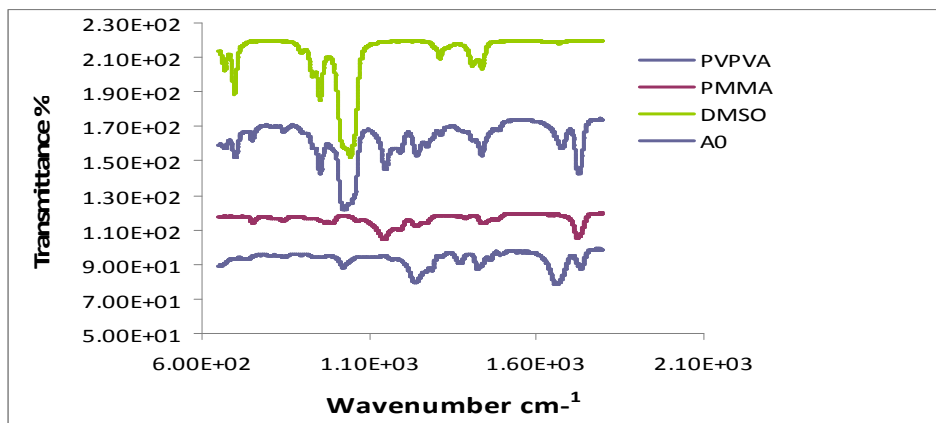
For the blended polymers (PVP-co-VAc)+ PMMA without salt the FTIR results Fig.(2-a), shows the shift in peaks position at 1435.52 cm^{-1} due to O-H stretching , 2994.98 cm^{-1} as enhancement of dimethyl sulfoxide (DMSO) C-H stretching , whereas peak at 1725.74 cm^{-1} which is due to stretching vibration of C=O carbonyl groups still within limit of allowed change , and the peak ranging from $1300-1000\text{ cm}^{-1}$ has shifted due to stretching of C-O of ester bond as shown in Fig.(2-b). When the (PVP-co-VAc) host polymer is blended with PMMA, this absorption signal, which is assigned to the stretching vibration of a C=O group in the pyrrolidone ring, tends to shift to a position of somewhat lower frequency (Miscibility of cellulose acetate with vinyl polymers) . The broadening of the band associated with the hydroxyl group indicates the formation of intermolecular hydrogen bonds. At the same time, a small shift of the carbonyl stretch of (PVP-co-VAc) occurred in the blends in relation to the pure copolymer. These shift also suggest the formation of intermolecular hydrogen bonding, similarly to the results reported for blends of (PVP-co-VAc)+ PMMA [14].

Fig.2 show FTIR results for electrolyte A which content different weight percent of Tetra propyl -ammonium iodide (TPAI) vary from (0-50%) , complexation may shift the polymer cage peak frequencies. FTIR would be sensitive both in situations where complexation has occurred in crystalline or amorphous phase [13] . The relative intensity of the peak at 3435.52 cm^{-1} for polymer blend without TPAI increases with increasing TPAI content , especially for A2,A4 and A6 samples .These observations, that the broad peak becomes narrower after the addition of TPAI salt a remarkable broadening of the PMMA bands when the polymer blend is added as seen in the figures earlier indicates a significant broadening degree of interaction between the polymer host and the PMMA molecules. This emphasis the complexation between the (PVP-co-VAc) -PMMA blends and TPAI . To recognize the nature of the interactions in the polymer blend salt (TPAI), we choose the band at 1722.85 cm^{-1} ,

Fig.(3-b) which is due to the stretching vibration of the C=O group in PMMA as a characteristic peak of PMMA. This band shows a little shift to the higher frequencies and has become broader in both of the polymer blend without TPAI and with . These changes can be ascribed by the interaction between PMMA and (PVP-co-VAc) chains.

