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Effect of cation size on electrochemical properties of polymer electrolyte

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Abstract

This study investigates the ionic conduction reliance on the size of positively charged ions in electrolytes with double iodide can enhance by incorporating a salt having a bulky cation. Group of gel polymer electrolytes with polyethylene oxide (PEO) as a host matrix based on double salts potassium iodide (KI) and rubidium iodide (RbI) with different weight ratio prepared by using solution cast method. The maximum value of conductivity reaches (6.03×10^{-3} at 293 K) S/cm for an electrolyte which content (KI 45%, RbI 5%) from binary salt. The ionic conductivity of for gel polymer electrolytes gradually increases by increasing temperature. The real dielectric constant results confirm that the dielectric behavior of the PEO material is a thermally activated process. FTIR results confirm that the shifting of peaks is another way to prove the interactions between PEO and binary salt ascribed to the creation of a passing cross-linking complex between the ether oxygen of the PEO and the positively charged ions of the ionic liquids.

Key words

Conductivity, cation size, double salts, dielectric constant, polymer electrolyte.

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تـأثير حجم الايون الموجب على الخواص الكهروكيميائية للالكترولايت البوليمري

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قسم الفيزياء، كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصة

هذه الدراسة تستستقصي اعتماد التوصيلية الأيونية على حجم الايون الموجب في الالكترولايتات البوليمرية الهلامية المستندة على الأيوديد المزدوج وأمكانية تعزيزها من خلال دمج أملاح تمتلك كاتيون ضخم· تم تحضيرمجموعة من الالكترولايتات البوليمرية الهلامية مع البولي اثيلين اوكسايد (OEP) كمادة رابطة ترتكز على املاح مزدوجة من يوديد البوتاسيوم (KI) ويوديد الربيديوم (RbI) وبنسب وزنية مختلفة باستخدام تقنية صب السائل· وصلت أقصى قيمة لتوصيلية (6.03×10^{-3} سمنز/سم) عند درجة حرارة الغرفة للالكترولايت ذو المحتوى (KI 45%, RbI 5%) من الملح الثنائي· ازدادت الموصلية الأيونية للالكترولايتات البوليمرية الهلامية تدريجيا مع زيادة درجة الحرارة· أكدت نتائج ثابت العزل الكهربائي الحقيقي ان سلوك ثابت العزل الكهربائي لمادة البولي اثيلين اوكسايد عملية فاعله حراريا· اكدت نتائج طيف الأمتصاص للاشعة تحت الحمراء (RITF) ان القمم المزاحة فيه هي طريقة اخرى تثبت التفاعل بين اوكسيد البولي اثيلين و الملح الثنائي يعزى الى تكوين مجمع عابر يربط بين الايونات الموجبة للسائل الأيوني و اوكسجين الأيثر للبولي اثيلين اوكسايد.

Introduction

Polymer electrolytes are favorable candidates for electrochemical apparatus enforcement mainly because they mechanically conduct such as solids and the conductivity demeanor neatly resembles the liquid state [1]. However, liquid electrolytes are suffered from evaporating leakage and corrode, making them unstable for the long run, exactly gas formation during the operation, difficult to utilize for portable applications. The current study focused on enhancing the gel polymer electrolyte as a result of many coveted characteristics of gel electrolytes over liquid electrolyte [2]. The first polymer noticed to have the capability to dissolve alkali metal was polyethylene oxide (PEO) [3]. It shows significant conductivity and elastic chain structure at room temperature [4]. Advertised the presence of a material able of dissolving iodides to shape a new type of ionic conductors [5]. The primary feature of a PEO is its high dissolution strength. Consequently, it may create a complex readily with many iodides and equipping a direct track for positively charged ions migration as a result of the presence of $(–CH_2–CH_2–\ddot{O}–)n$ in the polymer chain. PEO is a linear polymer included the polar ether group $(–C=\ddot{O}–)$ with a lonely couple of electrons and has a powerful tendency to coordinate with salts to create PEs [6, 7]. Net PEO has a low conductance about 10^{-7} S cm^{-1} at room temperature, but as incorporating salts into the polymer, the conductivity can be enhanced [8, 9]. Addendum of binary iodide to reduce the degree of crystallinity of PEO by provides mobile ions which play a critical role in the ionic convey procedure of the electrolytes. The mobility of ion happens through the amorphous area supported by the segmental motion of the polymer chains[10]. The work aims to promote the conductivity of gel electrolytes through the variation of double salt weight ratio, addition to studying the effect of temperature.

