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Limiting Molar Conductivity Behaviour of ENR-50 Electrolyte in Mixed Solvent System at Ambient Temperature

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The present research investigates the behaviour of the limiting molar conductivity (Λ_o) of ENR-50/$LiClO_4$ in a mixed solvent system comprising tetrahydrofuran (THF) and acetonitrile (ACN) at ambient temperature. The study uses the power law, to determine the Λ_o value of ENR-50/$LiClO_4$/THF:ACN at a specific reference salt concentration. The ENR-50/$LiClO_4$ electrolyte system was prepared with a fixed THF:ACN ratio of 8:2, at different ENR-50 concentration of range between 0.001-0.003 g/cm^3. The correlation values obtained for the three polymer concentrations ranged from 0.9959 to 0.9966. Regression analysis revealed that as the polymer concentration increases, the Λ_o decreases, indicating an inverse relationship which suggesting an enhanced ion dissociation due to an increase in total free-moving ions within the liquid polymer electrolyte system. The characterization of ENR-50/$LiClO_4$/THF:ACN was verified through ATR-FTIR spectroscopy, confirming the ion dipole interaction between the C-O-C group of ENR-50 and Li ions.

Keywords: ENR-50, Electrolyte, Mixed solvent system, Limiting molar conductivity, Tetrahydrofuran, Acetonitrile.

INTRODUCTION

The development of polymer electrolytes has received significant attention since Fenton's groundbreaking work, which revolutionized the field of ion-conducting polymers and their application as electrolytes in solid-state rechargeable lithium batteries [1]. This heightened interest is primarily driven by the wide range of potential applications that polymer electrolytes offer in various electrochemical devices, including high-energy density lithium-ion rechargeable batteries, fuel cells, sensors, electrochromic windows, and supercapacitors [2,3]. Recently, natural-based polymer electrolytes such polysaccharides (starch, chitosan, cellulose) and proteins (pectin-based electrolytes) are best candidate due to their abundance in environment [2,3] and have garnered growing significance over the past few decades as potential substitutes to conventional polymers like polyethylene oxide (PEO) and poly(methyl methacrylate) (PMMA), which originated from petroleum based. They serve as a vital solution to address numerous global challenges, including global warming, price instability in petroleum resources, environmental pollution and various economic and ecological issues [3-5]. Among the natural-based polymer electrolytes, there is a growing interest among polymer scientists in exploring the potential of ENR. Epoxidized natural rubber (ENR) is a chemically modified form of *cis* 1,4-polyisoprene rubber, where some of the unsaturated C=C bonds are converted into epoxide groups [6]. ENR possesses unique characteristics, such as its amorphous nature, low glass transition temperature, excellent elasticity and strong adhesive properties, which render it well-suited as a polymer host for polymer electrolytes by ensuring effective contact between the electrolyte layer and electrodes in electronic devices [7]. These properties have motivated further exploration of ENR's potential as a polymer electrolyte material. ENR has gained interest for its potential as a polymer electrolyte material and its compatibility with other polymers and ability to form coordination bonds with fillers and salts make it particularly promising [6-8].

Studies have shown that incorporating lithium salts into ENR improves its glass transition temperature and conductivity, with higher salt concentrations leading to improved ion

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mobility and a higher diffusion rate of charge carriers [9,10]. The presence of plasticizers enhances the entropy configuration of ENR-50, thus creating more free volume which facilitates ion mobility through the plasticizer-rich phase [11]. Furthermore, the enhancement in conductivity can be attributed to an increase in the segmental motion of the host polymer chains [12-14]. While most previous workdone on ENR has focused on solid polymer electrolyte (SPE) systems, recent attention has shifted towards liquid polymer electrolyte (LPE) systems which is a hybrid system involves the addition of salt to a polymer solution that is dissolved in a compatible solvent [15,16]. This shift is driven by the complexity of SPE systems, in which the interaction and interpretation of polymers are highly complex, requiring numerous indirect assumptions and speculations before any conclusive results can be drawn [17]. SPE systems often require the use of sophisticated instruments for characterization and interpretation, whereas the study of LPE systems tends to be relatively more straightforward and less complex. In comparison to SPE, the LPE systems offer several advantages over SPE systems such as high ionic conductivity (κ), high electrical resistance and excellent contact with the electrode [18].

