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FTIR and Electrical Behavior of Blend Electrolytes Based on (PVA/PVP)

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Abstract

Polymer electrolytes were prepared using the solution cast technology. Under some conditions, the electrolyte content of polymers was analyzed in constant percent of PVA/PVP (50:50), ethylene carbonate (EC), and propylene carbonate (PC) (1:1) with different proportions of potassium iodide (KI) (10, 20, 30, 40, 50 wt%) and iodine (I_2) = 10 wt% of salt. Fourier Transmission Infrared (FTIR) studies confirmed the complex formation of polymer blends. Electrical conductivity was calculated with an impedance analyzer in the frequency range 50 Hz–1MHz and in the temperature range 293–343 K. The highest electrical conductivity value of 5.3×10^{-3} (S/cm) was observed for electrolytes with 50 wt% KI concentration at room temperature. The magnitude of electrical conductivity was increased with the increase in the salt concentration and temperature. The blend electrolytes have a high dielectric constant at lower frequencies which may be attributed to the dipoles providing sufficient time to get aligned with the electric field, resulting in higher polarization. The reduction of activation energy (E_a) suggests that faster-conducting electrolyte ions want less energy to move.

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1. Introduction

Polymer electrolyte (PE) science is a broad field that includes polymer science, organic chemistry, electrochemistry, and inorganic chemistry [1]. It is a prominent issue in material science, particularly Gel Polymer Electrolytes (GPEs); it has many advantages, including no shape restrictions, faster charging/discharging, higher power density [2], and the flexibility to manufacture desired shapes [3]. Blending is an effective method for increasing polymer electrolytes' ionic conductivities and dimensional stability [4, 5].

Polymer salt complexes are frequently prepared by dissolving a trace quantity of salt in the required solvent with the host polymer to impact its ionic conductivity [6-8]. Because the electrolyte is composed of two or more different polymers, the device's thermal, mechanical, and conductive qualities may be enhanced by simple modulation and control of their physical properties [9, 10]. Polymer blend complexes may be used in electrochemical systems, such as stable electrolytes [11].

Modifications in the properties of polymer blends depend on the degree of compatibility and miscibility of the constituent polymers used in the blends. In this context, selecting compatible and miscible polymers for developing new polymeric material is an important aspect. Amongst different compatible polymers for the preparation of blends and composites, polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP) are widely used in various applications such as biosensors, nano-dielectrics, energy storage devices, supercapacitors, and batteries. PVA and PVP are eco-friendly, hydrophilic, biodegradable, nontoxic, and biocompatible polymers. These polymers are water-soluble, possess good mechanical strength, form flexible, and are transparent when prepared by solution-cast technique [12, 13]. This work aims to prepare electrolyte-based polymers and salt.

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2. Experimental Work

2.1. Materials and Method

PVA and PVP with a molecular weight of approx. MW= 14000 g/mol and approx. MW= 40000 g/mol, respectively, were used as host polymers. Dimethyl Sulfoxide (DMSO), Ethylene carbonate (EC), Propylene carbonate (PC), Potassium iodide (KI), and Iodine (I_2) with a purity of more than 98% were used to preparing the blend electrolytes. The samples were made using a fixed ratio of PVA:PVP (50:50), EC:PC (1: 1) with varying proportions of KI (10, 20, 30, 40, 50 wt%) and iodine I_2 = 10 wt% of salt as shown in Table 1.

First, the two polymers, PVA and PVP, were dissolved one by one in 3 ml of DMSO solvent in a glass container using a stirrer at (283 to 293 K) for 2 h, the salts KI, EC, and PC were then added one by one also into the homogenous solution and stirred continuously at the same temperature until the solution becomes viscous and gel-like. When this happened, heating was stopped, and iodine was added to the gel by stirring the solution for 1 h to complete homogeneity. Fig. 1 shows images of the prepared samples.

Table 1: Composition of electrolytes system.

Samples	PVA (g)	PVP (g)	DMSO (ml)	KI (wt%)	EC (g)	PC (g)	I_2 (wt%)
A	0.6	0.6	3	0	0.5	0.5	0
A1	0.6	0.6	3	10	0.5	0.5	10
A2	0.6	0.6	3	20	0.5	0.5	10
A3	0.6	0.6	3	30	0.5	0.5	10
A4	0.6	0.6	3	40	0.5	0.5	10
A5	0.6	0.6	3	50	0.5	0.5	10

Figure 1: Gel Polymer Electrolytes.