Materials and method

PEO with the molecular weight 100,000 g/mol used as a host polymer. Potassium iodide (KI) and rubidium iodide (RbI) with a molecular weight of (166, 212.37 g/mol), respectively. Ethylene carbonate (EC) and propylene carbonate (PC) as a solvents which has a molecular weight of (88.06, 102.09 g/mol), respectively, and iodine (I_2) with a molecular weight of 253.81 g/mol. All these materials have supplied from Sigma Aldrich. PEO based electrolytes with double salts prepared by using solution casting method. The ratio of binary salt (KI, RbI) to the whole electrolyte fixed to 50 wt%. The weight ratios of the salts were variation from (0 to 50 wt.%) as tabulated in Table 1. The prepared electrolyte systems have the configuration $\{(PEO)+(KI/RbI)\%+I_2\}$. First, the iodide was resolved separately into a medley of EC and PC with fixed ratio (1:1), in a glass bottle using magnetic stirrer. After dissolving the salt completely, then the appropriate amount of PEO was added to the medley was then stirred continuously for 60 min with heat up to 60 °C till it is homogenous. The electrolyte was left to cool to RT then added 10% I_2 and stirred for 1h till gating a homogenous gel electrolyte. However, the samples are allowed to evaporate slowly inside the fume hood for 24 hours and then put in a desiccator. The samples Exposure to frequency dependent behavior recorded range between 100 Hz and 1MHz by using HIOKI LCR Hi Tester 8110G/8105G impedance analyzer and calculate the conductivity by using Eq.(1) [11]:

$$\sigma = L/AR_b \qquad (1)$$

where L is thickness for the sample, A is the area of the electrode, and R_b is the bulk resistance of the electrolyte measured by impedance analyzer. FTIR has been measured using model prestige-21 Teaster.

Table 1: Illustrate the composition of electrolytes SH.

Assignments	RbI%	KI%	Composition
SH1	45	5	50%PEO+(45%RbI+5%KI)
SH2	40	10	50%PEO+(40%RbI+10%KI)
SH3	35	15	50%PEO+(35%RbI+15%KI)
SH4	30	20	50%PEO+(30%RbI+20%KI)
SH5	25	25	50%PEO+(25%RbI+25%KI)
SH6	20	30	50%PEO+(20%RbI+30%KI)
SH7	15	35	50%PEO+(15%RbI+35%KI)
SH8	10	40	50%PEO+(10%RbI+40%KI)
SH9	5	45	50%PEO+(5%RbI+45%KI)

