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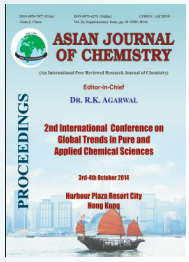

Molar Conductivity Behaviour of $LiClO_4$ in Poly(ethylene oxide) Solutions

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This article presents a study of the molar conductivity (Λ_0) behaviour of $LiClO_4$ in PEO_X solutions at 25 °C. The specific conductivity (κ) of the electrolyte systems were studied as a function of lithium salt concentration (C_{salt}), polymer concentration (C_{Poly}) and molecular weight (M_η). The electrolyte system of poly(ethylene oxide) (PEO_X) (M_η = 600, 1,000 and 4,000 Kg mol^{-1}) in acetonitrile has been prepared in a range of 0.0010-0.0030 g cm^{-3}, respectively was used as solvents to dissolved lithium perchlorate ($LiClO_4$). The κ of PEO_X solutions, has been measured as a function of C_{salt} at 25.0 °C using AC conductivity meter. The Λ_0, equilibrium constant (K_{eq}) and critical ion-pairs concentration (β) for $LiClO_4$ in PEO_X solutions at different C_{Poly} and molecular weight were determined after Ostwald's dilution law. It was noticed, as PEO_X concentration increased the Λ_0 value showed a decreasing trend, indicated the change of solvent properties to a better electrolyte system relative to $LiClO_4$ in acetonitrile (176.68 S cm^2 mol^{-1}) with an acceptable small error. This decreasing trend of Λ_0 gives a significant improvement in the total $LiClO_4$ dissociation particularly at higher PEO_X concentration in the electrolyte system. This been noticed with a much lower K_{eq} values relative to $LiClO_4$ in acetonitrile system at 25 °C. A similar observation was also noted for higher M_η PEO_X solutions. However, from β calculation it is noted that the low molecular PEO_X at lower C_{Poly} act as a better electrolyte compare to higher molecular PEO_X and a *vice versa* observation is noted at higher C_{Poly}. In conclusion, the addition of PEO_X into the $LiClO_4$ solution leads to the decreases of the Λ_0 value and enhances $LiClO_4$ dissociation particularly for higher PEO_X concentration at higher M_η. This might due to changes in its viscosity of the solution that interrelated with the Walden rule.

Keywords: Poly(ethylene oxide), Ostwald's dilution law, Critical ion-pairs concentration and equilibrium constant (K_{eq}).

INTRODUCTION

The study of salt-polymer solution serves as a powerful fundamental knowledge base for many advance application. Studies of salt-polymer solutions mainly contribute for a better understanding particularly for polymer electrolyte system that mostly applied in secondary battery system[1]. Salt-polymer solution is a hybrid system comprises of inorganic salt and polymer that dissolved in a solvent[2]. The individual components of the inorganic salt will dissociate due to the thermodynamic interactions between solvent and solute molecules in the electrolyte system. Hence, the added salt provides ions and the polymer help provide a medium for ion conduction[3,4]. Normally, in a salt-polymer solution system ions are said to coordinate to the polymer backbone and transport through the polymer medium *via* the long-ranged segmental motion of the polymer chains[5]. Examples of salt-polymer solution are lithium perchlorate ($LiClO_4$) in aqueous poly(ethylene oxide) (PEO) solution[6], $LiClO_4$ in solution of poly(ethylene oxide) and methanol[5] and sodium chloride in aqueous poly(vinyl alcohol) solution[7].

For a solid polymer electrolyte consists of semi-crystalline polymer added with salt, it is widely accepted that salts are molecularly dispersed in amorphous regions of the polymer. At low salt concentration, the crystalline phases do not contribute to conductivity and the ion dynamics is essentially governed by the segmental motion of the amorphous phases in semi-crystalline polymer. Dissolution of the salt is accompanied by solvation of cation by monomer units of the chain molecules[8-14]. Poly(ethylene oxide) is one the most popular polymer hosts used in solid polymer electrolyte[15-21]. The evaluation of ion-polymer and ion-ion interactions in PEO-based solid polymer electrolyte was studied by FTIR by monitoring interaction between metal ion and oxygen atom from the poly(ethylene

oxide)[13,14,22]. The complication of interpretation of results for ion-polymer and ion-ion interactions is mainly due to the co-existing of crystalline and amorphous phases in the systems.

The solid polymer electrolyte consists of semi-crystalline polymer, the ionic conduction mainly occurs in amorphous regions of the salt-polymer complexes and the local polymer segmental motion plays an important role in the ions transport mechanism[23,24]. This argument is supported by the work of Harris *et al.*[24], for sodium triflate ($NaCF_3SO_3$) in poly(ethylenimine) by NMR study. The segmental motion of the polymer and ions mobility belonging to the amorphous phase is higher than crystalline phase. Thus, the amorphous phase of polymer-salt system for solid polymer electrolyte is mainly responsible for the ionic percolation pathway[23,25,26].