2.2. Characterization of Materials

FTIR spectra were acquired at room temperature with a PerkinElmer Spectrum over a range of 400-4000 cm^{-1}. The samples resistance were calculated with an LCR - 8110G/8105 impedance analyzer in the 50 Hz -1 MHz frequency range. Eq. (1) shows the ionic conductivity σ in relation to the bulk resistance R_b [14]:

$$\sigma = \frac{L}{R_b\ A} \tag{1}$$

where: L (cm) is the distance between the electrodes and A (cm^2) is the electrode area. The temperature of the sample ranged between 293 and 343 K. The real part of the dielectric constant (ε_r) was determined using Eq. (2) [15]:

$$\varepsilon_r = \frac{Zi}{\omega\, C_\circ\, [Z_r^2 + Z_i^2]} \qquad \textbf{(2)}$$

where: ω is the angular frequency ($\omega = 2\pi f$), $C_\circ$ is the vacuum capacitance and Z_r and Z_i are the real and imaginary parts of resistance, respectively.

3. Results and Discussion

2.1. FTIR Results

FTIR spectroscopy is a fundamental tool for analyzing the band structure of materials, which changes depending on their formulation. It may reveal the complexity and interaction between various components such as polymers, ions, and cations [14]. Fig.2 shows the FTIR spectra of a pure blended and gel electrolyte with different concentrations of KI salt listed as (A, A1, A2, A3, A4, and A5). The transmittance fluctuation and the identified band shifting in the FTIR spectrum in a salt-complexed system shows that the salt has been completely complexed and dissolved in the polymer mix. Complexation may be linked to changes in the infrared spectrum, such as band shifting and the introduction or extinction of an infrared spectrum band [16, 17].

This study relied extensively on changing the FTIR spectral band assigned to explain polymer blends and their interactions with varying KI wt.% concentrations. The hydroxyl groups of the (PVA-PVP) blend shifted slightly (3425.34 - 3452.34 cm^{-1}) with the increase of the KI wt% concentrations, as seen in Table 2 [12, 13]. There were no significant shifts in the absorbance of the C=C bond at 1575 cm^{-1}. The C-H stretching bond shifted from 2977.89 cm^{-1} to a lower wavenumber of 2972.10 cm^{-1}, indicating that hydrogen bonding interactions have developed. The CH_2 peak for the (PVA-PVP) has not disappeared entirely for (A3, A4, and A5) samples, indicating that some of the vinyl groups have been left unreacted during the polymerization process [13-17].

2.2. Electrical Conductivity Results

At two different temperatures, the Nyquist plots for blend gel electrolyte samples with different weight percentages of KI (10, 20, 30, 40, and 50 wt%) are shown in Figs.3 (a and b). The graphs show a semicircle in the high-frequency domain and a spike in the low-frequency for all samples and temperatures. The semicircle is formed by the electrolyte's volume effect, but the spike is caused by the electrodes' blocking action [18]. The bulk resistance of each sample was calculated using the intercept between the semicircle and the spike [19].

The addition of 50 wt% KI to the PVA-PVP blend significantly reduced the diameter of the semicircle, implying a reduction in bulk resistance in the KI-based polymer blend electrolyte. This drop might be attributed to the increase in ionic charges caused by adding KI. It was found that raising the temperature and/or KI wt% lowers the width of the semicircle, indicating active participation of the ionic conductivity across the samples [5, 18]. These results indicate a non-Debye relaxation nature (a single relaxation time) for electrolyte blend samples [20].