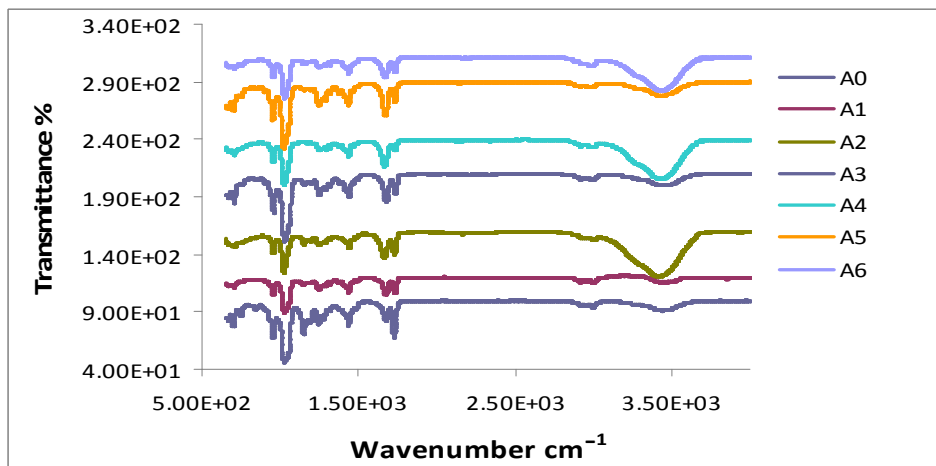


(a)

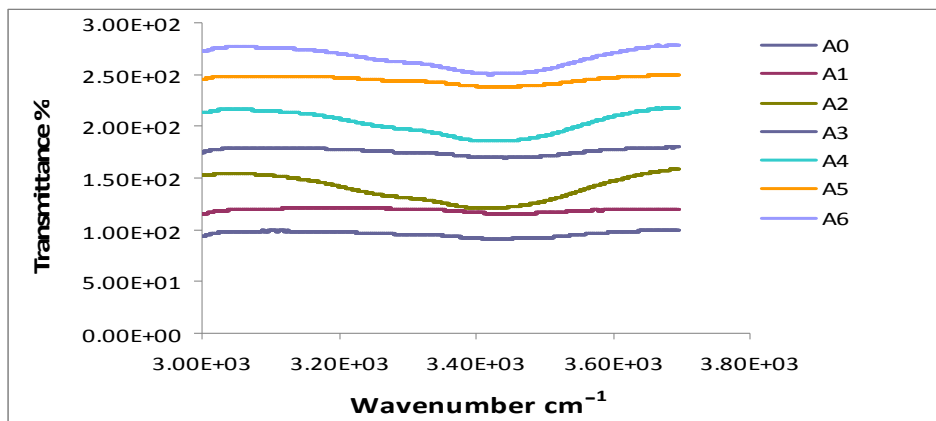


(b)

Fig.2: FTIR for (PVP-co-VAc), PMMA,DMSO and Polymer blend A0,(a)for wavenumber range 400-4000 cm^{-1} , (b) 600-1700 cm^{-1} .



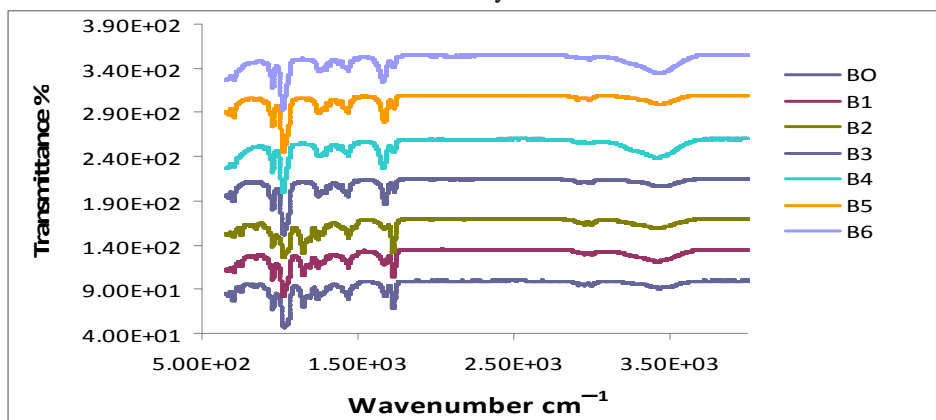
(a)