Most of the time, indirect methods were used to interpret the salt dissociation and interaction of salt with polymer for polymer electrolytes in solid polymer electrolyte that subjected to lot of theories and assumption. As an alternative for above situation, measurement of conductivity for dilute-solution of salt-polymer system serves as an alternative and a powerful tool in elucidation of the ion-ion and ion-polymer interactions. Such system may adequately reflect the ion-ion and ion-polymer interactions in amorphous regions of the solid polymer electrolyte consist of semi-crystalline polymer.

Therefore, in the present study, poly(ethylene oxide) with different mass-average molecular weights (M_η) doped with $LiClO_4$ in acetonitrile was chosen to elucidate the solubility behaviour of $LiClO_4$ in poly(ethylene oxide) solutions at 25 °C. A simple AC conductivity meter was adopted in measuring the specific conductivity (κ) of the $LiClO_4$-PEO_X solutions. Ostwald's dilution law for weak electrolytes is applied for estimation of limiting molar conductivity (Λ_0) value and dissociation behaviour of $LiClO_4$ in PEO_X-dilute solutions in a range of poly(ethylene oxide) concentrations (C_{poly}), $LiClO_4$ concentrations (C_{salt}) and M_η of poly(ethylene oxide).

Theoretical background: Electric conductivity was studied in polymer solutions as a function of salt concentration. Suppose, we have an electrolyte of the type $K_{v+}^{z+}A_{v-}^{z-}$ that may dissociate in the following way

$$K_{v+}^{z+}A_{v-}^{z-} \rightarrow v_+K^{z+} + v_-A^{z-}$$

The electrochemical valence is defined as follows:

$$n_e = v_+z_+ = v_-|z_-|$$

The concentration c of an electrolyte in a solution is usually given by

$$c = \frac{\text{number of moles of electrolyte}}{\text{volume of solution}} = \frac{n}{\text{liter(solution)}}$$

The quantity $n_e \cdot c$ is called equivalent concentration. It serves to define the so-called molar conductivity Λ. It is given by

$$\Lambda = \frac{\kappa}{n_e c} \quad (1)$$

where κ is the specific conductivity which is the reciprocal of specific resistance. Molar conductivity is usually given in units as follows:

$$[\Lambda] = \Omega^{-1}\ cm^2\ mol^{-1} \quad (2)$$

The degree of dissociation α might be defined as follows:

$$\alpha = \frac{\Lambda_{c'}}{\Lambda_o} \rightarrow \alpha = \frac{\Lambda_c}{\Lambda_o} \text{ for } c \rightarrow 0 \quad (3)$$

where quantity $\Lambda_{c'}$ symbolizes the equivalent conductance at ionic concentration c' in a system with electrolyte concentration c and Λ_o is the equivalent conductance in the limit $c \rightarrow 0$. The ionic concentration c' is unknown, however, $c' \rightarrow c$ for $c \rightarrow 0$. Eqn. 3 can be seen as valid only if the concentration of ions in the system is very small. At finite electrolyte concentration c, when also the ionic concentration is not small anymore, one has to generalize eqn. 3 by introducing a so-called conductance coefficient (f), we say

$$c' = f\alpha c \quad (4)$$

$$f\alpha = \frac{\Lambda_c}{\Lambda_o} \text{ or } f = \frac{\Lambda_c}{\Lambda_o} \quad (5)$$

With the second equation, the part of the non-dissociated electrolyte is neglected, *i.e.*, $\alpha \approx 1$. This is justified since only ions contribute to conductivity. The conductivity coefficient is not identical with the (thermodynamically defined) activity coefficient, but describes also deviations from infinite dilution. It refers to deviation of conductivity Λ from the stage of infinite dilution.

Let us formulate the equilibrium constant for dissociation of $LiClO_4$. It reads with introducing the degree of dissociation (α):

$$K_{eq} = \frac{C_{Li} + C_{ClO_4^-}}{C_{LiClO_4}C_0} = \frac{\alpha C \alpha C}{(1-\alpha)CC_0} \quad (6)$$

where c is the (total) concentration of $LiClO_4$ in the solvent in moles per liter. In eqn. 6 concentrations were inserted in c/c_o (with c_o = 1 mol/L) to keep K_{eq} dimensionless. Introducing the equivalent conductance according to (3), we get

$$K_{eq} = \frac{(\Lambda/\Lambda_0)^2 c}{(1-\Lambda/\Lambda_0)c_0} \quad (7)$$

Upon rearranging, eqn. 7, becomes

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + \frac{\Lambda}{\Lambda_0}\frac{C}{K_{eq}\Lambda_0 C_0} \quad (8)$$

Since (3) can only be used in the limit $c \rightarrow 0$, we have $\Lambda/\Lambda_o \approx 1$. Therefore, it follows

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + \frac{C}{K_{eq}\Lambda_0 C_0} \text{ for } c \rightarrow 0 \quad (9)$$

A plot of Λ^{-1} *versus* in the limit $c \rightarrow 0$ will give a straight line with the intercept Λ_o^{-1} and the slope[27-29] $(K_{eq}\Lambda_0)^{-1}$.