Results and discussion

The infrared vary is based on their structure and may be able to show the appearance of complexation and interaction between the different constituents, like polymer-ion, ion-ion. FTIR for pure components (EC, PC, PEO, KI, and RbI) are shown in Fig.1. The major absorption bands for solvent EC has O-H stretching at (3552 cm^{-1}), stretching vibration of carbonyl group C=O at (3039, 2997, 2931 cm^{-1}), C=O stretching find at (1801, 1774 cm^{-1}), CH_3 asymmetric stretching & C-H stretching find at (1392 cm^{-1}), C- O-C stretching & O-CH_3 symmetric stretching find at (1165,1072 cm^{-1}) and symmetric rocking of CH_2 & C–H bending wagging vibration find at (775 cm^{-1}). PC has O-H stretching at (3579 cm^{-1}), C=O stretching find at (2989, 2920, 2639 cm^{-1}), C-O-C stretching & O-CH_3 symmetric stretching find at (1184, 1118, 1041 cm^{-1}) and symmetric rocking of CH_2 & C–H bending wagging vibration find at (775 cm^{-1}). The stretching mode of the carbonyl (C=O) group in PC is assigned to the characteristic frequency shown at (1789 cm^{-1}). The pure PEO has a CH_2 stretching in the wavenumbers at (3468, 2881 cm^{-1}) and a C-O-C stretching vibration in the wavenumbers at (1145, 1103 cm^{-1}) and a CH_2 twisting shaking at (950 cm^{-1}), and a CH_2 wagging vibration at (844 cm^{-1}). FTIR spectrum of KI salt was associated with O-H stretching at (3471, 3421 cm^{-1}). At (1797, 1774 cm^{-1}) stretching vibration of carbonyl group C=O, C=O stretching at (1111, 1075 cm^{-1}). RbI salt also has O-H stretching at (3471 cm^{-1}), stretching vibration of carbonyl group C=O at (1774, 1624 cm^{-1}), and C=O stretching at (1080 cm^{-1}).

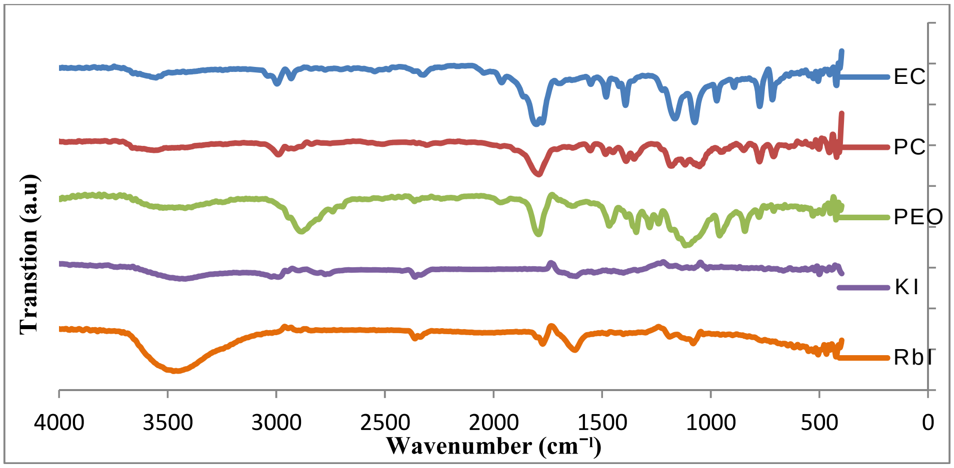

Fig. 1: FTIR for Raw material.

Fig.2, illustrate FTIR of electrolytes (SH1, SH5, and SH9), one can observe the shifting in CH2 stretching of PEO at wavenumbers from (3468 cm^{-1}) to (3483 cm^{-1}) for electrolyte SH1 and to (3437 cm^{-1}) for SH5 and SH9. This shifting of peaks is another way to prove the interactions between PEO and binary salt ascribed to the creation of a passing crosslinking complex between the ionic liquids and the ether oxygen of the PEO. However, the created moving state will dampen C-O-C stretching vibration, and the crystallization of PEO will reduce [12]. That reveals the amorphous behavior of PEO forms disorder arrangement in the polymer matrix. The difference in the shifting peaks of SH1 from SH5, SH9 causes by KI salt addition, which has a ratio of 45% while 5% for RbI. In contrast, SH5 electrolyte shows shifting at (1180 cm^{-1}) peak and become sharper. At equal weight concentration of the two salts that making the interactions between them more than the interactions each one of them with the polymer itself, this forms a less amorphous face.