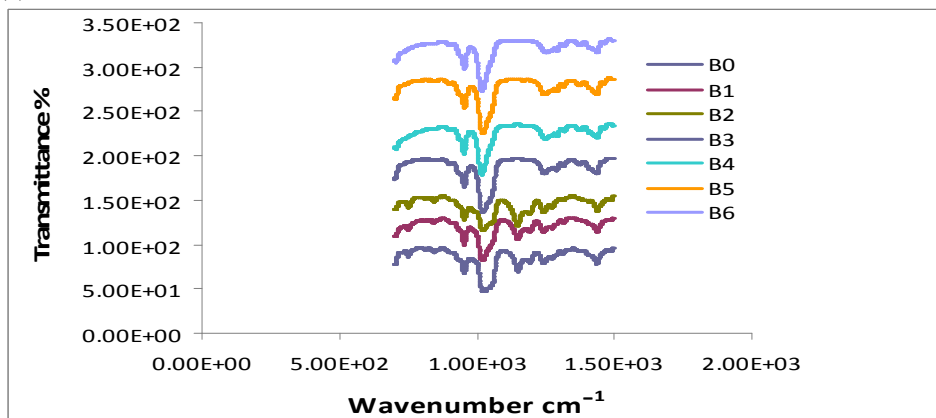
(b)

Fig.3: FTIR for electrolyte A, (a) with and without TPAI salt, with different weight ratio, (b) Stretching vibration of the C=O of electrolyte A.

Fig.4 shows FTIR results for electrolyte B which content different weight percent of Potassium iodide (KI) vary from (0-50%) ,in the range 3600-3000 cm^{-1} the broadening of the band associated to O-H stretching , clearly observe for electrolytes B3,B5 and B6 , this can be related to the enhancement of K^+ ion which increase the ionic conductivity as shown in Fig.(4-a) , the mean behavior of the spectrum same in the range(3600- 1600 cm^{-1}) no new peaks appear . In the wavenumber range (1600-600 cm^{-1}) , as shown in Fig.(4-b) , the peak (1148.35 cm^{-1}) for sample B0, (1147.62 cm^{-1}) for B1 and (1146.54 cm^{-1}) for B2 disappears in other samples B3,B4,B5 and B6 , those bonds was related to stretching of C-O of ester bond . The disappears process may due to form new chemical bond group as a results of the interaction between the polymer blend in addition to the contribution of potassium iodide when increase the weight percentage in the electrolytes . We can observed also from Fig.(4-b) little shift in peak position (1003 cm^{-1}) and the broad peak becomes narrower and sharp with addition more amount of KI salt in the electrolytes .



(a)



(b)

Fig.4: FTIR for electrolyte B (a) with and without KI salt ,(b) Stretching of C-O of ester bond.

3.2 Ionic conductivity Results

The bulk resistance of electrolytes can be obtained from the oblique line at high frequency that intercepts the real axis in the Nyquist plot. The conductivity σ is inversely related to the real part of the bulk impedance (Z) according to eq.1. Ionic conductivity plays a predominant role to produce better polymer electrolytes leading to battery applications. The ionic conductivity in polymer electrolytes is assumed to occur by Lewis acid–base interaction between cation and polymer [10]. The resulting conductivity is mainly due to the overall mobility of ions and polymer, which is determined by the free volume, and this leads to the increase in ionic conductivity and segmental mobility. This assists ion transport and compensates the retarding effect of the ionic clouds [15]. Dimethylsulphoxide (DMSO) has been used as the solvent because of its high dielectric constant, and its role as good plasticizer. The presence of DMSO in the prepared polymer electrolyte has been confirmed from FTIR spectroscopy studies. DMSO is a good electron donor and therefore expected to fully coordinate the cations and consequently enhances the conductivity (in the present case proton conductivity of the system) [16]. The ionic conductivity was determined from the impedance plots. The conductivity of the gel electrolyte, Fig.(5-a) hence increases linearly with the increase in TPAI up to 50 wt% conductivity reaches the maximum value of (0.00139 S cm⁻¹) at room temperature. The increase in conductivity with temperature is mainly due to increase in free volume for the motion of ions through the polymer backbone. This can be understood with the emphasis that as temperature increases, the vibrational energy of segmental motion operates against the hydrostatic pressure imposed by its neighboring atoms. Consequently, it creates a small amount of space surrounding its own volume in which vibrational motion can occur. Therefore, free volume around the polymer chain causes augmentation in mobility of ions and hence enhances the conductivity [17]. The ionic conductivity of plasticized polymer electrolytes as a function of temperature is shown in Fig (5-b) which describe the increasing of ionic conductivity with increasing content of TPAI, reaching a maximum at 50 wt%. With the increase in the amount of TPAI, more conducting channels for charge transfer are constructed, and the conductivity of the gel electrolyte is hence enhanced. Polymer blending can avoid problems associated with low ionic conductivity of the systems with properties that could not be obtained with the use of a single polymer [18]. The electrolyte samples with high Tetrapropylammonium iodide (Pr₄N⁺I⁻) contents show relatively higher iodide ion conductivity, evidently due to the bulky Pr₄N⁺ cation which is expected to be much less mobile [19].