EXPERIMENTAL

Poly(ethylene oxide) with different M_ηs was purchased from Sigma-Aldrich Chemical Company with purity ≥ 99 %. PEO_{600}, PEO_{1000} and PEO_{4000} represent PEO_X with M_η = 600, 1,000 and 4,000 Kg mol^{-1}, respectively. All the PEO_X will only

use after the purification step. To purify PEO_X, a re-precipitation method by dissolving it in polar and precipitate in non-polar solvent has been applied. This has been done by dissolving an appropriate amount of the PEO_X in the analytical reagent grade of chloroform to make a 2 % weight/weight (w/w) solution. The solution is stirred continuously for 48 h at 50 °C to ensure complete dissolution. The solution was concentrated to half of its initial volume using a rotary evaporator.

The final viscous PEO_X solution was poured into the analytical reagent grade of *n*-hexane for the re-precipitation of the PEO_X. After decanting off the solvent, the PEO_X sample is transferred into a Petri dish and it was left dry overnight in a fume hood. Later, the solid sample of PEO_X is further dried in conventional oven for 48 h and then transferred into a vacuum oven for another 48 h, respectively at 50 °C. The purified poly(ethylene oxide) is kept in the electronic desiccator under an atmosphere of dry nitrogen to exclude any moisture absorption and the PEO_X sample will only take off from the desiccator before its further use.

Anhydrous $LiClO_4$ with purity > 99 % was obtained from Acros Organic and dried in a vacuum oven at 100 °C for 48 h to eliminate any traces of water before dissolution. High-performance liquid chromatography grade of acetonitrile with the purity > 99.99 % (Fisher Scientific, Leicestershire, UK) was used as supplied to dissolve $LiClO_4$ and PEO_X. The organic solvent was kept dry by addition molecular sieves (Merck, Darmstadt Germany) with pore diameter 3Å.

Apparatus and procedure: Preparation of the salt-polymer solution system for the conductivity measurement was carried out under a controlled environment to minimise error in κ measurements. The temperature of the laboratory was controlled at 25 ± 2 °C. This has been done in order to avoid variation in the cell constant value for the probe used for the conductivity measurements. The same cell constant value is used to determine the κ value for the electrolyte systems. Thus, an accurate determination of the cell constant at a relatively constant temperature will minimize errors in κ value. The κ measurements for the salt-polymer solution for series of C_{salt} concentrations (10^{-3} mol cm^{-3} – 10^{-6} mol cm^{-3}) were prepared from a stock solution of known PEO_X concentration (C_{Poly}) using acetonitrile as a solvent shown in Table-1. Subsequently, the solution was stirred for 48 h at 50 °C before further use.

TABLE-1
C_{Poly} RANGE FOR DIFFERENT POLY(ETHYLENE OXIDE) IN ACETONITRILE AT 25 °C

Poly(ethylene oxide)	C_{Poly} (g cm^{-3})
PEO_{600}	0.0010-0.0030
PEO_{1000}	0.0010-0.0030
PEO_{4000}	0.0010-0.0030

Then, approximately 12-15 subsequent dilutions were carried out from the stock solution for the conductivity measurement. Thus, the conductivity measurement is carried out using Mettler-Toledo Seven Compact S230 Conductivity meter (Schwer-zenbach, Switzerland) with its dip-type conductivity probe (electrode) InLab®741 (measuring range 0.001-500 μS cm^{-1}). This probe comprise of built-in temperature sensor with an accuracy of ± 0.4 °C. This conductivity meter has the feature of automatic temperature compensation. All the displayed κ from the conductivity meter is the κ at referred temperature of 25.0 ± 0.4 °C. The cell constant of InLab® 741 were estimated by automatic calibration on a daily basis. The primary standard of an aqueous solution of potassium chloride (KCl) (Mettler-Toledo, Schwerzenbach, Switzerland) at concentration 0.0005 mol dm^{-3} with the quantities κ at 84 μS cm^{-1} at 25.0 °C was used for the calibration with the conductivity meter attached[30,31] to InLab® 741.

All of the preparation steps of the liquid electrolyte solution and conductivity measurements are carried out in a glove box under nitrogen gas condition to avoid the absorption of carbon dioxide gas into the salt solution that might cause an error in conductivity measurement particularly at a low salt concentration. All the glassware used was cleaned with concentrated chromic sulphuric acid. Then, it was further cleaned with Extran® detergent solution (Merck, Darmstadt, Germany) and rinsed with tap water and finally with deionized water. The glassware was dried in the conventional oven at 100 °C for 24 h. The glassware was thermally equilibrated to the laboratory room temperature before use[31].

RESULTS AND DISCUSSION

Polymer has low conductivity in its natural state. However, the conductivity can be improved by incorporating additive in the form of inorganic salt and/or solvent into the polymer matrix to enhance the ions mobility in the electrolyte system. Therefore, the basic electrochemical quantity that allows for study of variation of molecular mass of PEO_X for optimization of the properties of the electrolyte system is the molar conductivity (Λ). This quantity was determined as a function of $LiClO_4$ concentration (C_{salt}) at different PEO_X concentration (C_{Poly}) and constant temperature. The critical point is the accurate determination of electrolytic conductivity (κ) at sufficiently low C_{salt} ($C_{salt} \leq 10^{-5}$ mol cm^{-3}) at 25.0 °C. It is important since this is a prerequisite for extrapolation of molar conductivity to zero salt concentration. Fig. 1 is plotted after eq. 9 for $LiClO_4$ in acetonitrile and $LiClO_4$ in PEO_{600} for different C_{Poly} at 25 °C.