Understanding ion transport mechanisms in LPE can provide valuable insights for the development of high-performance polymer electrolyte systems. The measurement of conductivity in a dilute solution of salt-polymer system serves as an effective tool for understanding the interaction between ions and polymers in the amorphous regions of solid polymer electrolytes [16-19]. Therefore, analyzing polymers in a solvent (dilute polymer) system can provide a fundamental basis for better clarification of polymer interactions. This approach allows for a more comprehensive understanding of the underlying mechanisms and behaviour of polymer electrolytes [18,19]. Researchers have explored the limiting molar conductivity (Λ_o) and equilibrium constant for $LiClO_4$ in a different concentration of poly(methyl methacrylate) (PMMA-*co*-MA) solution at 25 ºC, revealing the influence of polymer concentration and type on ion mobility and conductivity [15]. They investigated the molar conductivity of the LPE system using Ostwald's equations to calculate Λ_o. Their findings revealed a decreasing trend in Λ_o as the concentration of PMMA-*co*-MA increased. This suggests that the strength of the solution improved, leading to enhanced salt dissociation within the LPE system.

Hanibah *et al*. [16] studied the effect of $LiClO_4$ in polyethylene oxide (PEO) solutions at ambient temperature and it was found that the reciprocal of molar conductivity increased as $LiClO_4$ concentration increased across all the different electrolyte systems studied at various PEO concentrations [16]. These results indicate that the polymer plays a crucial role in enhancing ion mobility within the polymer electrolyte system. Furthermore, the study demonstrated that at higher C_{poly}, the use of PEO significantly contributed to the enhancement of salt dissociation and the coordination of ions at the active site of the ether oxygen of PEO [16,17].

To the best of our knowledge, there is no available data pertaining to critical parameters such as limiting molar conductivity, salt dissociation and the interaction between ions and polymers within the ENR electrolyte based on LPE system. Moreover, it is well-established that ENR exhibits solubility only in a restricted range of organic solvents such as tetrahydrofuran (THF), which exhibits low dielectric constant and poor salt solvation properties. In previous studies [15-19], the potential benefits of using acetonitrile (ACN) owing to its high dielectric constant and excellent capabilities for salt dissociation, particularly with $LiClO_4$ [17] has been reported. However, the compatibility and solubility of ACN with ENR have not been thoroughly investigated. To address this limitation, there is a necessity to employ a mixed solvent system albeit there is a lack of comprehensive research on the impact of mixed solvents in ENR electrolyte systems, especially in the context of LPE systems. The existing knowledge gap highlights the necessity for additional research with the objective of gaining a more comprehensive understanding of the mechanisms by which mixed solvents can improve the performance of ENR-based LPE systems.

Hence, in this work, the behaviour of the limiting molar conductivity (Λ_o) in a liquid polymer electrolyte system based on ENR is investigated. An ENR-50/$LiClO_4$ electrolyte system was prepared in the mixed solvent system of THF and ACN. The limiting molar conductivity of this system were determined at different ENR-50 concentrations using the power law method [17,18]. Characterization of ENR-50/$LiClO_4$/THF:ACN was performed by ATR-FTIR spectroscopy.

EXPERIMENTAL

Epoxidized natural rubber, ENR-50 (denotes 50% mole of epoxidation level) was supplied by Malaysian Rubber Board (Sungai Buloh, Malaysia). Anhydrous lithium percholrate (M_w = 106.39 g/mol) with purity > 99 % was obtained from Acros Organic and dried in a vacuum oven at 100 ºC for 48 h to eliminate any traces of water that may trapped in the salt prior to be dissolved in the mixed solvent. The salt was kept in the electronic dessicator with relative humidity < 40%. Organic solvent, THF with purify > 99.99% (Merck, Germany) was used for dissolution of ENR. High performance liquid chromatography (HPLC) grade of acetonitrile (Fisher-Scientific, U.K.) with purity > 99.99% and THF were used as supplied. The water used in this study was prepared by passing through the double distilled water to water deionizing system (Sartorius, Germany) resulting in 18 × 10^6 MOhm cm at 25 ºC.