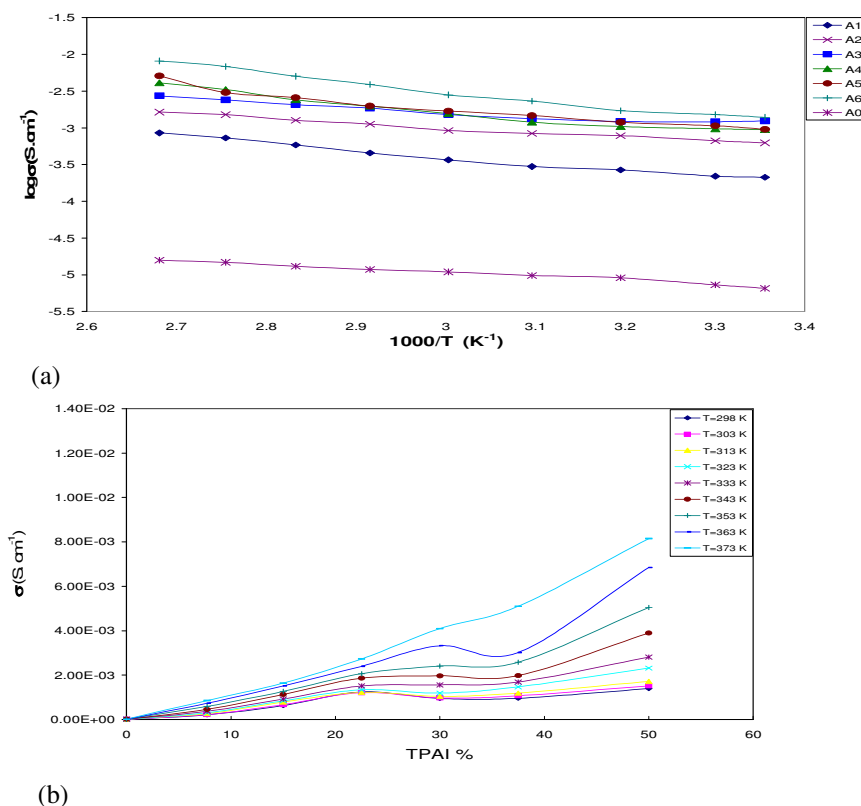