From Fig. 1, it is noted as C_{salt} increases the Λ^{-1} value increases too. This been observed for all electrolyte system at different C_{Poly}. The same observation also been noted for PEO_{1000} and PEO_{4000} as shows in Figs. 2 and 3. This indicates polymer play a significant role in ions mobility for polymer electrolyte system. On top of this, used of PEO_X at higher C_{Poly} have further proved to contribute enhancement in ions conductivity in polymer electrolyte system.

Regression analysis after eqn. 9 for Figs. 1-3 is shown in Tables 2 to 4. The Λ_0 and the equilibrium constant (K_{eq}) value for $LiClO_4$ in acetonitrile and $LiClO_4$ in PEO_{600}, PEO_{1000} and PEO_{4000} at 25 °C is determined after the extrapolation to zero concentration and recalculation after eqn. 9. Quantity Λ_0 for $LiClO_4$ in acetonitrile in this study is 176.68 S cm^2 mol^{-1} is only at 2 % of error as compared to that of the expected value[32] at 173 S cm^2 mol^{-1}. This may suggest the experimental data and the method applied in determination of Λ_0 for this study

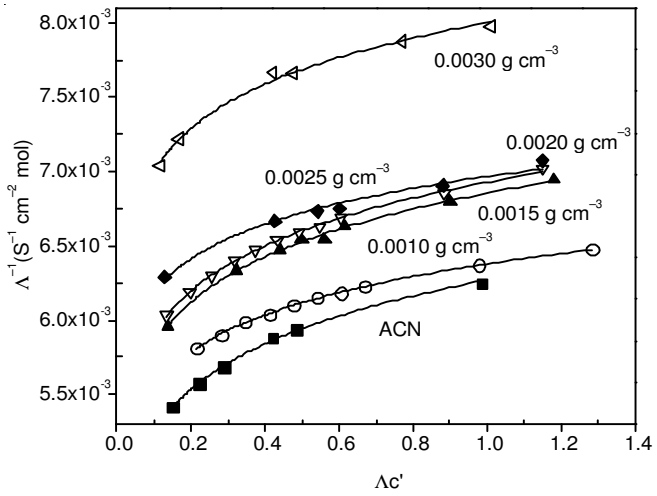

Fig. 1. Λ^{-1} *versus* $\Lambda c'$ for $LiClO_4$ in acetonitrile and in PEO_{600} for different C_{Poly} at 25 °C

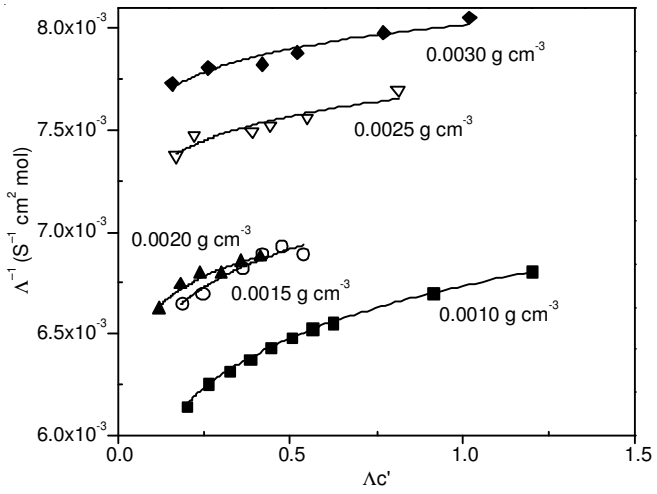

Fig. 2. Λ^{-1} *versus* $\Lambda c'$ for $LiClO_4$ in PEO_{1000} for different C_{Poly} at 25 °C

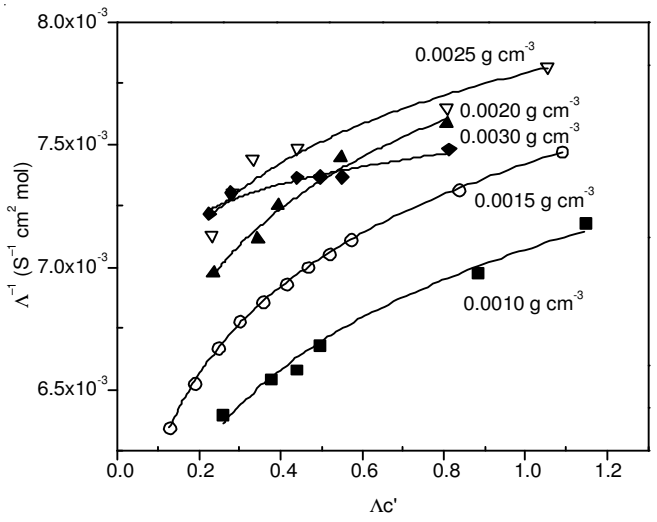

Fig. 3. Λ^{-1} *versus* $\Lambda c'$ for $LiClO_4$ in PEO_{4000} for different C_{Poly} at 25 °C

is acceptable with a relatively small error. Hence, the same approach is further adopted for all remaining electrolyte systems.