Conductivity meter: The Mettler Toledo Seven Compact S230 AC conductivity meter (Schwerzenbach, Switzerland) with conductivity probe Inlab® 741 (measurement range of 0.001-500 µS cm^{-1} and the temperature range of 0-70 ºC), was used to measure the quantity of ionic conductivity for the system consisting of organic solvent at ambient temperature (25 ºC). The cell constant of conductivity meter was determined through an automatic calibration process performed on a daily basis. The aqueous solution of potassium chloride (KCl) supplied by Metler Toledo (Schwerzenbach, Switzerland) and had concentrations of 0.1, 0.01 and 0.005 mol L^{-1}, with corresponding conductivity values of 12.88 mS cm^{-1}, 1413 µS cm^{-1} and 84 µS cm^{-1}. The calibration process was carried out with the conductivity meter connected to an Inlab® 741 electrode.

Following the successful calibration of the conductivity meter, the measurement of electrolytic conductivity was performed for sample solutions (ENR-50/$LiClO_4$/THF:ACN) at a reference temperature of 25 ºC. Each measurement was performed at least three times (triplicate analysis) and subsequently, the mean values of κ (with a coefficient of variation less than 5%) were reported.

Sample preparation (purification of ENR-50): ENR-50 (2 wt.%) was fragmented into small grains to facilitate the dissolution of ENR in THF. The solution was continuous stirred at 50 ºC for 72 h to ensure complete dissolution until no further changes in the solution. A viscous solution of ENR rubber was formed. To separate the soluble ENR from the insoluble gel content, the viscous solution was passed through a 100-mesh steel gauze sieve *via* a double filtration process. The filtrate, containing the viscous soluble ENR solution, was collected and its volume was reduced to one-third using a rotary evaporator at 50 ºC. The concentrated viscous solution was subsequently re-precipitated by adding *n*-hexane in a 1:5 ratio. Once the ENR had precipitated, it was carefully transferred into petri dishes. The precipitated ENR samples were then subjected to further drying in a vacuum oven at 50 ºC for 24 h to remove any residual solvent. The purified ENR samples were finally stored in an electronic desiccator with a relative humidity of approximately 40%, ensuring their preservation until further used.

Solubility of purified ENR-50 with various solvents: The purified ENR-50 (2 wt%) was fragmented into small pieces to facilitate its dissolution in three different solvents: (a) THF, (b) ACN and (c) a mixed solvent consisting of THF and ACN in various ratios. These solvent mixtures were continuously stirred at 50 ºC for 72 h to ensure complete dissolution. The process continued until a fully homogeneous and transparent solution was achieved. In addition, to investigate the compatibility of both solvents, a study was conducted by mixing different ratios of THF and ACN solvents. The homogeneity of these mixtures was observed while varying the ratios of the mixed solvent. The detailed findings from this investigation will be discussed further in the results and discussion section, specifically under the subsection addressing the effect of the mixed solvent system. Consequently, it was concluded that a mixed solvent composed of THF:ACN in an 8:2 ratio will be utilized throughout the experiment for the preparation of ENR-50/LPE.

Preparation of ENR-50 liquid polymer electrolyte (LPE): The preparation of the salt solution and salt-polymer solution (specifically an ENR-50/$LiClO_4$/THF:ACN) system for conductivity measurement was done in a controlled environment to minimize the error in K measurement. The temperature in the laboratory was controlled at 25 ± 2 ºC. Purified ENR-50 samples were cut into the small pieces and weighed at various masses, approximately 0.5 g, 1.0 g and 1.5 g. These samples were then dissolved in 500 mL of a mixed solvent consisting of THF and ACN in an 8:2 ratio. This resulted in the formation of polymer solutions with different concentrations (C_{poly}): 0.001 g/cm^3, 0.002 g/cm^3 and 0.003 g/cm^3, respectively. The mixtures of ENR-50 and the mixed solvent were continuously stirred for 24 h at 50 ºC, until homogeneous and transparent solution formed. These solutions are referred to as stock solutions and will be used for further experiments.