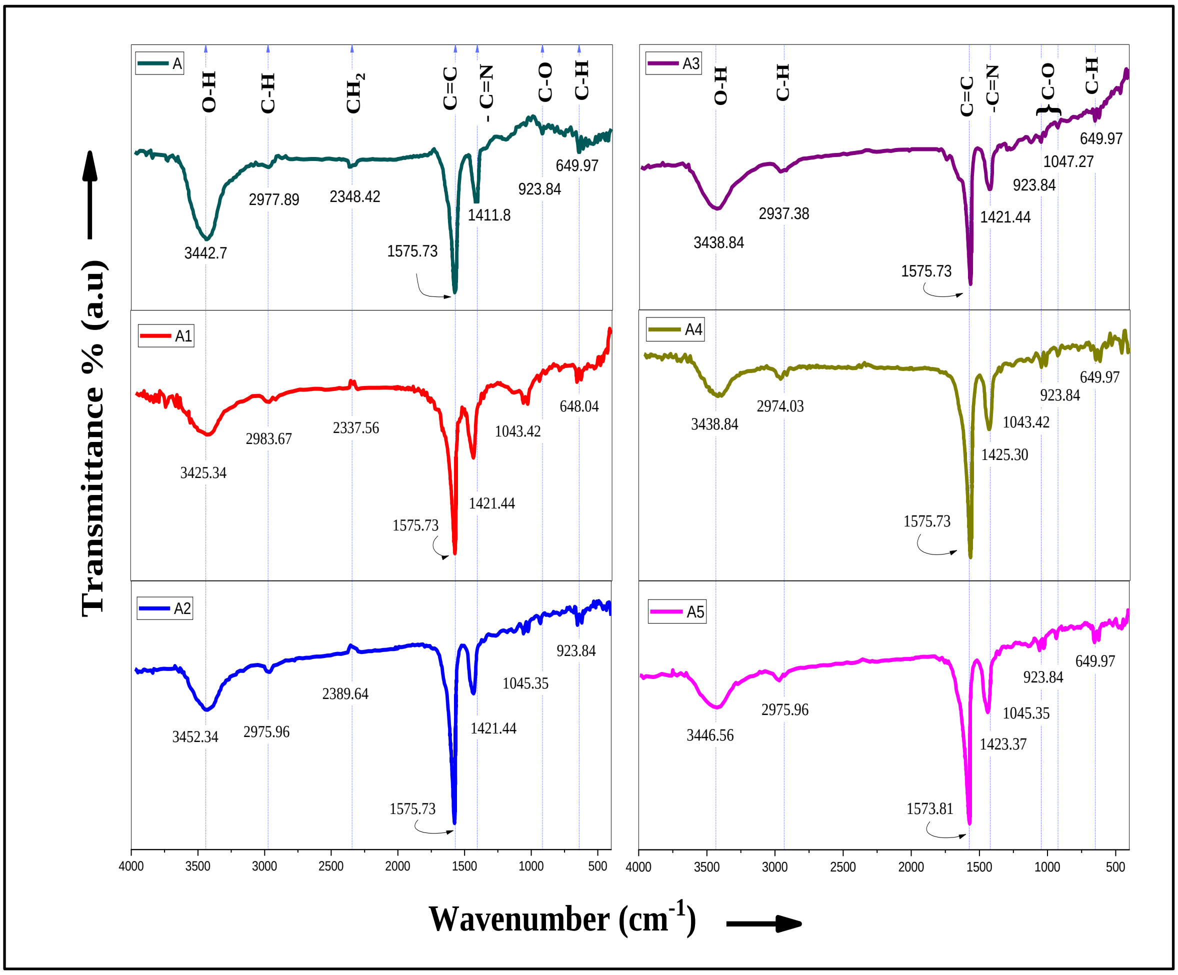

Figure 2: FTIR spectra of pure polymer blends PVA/PVP and blends with varying KI concentrations.

Table 2: Assignments of the FTIR characterization bands of the PVA/PVP blend and gel electrolytes with different wt% of KI.

Wavenumber (cm^{-1}) of pure PVA-PVP blend with different concentrations of KI wt%						Assignments	Ref.
0%	10 %	20%	30%	40%	50%		
3442.70	3425.34	3452.34	3438.84	3438.84	3446.56	-OH Stretching/vibration	13,12
2977.89	2983.67	2975.96	2937.10	2974.03	2975.96	C-H stretching	5
2348.42	2337.56	2389.64	2391.57			CH_2 asymmetric stretching	16
1575.73	1575.73	1575.73	1575.73	1575.73	1573.81	CH_2 wagging and C=C stretching	13
1411.80	1421.44	1421.44	1421.44	1425.30	1423.37	-C=N pyridine ring / stretching	12,14
	1043.42	1045.35	1047.27	1043.42	1045.35	C-C Stretching vibration	17
923.84	925.77	923.84	923.84	923.84	923.84	C-O stretching	17
649.97	648.04	648.04	649.97	649.97	649.97	C-H out of phase bending	13