TABLE-2
REGRESSION FUNCTION AFTER EQN. 9, QUANTITY Λ_0 AND K_{eq} FOR $LICLO_4$ IN ACETONITRILE AND PEO_{600} SOLUTIONS AT 25 °C

System (g cm^{-3})	Regression function After Eq. (11)	Λ_o (S cm^2 mol^{-1})	K_{eq}	r^2 (Correlation)
Acetonitrile	$\Lambda^{-1} = 5.45\times10^{-4}\,\Lambda c' + 5.66\times10^{-3}$	176.68	5.88×10^{-2}	0.9964
0.0010	$\Lambda^{-1} = 7.33\times10^{-4}\,\Lambda c' + 5.74\times10^{-3}$	174.22	4.49×10^{-2}	0.9906
0.0015	$\Lambda^{-1} = 1.07\times10^{-3}\,\Lambda c' + 5.98\times10^{-3}$	167.22	3.34×10^{-2}	0.9731
0.0020	$\Lambda^{-1} = 9.67\times10^{-4}\,\Lambda c' + 6.11\times10^{-3}$	163.67	3.86×10^{-2}	0.9887
0.0025	$\Lambda^{-1} = 7.78\times10^{-4}\,\Lambda c' + 6.30\times10^{-3}$	158.73	5.10×10^{-2}	0.9918
0.0030	$\Lambda^{-1} = 6.91\times10^{-4}\,\Lambda c' + 7.37\times10^{-3}$	135.69	7.86×10^{-2}	0.9917

TABLE-3
REGRESSION FUNCTION AFTER EQN. (9), QUANTITY Λ_0 and K_{eq} FOR $LiClO_4$ IN PEO_{1000} SOLUTIONS AT 25 °C

System (g cm^{-3})	Regression function After Eq. (11)	Λ_o (S cm^2 mol^{-1})	K_{eq}	r^2 (Correlation)
0.0010	$\Lambda^{-1} = 8.93\times10^{-4}\,\Lambda c' + 6.03\times10^{-3}$	165.84	4.07×10^{-2}	0.9947
0.0015	$\Lambda^{-1} = 9.91\times10^{-4}\,\Lambda c + 6.46\times10^{-3}$	154.80	4.21×10^{-2}	0.9926
0.0020	$\Lambda^{-1} = 7.66\times10^{-4}\,\Lambda c' + 6.58\times10^{-3}$	151.98	5.65×10^{-2}	0.9922
0.0025	$\Lambda^{-1} = 6.10\times10^{-4}\,\Lambda c' + 7.25\times10^{-3}$	137.93	8.62×10^{-2}	0.9834
0.0030	$\Lambda^{-1} = 3.66\times10^{-4}\,\Lambda c' + 7.69\times10^{-3}$	130.03	1.62×10^{-1}	0.9759

TABLE-4
REGRESSION FUNCTION AFTER EQN. (9), QUANTITY Λ_0 AND K_{eq} FOR $LiClO_4$ IN PEO_{4000} SOLUTIONS AT 25 °C

System (g cm^{-3})	Regression function After Eq. (11)	Λ_o (S cm^2 mol^{-1})	K_{eq}	r^2 (Correlation)
0.0010	$\Lambda^{-1} = 8.69\times10^{-4}\,\Lambda c' + 6.21\times10^{-3}$	161.03	4.44×10^{-2}	0.9917
0.0015	$\Lambda^{-1} = 1.22\times10^{-3}\,\Lambda c + 6.42\times10^{-3}$	155.76	3.38×10^{-2}	0.9961
0.0020	$\Lambda^{-1} = 1.95\times10^{-3}\,\Lambda c' + 6.49\times10^{-3}$	154.08	2.16×10^{-2}	0.9835
0.0025	$\Lambda^{-1} = 4.46\times10^{-4}\,\Lambda c' + 7.32\times10^{-3}$	136.61	1.20×10^{-2}	0.9882
0.0030	$\Lambda^{-1} = 4.18\times10^{-4}\,\Lambda c' + 7.21\times10^{-3}$	138.70	1.24×10^{-1}	0.9817

Tables 2-4 summarizes the regression function after eqn. 9, quantity Λ_0 and K_{eq} for all the electrolyte system at 25 °C. In general, the addition of PEO_X cause decreases in quantity Λ_0 in respective to Λ_0 of $LiClO_4$ in acetonitrile. It is also noted, higher M_η of PEO_X at C_{Poly} = constant demonstrate a descending Λ_0. This indicates that the polymer solution is approaching to the behaviour of strong electrolyte at higher C_{Polys}. In addition, as the C_{Poly} increases the K_{eq} increases too, this indicate the dissociation of $LiClO_4$ into it individual ions are take place especially at higher C_{Polys} particularly for higher M_η PEO_X. Therefore, it can be suggest that PEO_X not only used as a backbone for the ion transport in polymer electrolyte, but it also play significant role to enhance dissociation of $LiClO_4$ and change solvent properties of the electrolyte to a much better electrolyte system respective to $LiClO_4$ in acetonitrile.