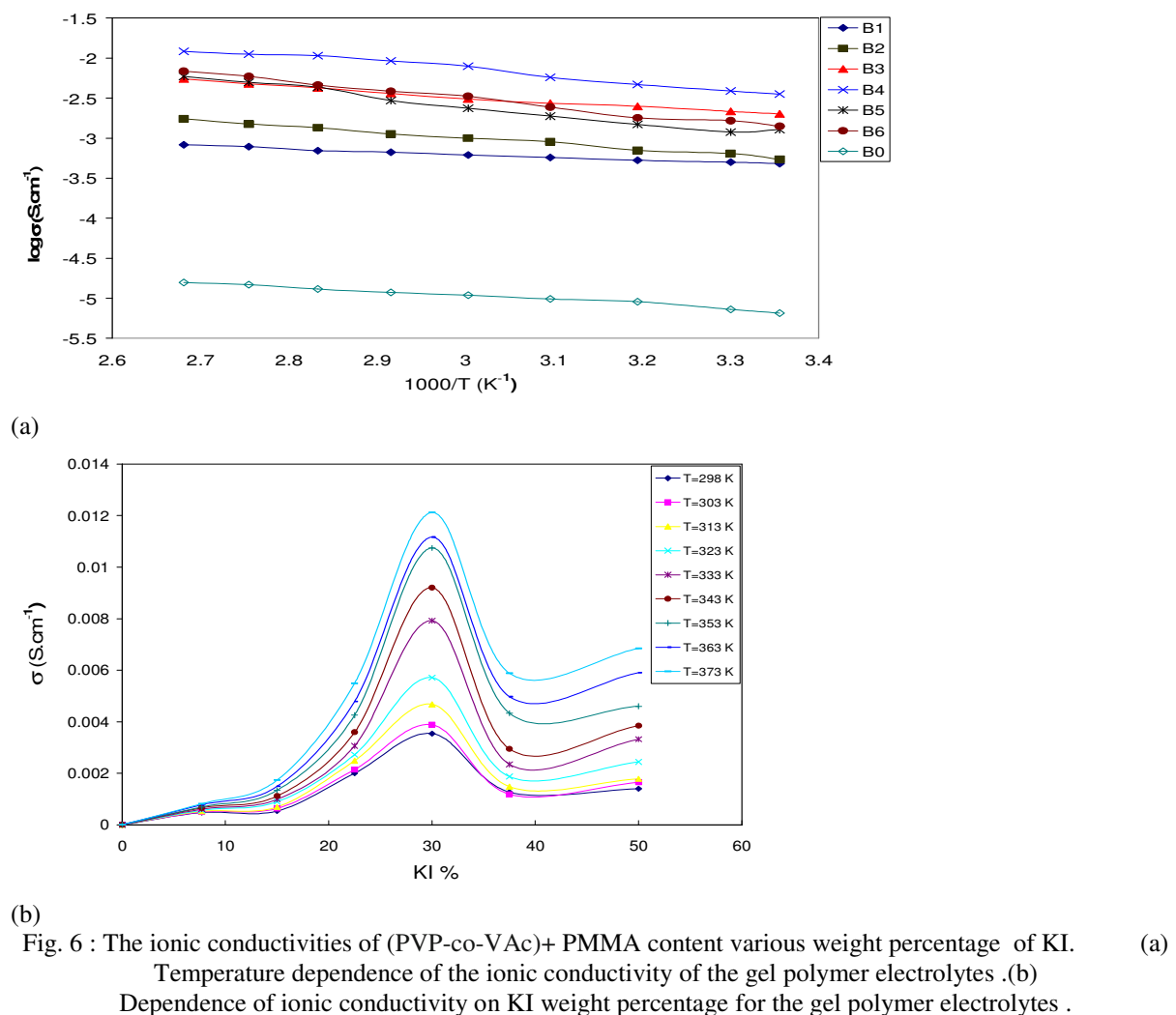