The preparation of a salt-polymer solution, specifically an ENR-50/$LiClO_4$/THF:ACN system, with a salt concentration of 0.1 mole (1×10^{-4} mol/cm^3), was carried out. The choice of employing low salt concentrations was a crucial aspect of this study. It allowed to evaluate the limiting molar conductivity of the electrolyte system at a state of infinite dilution, where there is minimal electrostatic attraction among the dissociated Li^+ ions within the system [18,19]. The general formula (eqn. 1) used to calculate the salt-polymer solution at different concentrations is as follows:

$$C_{salt} = \left(\frac{M_{salt}}{M_w \times V} \right) \quad (1)$$

where C_{salt} represents the concentration of the $LiClO_4$ stock solution in mol/mL, M_{salt} denotes the mass of $LiClO_4$ in grams, M_w represents the molar mass of $LiClO_4$ in g/mol and V represents the volume of the solution in mL. To prepare the stock solution with a salt concentration of 1.0×10^{-4} mol/mL, approximately 0.5319 g of $LiClO_4$ were weighed and dissolved in 50 mL of the mixed solvent composed of THF and ACN in an 8:2 ratio. The solution was continuously stirred at 50 ºC for 24 h or until a homogeneous transparent solution was formed. A series of 12-15 dilutions was performed to obtain a range of $C_{salt} \approx 10^{-4}$-10^{-7} mol/cm^3 for the conductivity measurements. Each dilution involved transferring a specific volume of the stock solution and adjusting the volume with the polymer solution in the volumetric flask, ultimately resulting in different concentrations of the salt-polymer solution (ENR-50/$LiClO_4$/THF: ACN) for the conductivity measurements.

FTIR analysis: The comparison of three different polymer concentration of ENR-50/$LiClO_4$ and mixed in THF:ACN (8:2) was verified by FTIR spectroscopy. The samples were directly placed on a diamond plate. The FTIR spectra were recorded with an attenuated total reflectance (ATR) equipped Thermo-Nicolet (IS50-FT-IR) spectrometer in the range of 4000–800 cm^{-1}.

RESULTS AND DISCUSSION

Effect of mixed solvent system (THF:ACN): The choice of solvent for dissolving a polymer is a critical factor that significantly influences the structure of the polymer chain in the solution. It is well-established in the literature that ENR dissolved only in limited organic solvent such as THF, which has been recognized as good solvent for ENR [20]. However, when considering applications that require high electrolytic conductivity, the sole use of THF in the electrolyte solution needs to be avoided due to its limitations in enhancing salt dissociation. As such, the use of a polar solvent such as ACN is strongly recommended as it ensure maximum expansion of the polymer chain in the solution, creating a larger hydrodynamic volume compared to non-polar solvents [21]. This maximum expansion is particularly crucial in LPE systems. With a fully expanded polymer chain, ion coordination to the active sites of polymer is optimized, leading to improved ion mobility within the system. Consequently, this enhancement of ionic conductivity in the electrolyte system is predicted to be at its optimum condition [17,18,21].

In the preliminary work, it was observed that the purified ENR-50 rubber sample did not dissolve in the polar solvent ACN (with a polarity index of 5.8) [22]. This lack of dissolution was likely attributed to the non-polar characteristics of ENR-50 rubber and the high polarity of ACN. To overcome this challenge, an experimental trial was conducted using THF, which has a lower polarity (with a polarity index of 4.0) [22,23] compared to ACN. Interestingly, it was observed that purified ENR-50 sample dissolved completely in THF. Although THF is not ideal for salt dissociation due to its poor dielectric constant ($\varepsilon = 7.58$) [24] compared to ACN ($\varepsilon = 35.96$) [25], which has a relatively high dielectric constant and good solvation ability for salts, it was essential to find a balance between dissolving the ENR and facilitating ion salt dissociation. Hence, a mixture of THF:ACN was employed to address these considerations. The miscibility of THF and ACN were studied and it was observed that no distinct layers formed, indicating that THF and ACN were completely miscible. Encouraged by these results, the experiment was proceeded by varying the ratios of the mixed solvent and the outcomes are recorded in Table-1.