Fig. 4 suggests addition of PEO_X cause decreases in quantity Λ_0 respective to Λ_0 of $LiClO_4$ in acetonitrile at different C_{Poly} at 25.0 °C. It is obvious that Λ_0 (C_{Poly}) varies linearly with polymer concentration in the range of sufficiently low polymer concentration. Ideally, the extrapolation of the Λ_0 (C_{Poly}) to zero concentration should match the Λ_0 value of $LiClO_4$ in acetonitrile (176.68 S cm^2 mol^{-1}) as indicated by arrow in Fig. 4. However, this extrapolation much shifted from the expected value. Therefore, this is assumed solely caused by imprecise selection of Λ^{-1} data during the extrapolation after

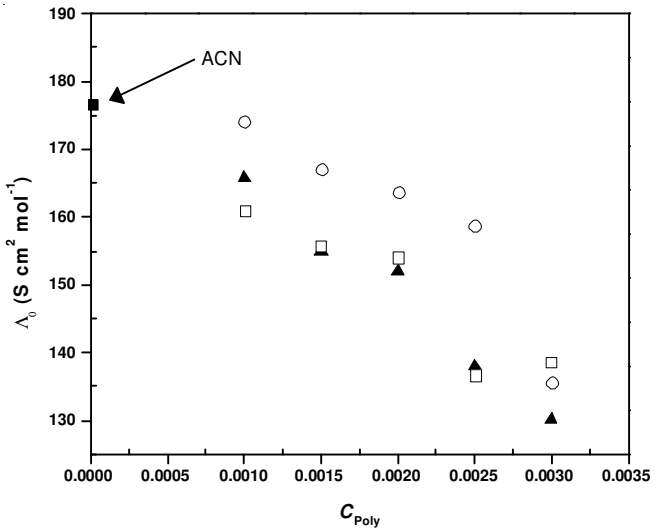

Fig. 4. Regression curves for quantity Λ_0 *versus* C_{PEO600} (○), $C_{PEO1000}$ (▲) and $C_{PEO4000}$ (□) in acetonitrile at 25 °C

eqn. 9 and its independent of C_{Poly}. Accepting this assumption, the normalization of Λ_0 (C_{Poly}) has been carried out. Table-5 shows the regression function after normalization, limiting molar conductivity value after normalization (Λ_0') and critical ion-pairs concentration (β) for $LiClO_4$ in PEO_X solutions at 25 °C.

TABLE-5
REGRESSION FUNCTION AFTER NORMALIZATION, LIMITING MOLAR CONDUCTIVITY AFTER NORMALIZATION (Λ_0') AND CRITICAL ION-PAIRS CONCENTRATION (β) FOR $LiClO_4$ IN PEO_{600} to PEO_{4000} SOLUTIONS AT 25 °C

System (g cm^{-3})	Regression function (after normalization)	Λ_0'	$10^6\beta$ (mol cm^{-3})
PEO_{600}			
0.0010		166.68	2.12
0.0015	Λ_0' = 176.68 S cm^2 mol^{-1}– 10004	161.67	1.19
0.0020	cm^5 g^{-1} mol^{-1} C_{Poly}	156.67	1.80
0.0025		151.67	2.49
0.0030		146.67	5.45
PEO_{1000}			
0.0010		162.82	0.769
0.0015	Λ_0' = 176.68 S cm^2 mol^{-1}- 13860	155.89	0.293
0.0020	S cm^5 g^{-1} mol^{-1} C_{Poly}	148.96	1.17
0.0025		142.03	2.42
0.0030		135.10	5.83
PEO_{4000}			
0.0010		161.69	0.180
0.0015	Λ_0' = 176.68 S cm^2 mol^{-1}- 14988 S	154.20	0.346
0.0020	cm^5 g^{-1} mol^{-1} C_{Poly}	146.70	1.14
0.0025		139.21	2.20
0.0030		131.72	6.93

From Table-5, it can be summarizes that PEO_X in the electrolyte system has contributed for better dissociation of $LiClO_4$ (α) eqn. 5 and enhance ionic conductivity. This can be monitor with the decreasing trend of Λ_0 value as the C_{Poly} increases. In addition, it is also noted that molecular weight of PEO_X also an important factor that contribute for the changes in Λ_0 value. Therefore, this trend eventually influence the salt dissociation behaviour in the electrolyte system at different C_{Poly}. It is well understood that concentration of $LiClO_4$ that correspond to Λ_0 that been determine after eqn. 9 for each system is assumed as a point to have 100 % of $LiClO_4$ dissociation. Any concentration of $LiClO_4$ above the corresponded Λ_0 might result ion-pairing in the electrolyte system.