Fig. 5: The ionic conductivities of (PVP-co-VAc)+ PMMA with various weight ratio of TPAI.

(a) Temperature dependence of the ionic conductivity of the gel polymer electrolytes.

(b) Dependence of ionic conductivity on TPAI weight ratio for the gel polymer electrolytes.

Ionic conductivity results for the gel electrolyte with different weight ratio of potassium iodide (KI) are shown in Fig.(6 a-b), it obvious that the ionic conductivity increase with the increasing KI weight percentage . As salt concentration is raised, ionic conductivity of the electrolyte solutions and gels increases steadily, acquires a maximum value and then decreases gradually. The enhancement in conductivity is due to the increase of conducting ion concentration in the system. The conductivity reaches the maximum value of 0.0035 S cm^{-1} at room temperature with 30 wt.% of KI salt ,and with different temperatures, from room and (298-373 K) , and further increase in the amount of KI adversely decreases the values for I3 ionic diffusion. When the salt goes to 37.5 wt.% the conductivity almost saturates and the rate of increase in conductivity becomes slower upon further addition of KI salt to the polymer. From the structural analysis it is predicted that K^+ ion is coordinated to five ether oxygens [20]. Ion transport occurs by hopping between preferred oxygen sites of polymer. The increase of salt concentration introduces more mobile ions. As a result of it, conductivity increases with increase in salt concentration. The saturation of conductivity at higher salt concentration may be due to ion-ion interaction. All ion species present in an electrolyte and their concentrations, as well as other charge exchange reactions can also contribute to the ion conductivity. Hence the conductivity decreases are more pronounced with increasing KI, mostly due to the obstructed segmental motion that inhibits migration of the electrons/ions, causing more difficulties in the transportation of charge carriers. At higher salt concentration, electrostatic crosslinking of the polymer substantially reduces the diffusion coefficients . However, above a limiting high salt concentration the segmental motion of the polymer chains is reduced due to an “ionic cross-linking” which decreases ionic conductivity . The ionic conductivity of the electrolyte B (only with KI salt) originates from two types of ions, namely K^+ ions and I^- ions and both these ions contribute to the highest conductivity seen for this electrolyte [19] .



To further enhance the understanding in conductivity trend, a graph of dielectric constant, ϵ_r against log frequency at room temperature is plotted, as shown in Figs. (7,8). Permittivity is a measure of the degree to which a medium can resist the flow of charge. Since ac conductivity is known to increase with frequency, permittivity must decrease with frequency so that the flow of charge will not encounter much resistance in the high frequency region. At lower frequency region, ϵ_r is observed to decrease with increasing frequency and level off at higher frequency region. This is because at lower frequency region, electrode polarization occurs due to the accumulation of ions at the electrode–electrolyte interface, confirming non-Debye dependence. Towards high frequency, the reversal of electric field occurs at faster rate so that most of the ions are located in the bulk of the sample which decreases the electrode polarization, hence decreasing the ϵ_r value. No relaxation peaks are observed suggesting that ϵ_r values may be used as the indicator to show that the increasing conductivity is mainly attributed to the increasing free mobile ions [19]. The ϵ_r represents the fractional increase in the stored energy per unit voltage, it mean that ϵ_r represents the fractional increase in charge, the charge must come from the proton of gel electrolytes. Therefore fractional increase in charge implies an increase in number of ions.

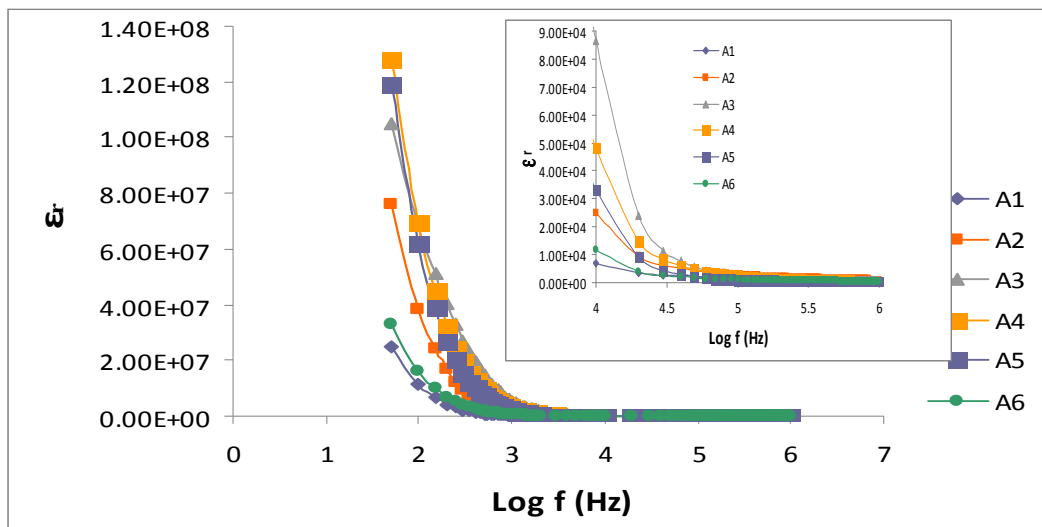


Fig. 7: Dielectric constant vs. Log frequency at room temperature for A electrolyte With different TPAI salt concentration.