TABLE-1
DISSOLUTION OF MIXED SOLVENT (THF AND ACN) WITH DIFFERENT RATIO ON SOLUBILITY OF PURIFIED ENR-50

Ratio of mixed solvent (THF:ACN)	Miscibility by visual evaluation (solvent miscibility)	Observation by visual evaluation (ENR miscibility)
9:1	Miscible	Dissolved (100%)
8:2	Miscible	Dissolved (100%)
7:3	Miscible	Partially dissolved (80-90%)
6:4	Miscible	Partially dissolved (60-70%)
5:5	Miscible	Sample did not dissolve

It was observed that at mixed solvent (THF:ACN) ratios of 9:1 and 8:2, purified ENR-50 dissolved completely. On the other hand, at ratios of 7:3 and 6:4, ENR-50 exhibited partial dissolution. Finally, at a ratio of 5:5, purified ENR-50 did not dissolve at all. Considering the high dielectric constant of ACN for salt dissociation, whereas the excellent polarity index of THF for dissolving the purified ENR rubber, a mixed solvent ratio (THF:ACN) of 8:2 instead of 9:1 was selected as the optimum condition for preparing a salt-polymer solution system (ENR-50/$LiClO_4$/THF:ACN).

While the 9:1 ratio can also dissolve purified ENR-50 completely, the lower volume of ACN in this ratio may limit its effectiveness in facilitating salt dissociation as compared to ratio 8:2, which is deemed the best compromise to achieve both the dissolution of ENR and the salt dissociation. The results showed that a ratio of 8:2 worked best, completely dissolving ENR-50 and facilitating salt dissociation. The capacity of THF to dissolve ENR, along with the strong solvation and high dielectric constant of ACN, provides for an ideal solvent combination that promotes salt dissociation and increases ion mobility in an electrolyte system.

Determination of limiting molar conductivity of $LiClO_4$ in mixed solvent system (THF:ACN) after power law at 25 ºC: It is well known that lithium perchlorate ($LiClO_4$), when dissolved in water, is a strong electrolyte due to the strong thermodynamic interaction between it and water molecules [26,27]. In an aqueous solution, $LiClO_4$ undergoes complete dissociation into its constituent cation and anion species, particularly at low salt concentrations below 0.1×10^{-3} mol cm^{-3}, as illustrated in eqn. 2 [17,18,27].

$$LiClO_4\,(s) \longrightarrow Li^+\,(aq.) + ClO_4^-\,(aq.) \qquad (2)$$

However, in the presence of an organic solvent such as THF or ACN, the electrolyte system acts as a weak electrolyte due to partial dissociation as supported by previous research utilizing Ostwald's dilution law [17-19]. These lithium salt undergo partial dissociation into their constituent ions (eqn. 3). It is widely recognized that in a weak electrolyte system, the concentration of ions is lower than that of the solutes. Thus, assessing the total free mobile ions within the system depends on the dissolution of solutes [18,19].

$$LiClO_4\,(s) \rightleftharpoons Li^+\,(aq.) + ClO_4^-\,(aq.) \qquad (3)$$

The power law is introduced due to the limitations of the adaptation of Ostwald's dilution law equation to estimate Λ_o (ionic conductance at infinite dilution) for weak electrolyte systems consisting of organic solvent [17-19]. To overcome these limitations, a double-logarithmic plot of κ (electrolytic conductivity) *versus* C_{salt} (solute concentration) mentioned in eqn. 4 might be the most effective approach to recalculate the Λ_o values for weak electrolyte systems. This approach provides a more accurate estimation by considering the non-linear relationship between κ and C_{salt}, which is often observed in weak electrolyte systems. To assess the validity and applicability of eqn. 4, $LiClO_4$ at 25 ºC was employed as a reference system to verify the work-ability and effectiveness of eqn. 4.