Therefore, this might suggest the present of ionic equilibria in the electrolyte solution as the C_{salt} increases. Hence, the critical ion-pairs concentration (β) is calculated, is a $LiClO_4$ concentration that respond as a separation point before the ion-pairing became demined in the electrolyte system. This salt concentration can be estimated using the Λ_0' for each electrolyte system. Below β the electrolyte system is assumed to have a 100 % of sal dissociation and the ions (cation and anion) in the electrolyte system is said to have minimum ion-ion interactions[33,34]. Consequently, due to less ion-ion interactions in the system the ions are believed to have better ions mobility in the electrolyte. Therefore, the β can be approximately equal to the C_{salt} that correspond to Λ_0' for salt-polymer system as calculated in Table-5.

Fig. 5 shows the critical ion-pairs concentration (β) of $LiClO_4$ in PEO_X solutions for different C_{Poly} at 25.0 °C. In overall, from Fig. 5 it can be suggest that the addition of PEO_X to acetonitrile has result in the increases of degree of dissociation of $LiClO_4$ at 25.0 °C in the electrolyte system particular at a higher C_{Poly}. The enhancement of α may be due to strong electrostatic interaction between the cation ion and lone pair electrons of the ether oxygen in PEO_X[35]. Besides, for higher M_ηs PEO_X solution its shows different dissociation behaviour of $LiClO_4$ when it change from dilute to concentrated electrolyte system. It is noted, the low molecular mass PEO_X at lower C_{Poly} act as a better electrolyte compared to higher molecular PEO_X. However, this behaviour shows a total changes at higher C_{Poly}, where at higher molecular mass PEO_X act as a much better electrolyte compare to lower molecular mass PEO_X. This behaviour is believed due to the changes in viscosity of the solution. In principle, the decreases in limiting molar conductivity of a given electrolyte in different solvent can be attributed to the viscosity effect that, according to the Walden rule, requires constant values of the viscosity-conductivity product[36].

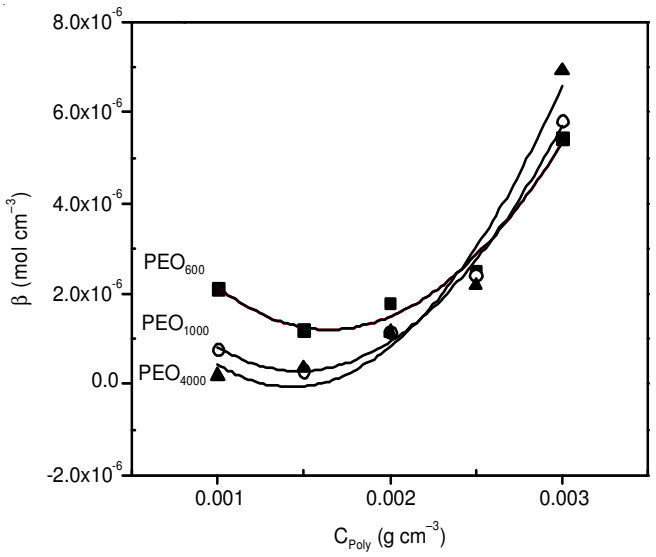

Fig. 5. Critical ion-pairs concentration (β) *versus* C_{Poly} for $LiClO_4$ in (■) PEO_{600}, (○) PEO_{1000} and (▲) PEO_{4000} at 25.0 °C

Conclusion

It was highlighted that the liquid polymer electrolytes have been proven to be especially fruitful in providing an improved understanding of the fundamental physical chemistry of salt-polymer system. In general, as the C_{Poly} increases, quantity Λ_0 tends to show a descending trend at constant M_η. Lower value of Λ_0 which is smaller than the Λ_0 value of $LiClO_4$ in acetonitrile, this suggests that the system are turning from a weak electrolyte to a stronger electrolyte system. The addition of PEO_X into $LiClO_4$ in acetonitrile solution increases the dissociation of $LiClO_4$ in acetonitrile particularly at higher C_{Poly}. The calculation of β for the electrolyte system shows a positive relationship that corresponds well at different C_{Poly} as well as at different M_η of PEO_X.