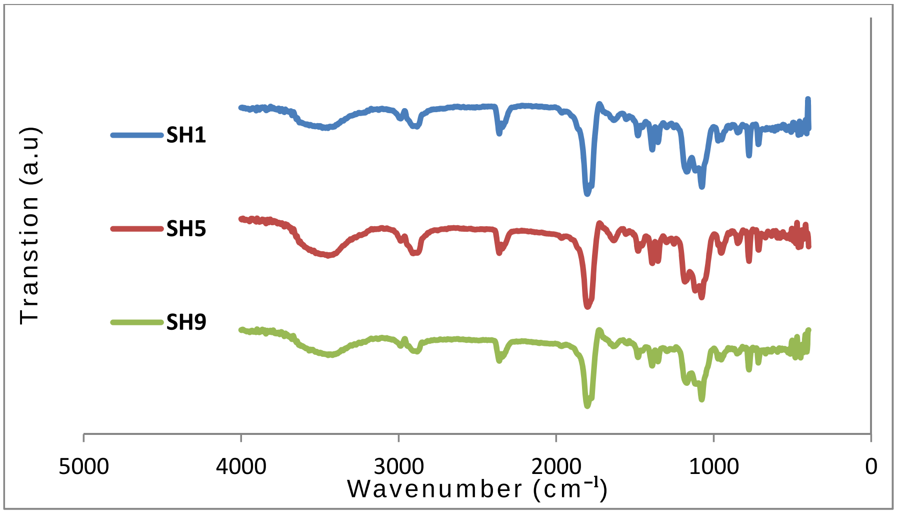

Fig. 2: FTIR for SH1, SH5, and SH9 electrolytes.

The conductivity of plasticized electrolytes (SH) as a function of temperature and different ratio (5-45 wt.%) for each binary salt (KI & RbI) over temperature range (293-343 K) illustrated in Fig.3. The conductance of gels polymer SH gradually increases by increasing temperature obeyed the Arrhenius type thermally activated process depending Eq. (2):

$$\sigma = \sigma_o \exp\{\frac{Ea}{KT}\} \tag{2}$$

where σ_o is a pre-exponential factor, Ea is activation energy for ionic mobility, K is Boltzmann constant, and T absolute temperature in Kelvin scale [13, 14]. In-gel polymer, the size, shape, and charge density of ions have independent and profound influences on the conductivity and the ionic strength [15]. With increasing temperature, the random phase turns into additional elastic, resulting in raised portion motion of the polymer chains as reflected by promoting conductance [16, 17]. As temperature increases, the electrolytes are easily expanded, therefore producing addition free volume [18, 19]. The conductivity is boosting as a result of promoting the mobility of ions and the segmental motion of polymer [20]. The highest value of conductivity reaches

(6.03×10^{-3} at 293 K and 2.246×10^{-2} at 343 K) S/cm for SH9 electrolyte which content (45%KI/5%RbI) from binary salt.

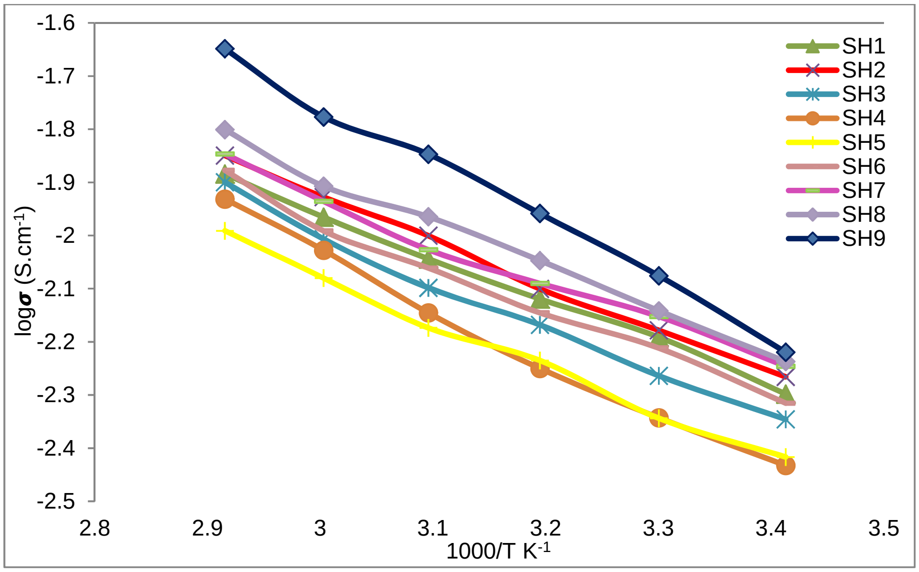

Fig.3: Temperature dependence of the ionic conductivity of the gel polymer electrolytes SH.