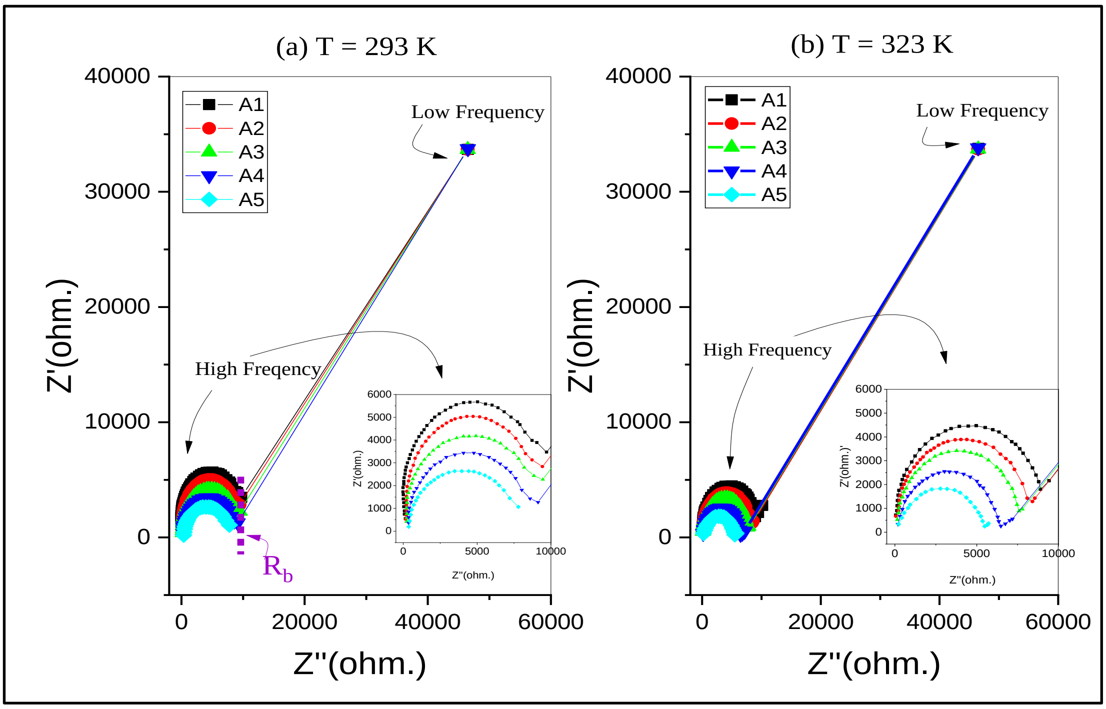

Figure 3: Nyquist plots of polymer blend electrolytes at: (a) T=293 K (b) T=323 K.

The conductivity results for pure blend and electrolytes with a specific percent of KI, (see Fig. 4), displayed an increase in the ionic conductivity as the concentration of KI salt rose. Increased conductivity is due to an increase in the mobility of the charge carriers [21].

At ambient temperature, specimens with 50 wt% KI had maximum conductivity of (5.309×10^{-3} S/cm). The transfer of ions happens by shuttling in the midst of the distinguished oxygen locations of the polymer. At the maximum salt concentration, conductivity saturation may be caused by ion-ion interaction [22].

As the salt percentage increased, polymer electrostatic crosslinking significantly decreased the diffusion coefficients. The movement of the polymer chains, however, is decreased by the "ionic cross-link" above the small rise in salt concentration, which decreases ionic conductivity [23].

The ionic conductivity of an electrolyte is caused by two kinds of ions, namely K^+ and I^- ions, and each of these ions contributes to the maximum conductivity of that electrolyte [24]. The conductivity of all electrolytes has increased in the temperature range of 293 to 343 K. An increase in conductivity with temperature causes an increase in free volume for ion mobility over the polymer backbone. Temperature raises the vibrational energy of segmental mobility effort compared to the hydrostatic pressure its neighbors need [20]. As a result, it encircles its volume with a limited scale in which vibrational motion can occur. As a result, the free space around the polymer chain increases, increasing ion mobility and therefore facilitating conductivity. Similar findings have been obtained by Barbosa et al. for other types of polymer electrolytes [8].