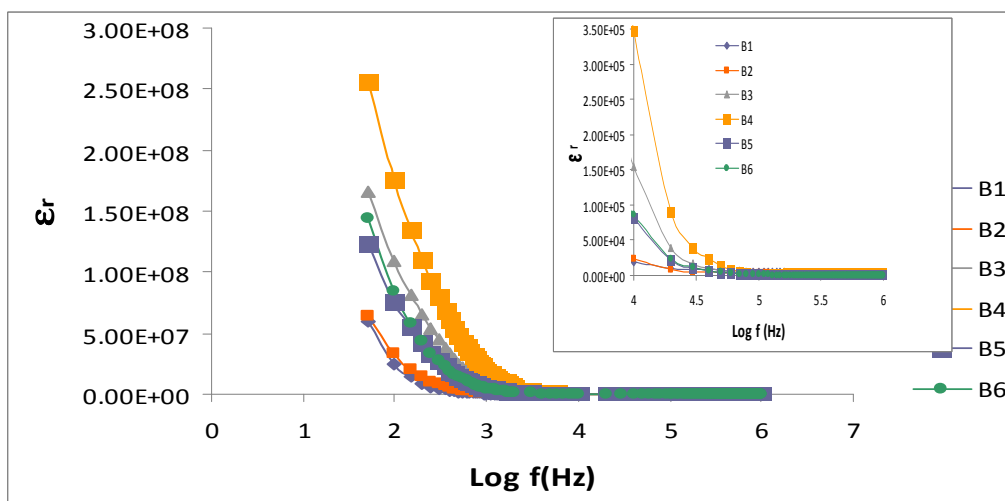


Fig. 8: Dielectric constant vs. Log frequency at room temperature for B electrolyte With different KI salt concentration.

4. Conclusions

A new proton-conducting polymer electrolyte, composed of (PVP-co-VAc) as a host polymer blend with (PMMA), were prepared by incorporating the salts TPAI and KI and characterized using FTIR and ac impedance spectroscopic techniques. From the FTIR result, we have confirmed the interaction between the added salt and the host polymer matrix gel polymer electrolytes. The results indicated that the ionic conductivity

values increase with increasing salts weight ratio up to (30%KI and 50%TPAD), and maximum ionic conductivity value is 0.0035 S cm^{-1} for electrolyte B with 30%KI at ambient temperature .

Acknowledgments

The authors would like to thank the University of Malaya. All preparation process and measurements are done in University of Malaya , Center of Ionics .