Fig.4, display of the effect for binary salts concentrations as a function of temperature on ionic conductivity. The curves beginning give the highest values for conductivity at the maximum amount of KI salt (45 %) and minimize the amount of RbI salt (5 %) of the binary salt. That indicates the contribution for KI salt more than RbI salt due to the big cation for Rb^+ where the ionic conductivity elevated with the rises of positively charged ion radius. That disagrees with the Stokes-Einstein relation, which clarifies the improvement of conductance for small radii K^+ cation [21].

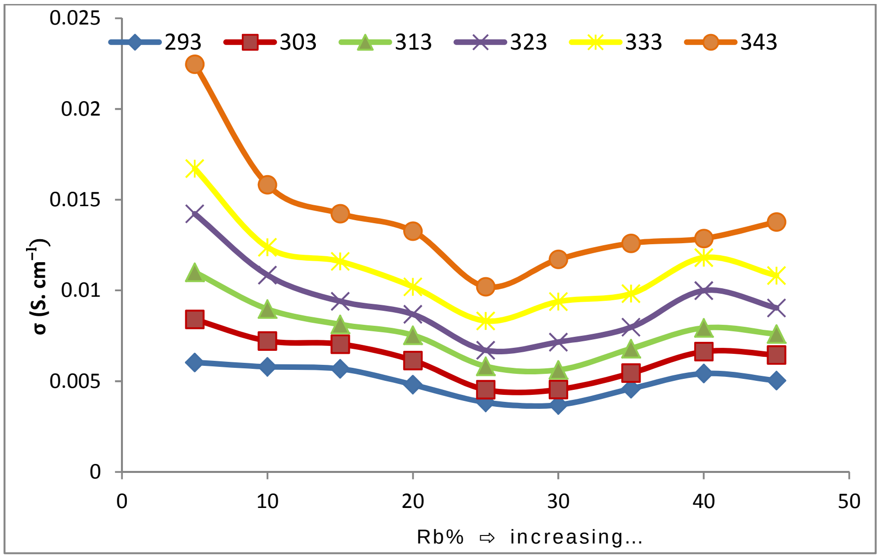

Fig. 4: Dependence of ionic conductivity on KI & RbI weight ratio in the gel polymer electrolytes SH.

The positively charged ion with a bigger size has lesser surface charge density, which results in low ion-dipole interaction force, and so the quicker positively charge migration, as shown in Fig.5. As the size of the bigger positively charges ion boost makes the polymer chains splay apart producing in a rise in polymer elasticity and capacity of voids by increases ionic dissociation leads to raising the separation of the polymer chains. The segmental motion of the polymer chains and the transport of ions improve, as the viscosity decreases producing in a drop in the mobility of the ions, thus increasing the activation energy. Salt dissolved enhances the ion conduction decreases the positively charged ion conduction, and negatively charged ion conductivity promotes the carrier density, and conductivity improves the ion conduction. For that types of electrolytes, the cation motion is related to the making and breaking of coordinate bonds thus resulting in transfer between coordinating positions whereas the negatively charged ion movement supported by an elastic and weak interacting surrounding [15].