The activation energy (E_a) of an ion is the required energy to detach from its original location and become a free ion. The influence of temperature on conductivity was examined to calculate E_a for all electrolytes [15]. According to Fig.4 (a), conductivity increased as temperature increased. The conductivity increases rapidly as the temperature rises, resulting in more free volume [25]. This effect improves the conductivity of ionic mobility and polymer segmental motion [26]. As a result, the regression coefficients in Fig.4 (a) are close to unity, and the conductivity temperature plots will be well matched with the Arrhenius equation [27]:

$$\sigma = \sigma_\circ \, e^{-E_a/KT} \tag{3}$$

where: $\sigma_\circ$ is a pre-exponential factor, k is Boltzmann constant and T is the absolute temperature. Whereas, (- $\frac{E_a}{KT}$) represents the graph slope. The value for $\sigma_\circ$ and E_a can be determined from Fig.4 (a) which illisterated the relation between log σ versus 1000/T. Table 2 lists the measured E_a and R^2 (the regression values) [28]. As conductivity increased, E_a decreased, implying that the ions in more conducting electrolytes require less energy to move [29]. The variance in activation energy strongly confirms the electrical conductivity transition. The low activation energy is considered a distinguishing property of the optimal conductivity value [30]. The adaptability of polymer electrolytes helps to enhance the rate of K+ dissociation. This enhances the movement of ions in the polymeric chain and increases the mobility of the charge carrier [31]. In Table 3, the variation of the activation energy values was tabulated.

Table 3: The conductivity, activation energy and R^2 the regression values at room temperature for electrolytes.

Electrolytes	**σ_{RT} (S/cm)**	**E_a (eV)**	**R^2**
A	1.8×10^{-4}	0.0937	0.991
A1	1.005×10^{-3}	0.0749	0.997
A2	1.597×10^{-3}	0.0716	0.999
A3	1.944×10^{-3}	0.0703	0.995
A4	2.600×10^{-3}	0.0694	0.996
A5	5.309×10^{-3}	0.0437	0.983