References

- [1] Agrawal ,R.C. & Pandey, G.P.,(2008) “Solid polymer electrolytes: materials designing and all-solid-state battery applications: an overview” *J. Phys. D: Appl. Phys.* 41, 223001 (18pp).
- [2] Murphy, S. B. R., (1998),“In *Polymer Networks—Principles of Their Formation, Structure and Properties*”, Stepto, R. F. T. (Ed.), Blackie Academic, London .
- [3] Abraham, K. M.,(1993), “In *Application of Electroactive Polymer*”, Scrosati, B. (Ed.), Chapman & Hall, London .
- [4] Wu, J. , Lan, Z. , Hao,S. , Li, P. ,Lin, J. , Huang, M., Fang, L. , & Huang, Y.,(2008), “Progress on the electrolytes for dye-sensitized solar cells” , *Pure Appl. Chem.* ,80(11) , 2241–2258.
- [5] Bandara, T. M. W. J. , Dissanayake, M. A. K. L., Jayasundara,W. J. M. J. S. R. , Albinsson, I. & Mellander,B.E.,(2012), “Efficiency enhancement in dye sensitized solar cells using gel polymer electrolytes based on a tetrahexylammonium iodide and MgI₂ binary iodide system”, *Phys. Chem. Chem. Phys.* , 14, 8620–8627.
- [6] Chan, Y.F. , Wang,C.C. , & Chen, C.Y. , (2013), “Quasi-solid DSSC based on a gel-state electrolyte of PAN with 2-D graphenes incorporated”,*J. Mater. Chem. A* , 1, 5479–5486 .
- [7] GRANQVIST, C. G.(1995), “*Handbook of Inorganic Electrochromic Materials*”,The Netherlands: Elsevier, .2 sv. (337, 296 s.) .
- [8] Razak, N.A.A., Winie, T.,Ghani F.S.A. & Ahmed, A.H.(2008) , “CONDUCTIVITY AND FTIR STUDIES ON PVA/CHITOSAN-LiCF₃SO₃”, *Solid State Science and Technology* , 16(1) ,1-7.
- [9] Vidal ,F., Plesse, C., Palaprat, G., J. Juger , Gauthier,J, Pelletier, J.M. , Varlot, K. M. , Chevrot, C., & Teyssié ,D.,(2013), “Influence of the poly(ethylene oxide)/polybutadiene IPN morphology on the ionic conductivity of ionic liquid” , *European Polymer Journal* 49, 2670–2679 .
- [10] Karuppasamy, K. , Antony, R. , Thanikaikarasan, S. , Balakumar, S. & Shajan, X.S.,(2013), “Combined effect of nanochitosan and succinonitrile on structural, mechanical, thermal, and electrochemical properties of plasticized nanocomposite polymer electrolytes (PNCPE) for lithium batteries”, *Ionics*, 19(5), 747–755.
- [11] Deepa,M., Sharma, N., Varshney,P., Agnihotry, S.A. & Chandra, R. ,(2000), “An Insight Into the Interactions Between LiN(CF₃SO₂)₂-RBL/DMF-PMMA by FTIR Spectroscopy”,*Ionics* , 6 , 408-414 .
- [12] Ramesh,S., Leen, K.H., Kumutha, K., &Arof, A.K. , (2007), “FTIR studies of PVC/PMMA blend based polymer electrolytes”, *Spectrochimica Acta Part A*, 66 ,1237–1242.
- [13] Zaccaron, C.M., Oliveira,R.V.B., Guiotoku, M., Pires, A.T.N., &Soldi, V.,(2005), “Blends of hydroxypropyl methylcellulose and poly(1-vinylpyrrolidone-co-vinyl acetate): Miscibility and thermal stability”, *Polymer Degradation and Stability*, 90, 21-27.
- [14] Padalia, D., Johri, U.C., & Zaidi, M.G.H. ,(2012), “Study of cerium doped magnetite (Fe₃O₄:Ce)/PMMA nanocomposites” , *Physica B*, 407, 838–843 .
- [15] Dey, A. , Karan, S. , & De, S.K., (2009) , “Effect of nanofillers on thermal and transport properties of potassium iodide_polyethylene oxide solid polymer electrolyte”, *J Phys Chem Solids* 71:329 .
- [16] Hema, Selvasekerapandian, M.S. , Hiran Kumar, G. , Sakunthala, A. ,Arunkumar, D.,& Nithya, H., (2009), “Structural and thermal studies of PVA:NH₄I” , *Journal of Physics and Chemistry of Solids*, 70, 1098–1103 .
- [17] Prajapati, G.K., Roshan, R., & Gupta, P.N.,(2010), “Effect of plasticizer on ionic transport and dielectric properties of PVA–H₃PO₄ proton conducting polymeric electrolytes” , *Journal of Physics and Chemistry of Solids*, 71, 1717–1723 .
- [18] Shukur, M.F. , Ithnin, R. , Illias, H.A. , & Kadir, M.F.Z. ,(2013), “Proton conducting polymer electrolyte based on plasticized chitosan–PEO blend and application in electrochemical devices” , *Optical Materials*, 35,1834–1841.
- [19] Dissanayake, M.A.K.L. , Thotawatthage, C.A. , Senadeera, G.K.R. , Bandara, T.M.W.J., Jayasundara, W.J.M.J.S.R., & Mellander, B.E. ,(2012), “Efficiency enhancement by mixed cation effect in dye-sensitized solar cells with PAN based gel polymer electrolyte” , *Journal of Photochemistry and Photobiology A: Chemistry*, 246, 29– 35 .
- [20] Dey, A. , Karan, S., Dey, A. , & De, S.K., (2011), “Structure, morphology and ionic conductivity of solid polymer electrolyte” , *Materials Research Bulletin*, 46, 2009–2015 .