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REFERENCES

1. J. Barthelt, H.J. Gores, R. Neueder and A. Schmid, *Pure Appl. Chem*., **71**, 1705 (1999).
2. G.G. Cameron and M.D. Ingram, in eds.: J.R. MacCallum and C.A. Vincent, Liquid Polymer Electrolytes, In: Polymer Electrolyte Reviews-2, Elsevier Applied Science, London, pp. 157-190 (1989).
3. S.S. Sekhon, *Bull. Mater. Sci*., **26**, 321 (2003).
4. L. Edman, M.M. Doeff, A. Ferry, J. Kerr and L.C. De Jonghe, *J. Phys. Chem. B*, **104**, 3476 (2000).
5. P.A. Banka, J.C. Selser, B. Wang, D.K. Shenoy and R. Martin, *Macromolecules*, **29**, 3956 (1996).
6. I.F. Hakem, J. Lal and M.R. Bockstaller, *J. Polym. Sci*., **44**, 3642 (2006).
7. H. Yang, Y. Yan, P. Zhu, H. Li, Q. Zhu and C. Fan, *Eur. Polym. J*., **41**, 329 (2005).
8. A. Ferry, G. Oradd and P. Jacobsson, *J. Chem. Phys*., **108**, 7426 (1998).
9. F.E. Bailey and J.V. Koleske, Poly(ethylene oxide), Academic Press Inc. Ltd., New York (1976).
10. J.R. Fried, in eds.: N. Radhuber, B. Goodwin, and M. Vincente, Polymer for Advanced Technologies, In: Polymer Science & Technology, Prentice Hall Professional Technical Reference, United State, edn. 2, pp. 485-529 (2008).
11. W. Wieczorek, A. Zalewska, D. Raducha, Z. Florjanczyk, J.R. Stevens, A. Ferry and P. Jacobsson, *Macromolecules*, **29**, 143 (1996).
12. D. Brandell, Understanding Ionic Conductivity in Crystalline Polymer Electrolytes, Digital Comprehensive Summaries, Faculty of Science and Technology, Uppsala Universitet, Uppsala, Sweden (2005).
13. S. Chintapalli, C. Zea and R. Frech, *Solid State Ion*., **92**, 205 (1996).
14. S.J. Wen, T.J. Richardson, D.I. Ghantous, K.A. Striebel, P.N. Ross and E.J. Cairns, *J. Electroanal. Chem*., **408**, 113 (1996).
15. Q. Xiao, X. Wang, W. Li, Z. Li, T. Zhang and H. Zhang, *J. Membr. Sci*., **334**, 117 (2009).
16. T.M.W.J. Bandara, B.E. Mellander, I. Albinsson and M.A.K.L. Dissanayake, *Solid State Ion*., **180**, 362 (2009).
17. G. Derrien, J. Hassoun, S. Sacchetti and S. Panero, *Solid State Ion*., **180**, 1267 (2009).
18. L. Wang, W. Yang, J. Wang and D.G. Evans, *Solid State Ion*., **180**, 392 (2009).
19. K. Hanai, K. Kusagawa, M. Ueno, T. Kobayashi, N. Imanishi, A. Hirano, Y. Takeda and O. Yamamoto, *J. Power Sources*, **195**, 2956 (2010).
20. Y. Zhao, R. Tao and T. Fujinami, *Electrochim. Acta*, **51**, 6451 (2006).
21. M. Marzantowicz, J.R. Dygas, F. Krok, A. Tomaszewska, Z. Florjanczyk, E. Zygad³o-Monikowska and G. Lapienis, *J. Power Sources*, **194**, 51 (2009).
22. M.Z.A. Yahya and A.K. Arof, *Eur. Polym. J*., **39**, 897 (2003).
23. M.E. Ries, M.G. Brereton, J.M. Cruickshank, P.G. Klein and I.M. Ward, *Macromolecules*, **28**, 3282 (1995).
24. C.S. Harris, D.F. Shriver and M.A. Ratner, *Macromolecules*, **19**, 987 (1986).
25. A. Johansson and J. Tegenfeldt, *Macromolecules*, **25**, 4712 (1992).
26. A.C. Bloise, J.P. Donoso, C.J. Magon, A.V. Rosario and E.C. Pereira, *Electrochim. Acta*, **48**, 2239 (2003).
27. K.J. Laidler, J.H. Meiser and B.C. Sanctuary, in eds.: R. Stratton, M. Papile and K. Dinovo, Solutions of Electrolytes, In: Physical Chemistry, Houghton Mifflin Company, New York, edn. 4, pp. 263-307 (2003).
28. P.W. Atkins, Molecules in Motion: The Motion of Molecules and Ions in Liquids, In: Physical Chemistry, Oxford University Press, USA, edn. 5, pp. 830-845 (1995).
29. S. Kislaya, in ed.: T. Wasan, Arrhenius Theory of Electrolytic Dissociation, In: Problems in Physical Chemistry, Discovery Publishing House Pvt. Ltd., Delhi, India, edn. 1, pp. 199-230 (2011).
30. H. Hanibah, A. Ahmad and N.H. Hassan, *Electrochim. Acta*, **147**, 758 (2014).
31. H. Hanibah, N.H. Hassan and A. Ahamad, *Asian J. Chem*., **26**, 4897 (2014).
32. J. Barthel, L. Iberl, J. Rossmaier, H.J. Gores and B. Kaukal, *J. Solution Chem*., **19**, 321 (1990).
33. M. Spiro, in ed.: A. Weissberger, Determination of Transference Number, In: Technique of Organic Chemistry, Interscience Publishers, Inc, New York, edn 3, vol. 1 (1960).
34. T. Shedlousky, in ed.: A. Weissberger, Conductometry, In: Technique of Organic Chemistry, Interscience Publishers, Inc, New York, edn. 3, vol. 1 (1960).
35. A. Chagnes, B. Carre, P. Willmann and D. Lemordant, *Electrochim. Acta*, **46**, 1783 (2001).
36. A. D'Aprano, B. Sesta, N. Proietti and V. Mauro, *J. Solution Chem.*, **26**, 649 (1997).