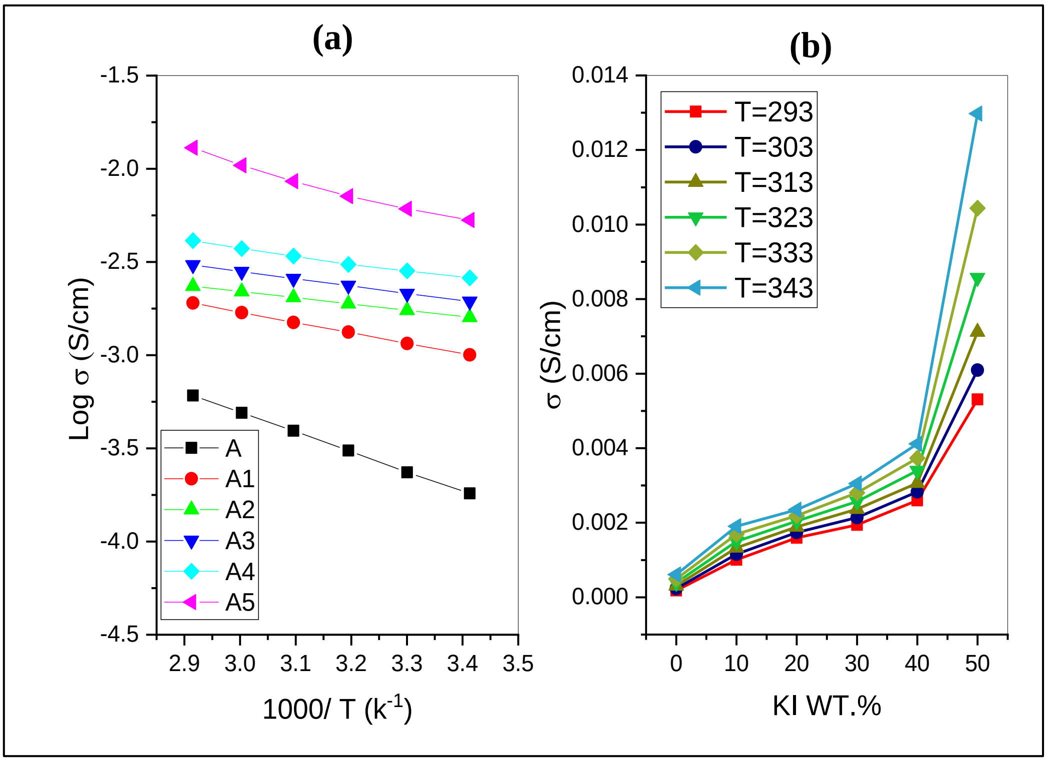

Figure 4: Ionic conductivity of blended electrolytes containing and not containing KI: (a) Temperature is dependent on conductivity; (b) ionic conductivity is dependent on KI wt%.

2.3. Dielectric Constant Results

The real dielectric constant (ε_r) was calculated to confirm the electrolyte conductivity. It denotes the dielectric material's capacity to store charges via conduction [32]. The dielectric constant (ε_r) demonstrates that an increase in conductivity is caused by the rise in the number of free mobile ions, which may be simplified as a fractional increase in charge. Fig.5 shows that for different weights per cent of KI, (ε_r) increases as frequency drops. Ion dissociation causes an increase in the number of accessible ions, while ion association causes a reduction [33]. The decrease in ε_r with frequency may be described as follows: at low frequencies, ε_r for polar materials is due to the contribution of many polarizability components (electronic, ionic, orientation, and interfacial) [34]. When the frequency is raised, the dipoles can no longer rotate quickly enough. As a result, their oscillations begin to lag behind the fields. With further increase in frequency, the dipole is unable to follow the field, and the orientation ceases; thus it adopts constant values [35].