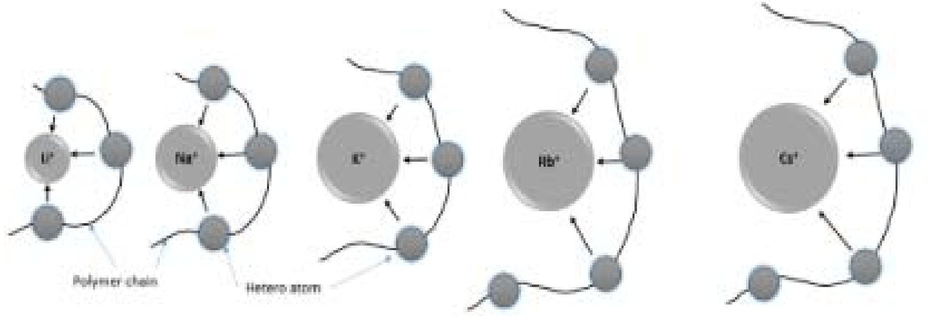

Fig.5: Schematic illustration in 2 dimensions to show the increase of polymer chain flexibility due to the swelling effect of the electrolyte with increasing size of the cation [15].

Larger cations facilitate ionic dissociation; besides, K^+ and Rb^+ are hard Lewis acids, and their forces lowered with increasing ionic radius. Consequently, the Lewis acid-base interactions with the heteroatoms in the polymer chain become weaker with the rising size of the positively charged ion. Subsequently, the ionic movement may elevate with rising positively charged ion volume. As for the conductivity, the decline at an equal ratio of to salt comes from reach to the saturation state which is attributable to decrees of iodide ion transport due higher concentration of large size cations species (KI^+, Rb^+) forms aggregation by effect ion-ion interaction or ionic multiples [22, 23]. The conductivity once again increased as a result of the decrease in RbI^+ cation, which has the most significant size cation in the concentration of the binary salt lead to reduce build aggregation.

The dielectric constant can estimate from Eq. (3):

$$\varepsilon_r = Z_i/ \omega C_o[Z_r^2 + Z_i^2] \qquad (3)$$

where ω is the angular frequency in Hertz (Hz), C_o is vacuum capacitance, and Z_r and Z_i are real and imaginary parts of impedance [24]. From Fig.6 at the slash frequency, the amounts of dielectric constant are elevated at room temperature. That was because of the polarization of dielectric substance which occurs in the frequency between

(100-10,000 Hz). Consequently, mobile ions that move about the polymer matrixes will collect at the surface between electrode and electrolyte. Thus, a different-charge layer is created [25, 26]. The mobile ions cannot orient with the direction of the applied field at higher frequency were a rapid cyclic inversion happens. The dielectric loss reduces along with a lowering in polarization as a result of the charge aggregation. This juvenile suggests a majority of relaxation mechanism [27, 28].

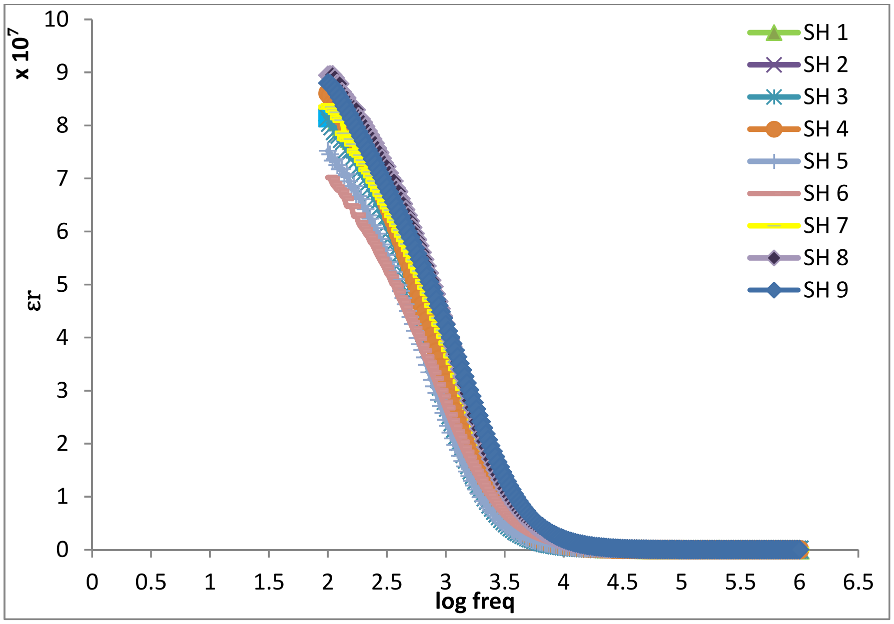

Fig.6: Dielectric constant vs. Log frequency at RT with different salts concentration for electrolytes SH.