$$\Lambda = K'\left(\frac{C_{salt}}{C_\theta}\right)^{\gamma-1} \qquad (4)$$

Theoretically, the power law presented in eqn. 4 should ideally exhibit linearity for a certain nite range of C_{salt}. Fig. 1 depicts a graph plotted after eqn. 4 for $LiClO_4$ at 25 °C for experimental data in this study. The plot demonstrates that the quantity κ for $LiClO_4$ increases consistently as a function of C_{salt} in accordance with the proposed power law [17-19]. This observation supports the effectiveness of the power law equation. However, it is worthnoting that in Fig. 1, below the sensitivity limit of the measurement probe, the quantities of κ start to deviate from linearity particularly at C_{salt} below 10^{-7} mol cm^{-3}. At these low salt concentrations, the values of κ become constant.

Regression function for $LiClO_4$ in Fig. 1

$$\log\kappa = 0.2661 + 0.7549\log\left(\frac{C_{salt}}{C^\theta}\right)(r^2 = 0.994) \qquad (5)$$

Or by rearranging:

$$\kappa = 1.845\left(\frac{C_{salt}}{C_\theta}\right)^{0.7549} \qquad (6)$$

Thus,

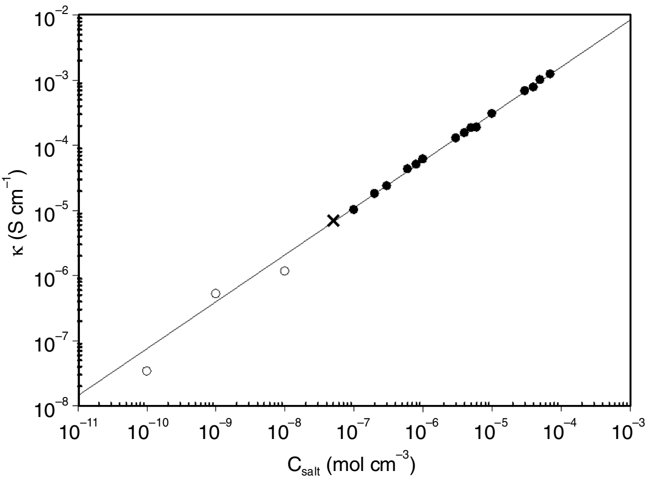

Fig. 1. Double-logarithm plot of κ *versus* C_{salt} for aqueous solution of $LiClO_4$ in mixed solvent (THF:ACN) at 25 °C after power law. Experimental data: (●) In the study: (○) where data deviate from power law; Solid curve represents the linear regression and (**x**) C_{ref} is this study after eqn. 8

$$\Lambda = \frac{1.845}{\left(\frac{C_{salt}}{C_e}\right)^{-0.2451}} \ (\text{S cm}^2\ \text{cm}^{-1}) \tag{7}$$

C_θ = mol cm^{-3}. After applying eqn. 7, the Λ_o value for $LiClO_4$ is recalculated at a fixed concentration. This fixed salt concentration used to calculate the Λ_o is known as salt reference concentration (C_{ref}). To calculate the Λ_o value using the power law, C_{ref} is approximately set to half of the lowest C_{salt} concentration that obeys the power law as proposed by Hanibah *et al.* [17,18]. This same approach is extended in an analogous manner for weak electrolyte systems to determine their respective Λ_o values. In summary, eqn. 8 is utilized to determine the Λ_o value through the application of the power law for both strong and weak electrolyte systems, employing the appropriate reference salt concentration.

$$\Lambda_o = K' \gamma C_{ref}^{\ (y-1)} \tag{8}$$

The value of C_{ref} is crucial to calculate Λ_o accurately for an electrolyte system. As mentioned earlier, the quantity of C_{ref} is approximately half of the lowest C_{salt} concentration which the power law holds true. This selection ensures that the power law equation is appropriately applied. The same approach will be applied to determine the Λ_o value for weak electrolyte system after the power law. The κ value was measured at various C_{salt} by carrying out a series of dilution of its stock solution until constant κ was attained [17-19]. These measurements are crucial for accurately applying the power law and determining the Λ_o value for weak electrolyte systems.