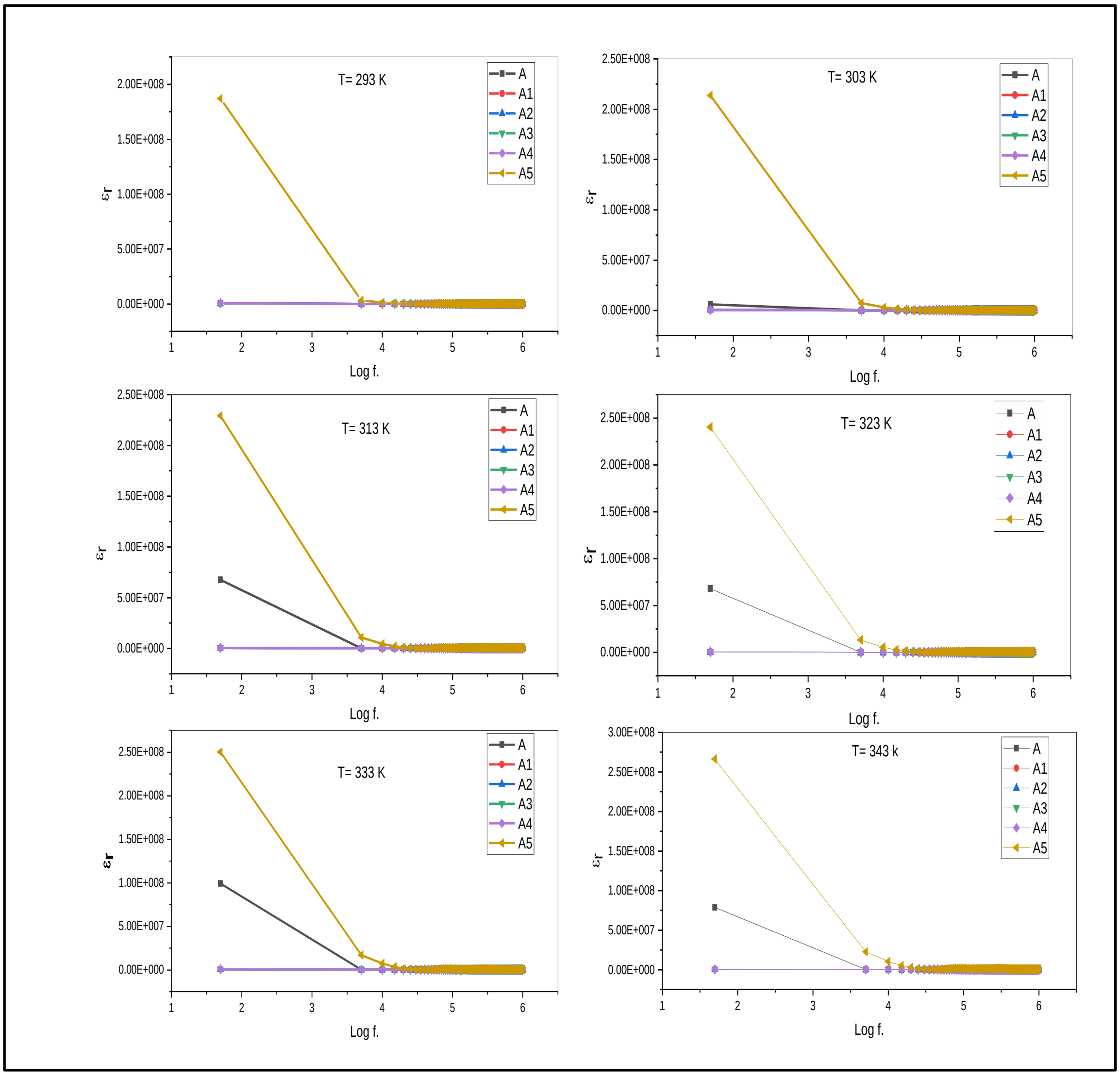

Figure 5: Dielectric constant vs. Log frequency for pure blend and gel electrolytes at different temperatures.

4. Conclusions

As part of this work, Gel Polymer Electrolytes were produced and characterized. FTIR electrolytes measurements demonstrated a significant interaction between polymer blends (PVA-PVP) and (KI) salts. Interactions between polymer blends and KI in electrolytes are associated with variations in the intensity, shape, and position of stretching modes. The maximum conductivity (5.3×10^{-3} S/cm) is attained at room temperature for electrolytes containing 50 wt% of KI. The activation energy reduces as the dielectric develops as the temperature rises, increasing the conductivity of the electrolyte. The results revealed that increasing the weight of the salts enhanced the ionic conductivity values. The highest conductivity was for the electrolyte containing the highest salt percentage, 50 wt% KI, at the highest temperature of 343 K, which was (1.29×10^{-2} S/cm). The temperature was shown to increase conductivity. As the temperature rises, the electrolytes expand, resulting in a greater free variation of the energy of defect formation and defect motion, which is the activation energy E_a. At room temperature, the polymer electrolyte A5 with 50 wt% KI has the highest dielectric constant value.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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طيف الأشعة تحت الحمراء والسلوك الكهربائي لإلكتروليت خليط البوليمر (PVA/PVP)

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الخلاصة

تم تحضير الالكترولايتات البوليمرية باستخدام تقنية صب السائل في ظل بعض الظروف، تم تحليل محتوى الالكترولايتات بنسبة ثابتة من البوليمرات (50:50) PVA/PVP و (1:1) PC/EC وبنسب وزنيه متفاوتة من KI يوديد البوتاسيوم (10%، 20%، 30%، 40%، 50%) اما نسبة اليود فكانت 10% من وزن الملح. أكدت دراسات طيف الاشعة تحت الحمراء (FTIR) التفاعل بين خليط البوليمر ويوديد البوتاسيوم KI. تم حساب الموصلية الكهربائية باستخدام محلل ممانعة في نطاق التردد 50 هرتز-1 ميجاهرتز وفي نطاق درجة الحرارة 293-343 كلفن. ولوحظ اعلى قيمة للتوصيل الكهربائي هي (5.3×10^{-3} سيمنز/ سم) لتركيز50 % من يوديد البوتاسيوم في درجة حرارة الغرفة. تزداد قيمة التوصيلية الكهربائية مع زيادة تركيز الملح وكذلك درجة الحرارة. تمتلك خلائط إلكتروليت اعلى ثابت عزل عند الترددات الواطئة. وان نقصان طاقة التنشيط (E_a) يشير إلى أن أيونات إلكترولايتات الأسرع توصيل تريد طاقة أقل للتحرك.