The effect of temperature variation as a representative sample with dielectric constant at a fixed frequency (100 Hz) illustrated in Fig.7. The real part of dielectric function ε_r has a little increase with the increase of temperature from 293 to 343 K. The results confirm that both the dielectric behavior and the structural dynamics of the PEO material are thermally activated processes. The crystallinity of the host polymer reduced [29], at higher temperatures, the dipoles become relatively free to trend readily to the applied electric field parallel to a highly cross-linked material. Consequently, the dielectric response raise, which lead to elevated polarization [30-33]. At the end of curves found the maximum values for ε_r at highest temperature can attribute to the dissociation of ion aggregates and a higher degree of salt dissociation. The electrolyte SH9 owned the highest dielectric constant than other electrolytes, which contains 45%KI/5% RbI salts. This lead to the number of cation K^+ higher than Rb^+ cation and also it has a large size can occupy more volumes compare with creating amorphicity in the polymeric material improvement of conductivity for small radii cation which having the large charge density. As a result increase in ε_r is observed [34], also reveals that on further addition of salts, there is decrement of ε_r due to a reduction in chain segmental mobility, This agrees with previous results obtained.

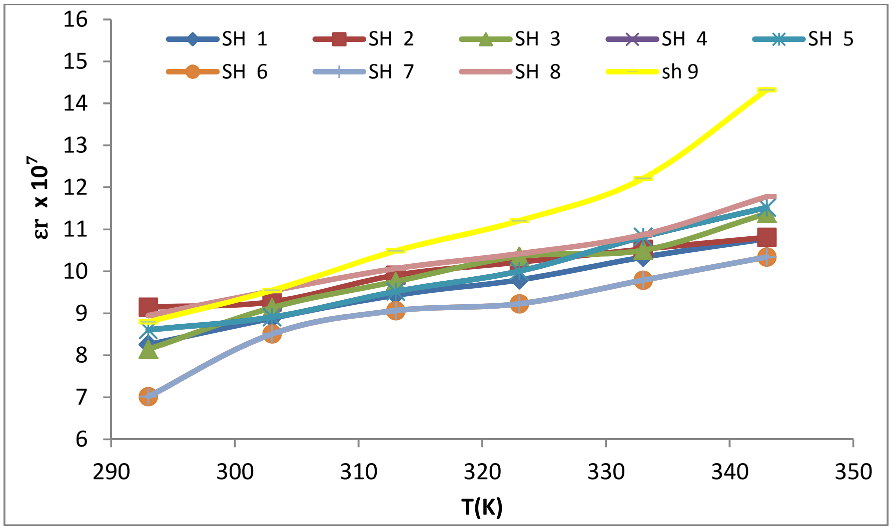

Fig.7: Dielectric constant vs. temperature with different salts weight ratio for electrolytes SH.

Conclusions

Serious of gel polymer electrolytes with PEO as a host matrix based on double salts (KI and RbI) prepared by using solution cast technique. The electrolyte SH9 which content (KI 45 %, RbI 5 %) owned higher value of conductivity of (6.03×10^{-3} at 293 K and 2.246×10^{-2} at 343 K) S/cm and the highest dielectric constant from the other electrolyte. This lead to the number of cation Rb^+ higher than K^+ cation and also it has a large size can occupy more volumes compare with creating amorphicity in the polymeric material improvement of conductivity for small radii cation which having the large charge density. Salt solvation improves the ion conduction reduces the cation conduction, and anion conductivity improves the carrier density, and conductivity improves the ion conduction.

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