It is observed that $C_{salt} = 1.00 \times 10^{-7}$ mol cm^{-3} is the last data that fixes well to the regression function (Fig. 2), therefore this data is taken to estimate the C_{ref} for this electrolyte system. At higher $C_{salt} \geq 10^{-7}$ mol cm^{-3} the data tends to deviate mostly due to the formation of ion-pairs as reported for same electrolyte system. Quantity C_{ref} for this system is half of the 1.00×10^{-7} mol cm^{-3} at $C_{ref} = 5.00 \times 10^{-8}$ mol cm^{-3}. The estimated quantity Λ_o for $LiClO_4$ in THF:ACN follows eqn. 8.

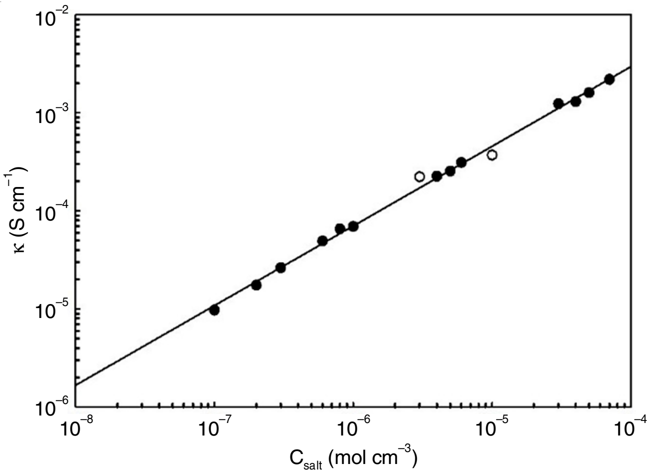

Fig. 2. Double-logarithm plot of κ *versus* C_{salt} for ENR-50/LiCiO$_4$/THF:ACN at different C_{poly} 0.001 g/cm^3 at 25 °C after power law. Experimental data: (●) In the study: (○) where data deviate from power law; Solid curve represents the linear regression

$$\begin{aligned}\Lambda_o &= (1.845) \times (0.7549) \times [(5.00 \times 10^{-8})^{(0.7549-1)}] \\ &= 85.78 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

Thus, the estimated Λ_o value for $LiClO_4$ in mixed solvent system (THF:ACN) at 25 ºC was 85.78 S cm^2 mol^{-1}.

Determination of limiting molar conductivity (Λ_o) ENR-50/LiClO$_4$/THF:ACN at different polymer concentrations after power law at ambient temperature (25 ºC): In this study, the power law method was employed to estimate the Λ_o of ENR-50/LiClO$_4$/THF:ACN at different polymer concentration (C_{poly}). Fig. 2 depicted the graph of double-logarithm of κ against C_{salt} at 25 ºC. A similar procedure was conducted to plot the graph for C_{poly} 0.002 g/cm^3 and 0.003 g/cm^3, respectively. The correlation (r^2) values obtained were ranged between 0.9959 to 0.9966 for the three polymer concentrations (C_{poly} = 0.001, 0.002 and 0.003 g/cm^3) system at 25 ºC, respectively. The summary of the regression function for ENR-50/LiClO$_4$ in mixed THF:ACN at 25 ºC for C_{poly} of 0.001, 0.002 and 0.003 g/cm^3 are tabulated in Table-2.

TABLE-2
SUMMARY OF THE Λ_o FOR ENR-50/LICIO$_4$ IN MIXED SOLVENT SYSTEM (THF:ACN) AT DIFFERENT POLYMER CONCENTRATIONS AT 25 °C

Polymer system (g/cm³)	Linear regression function	Correlation (r^2)	Limiting molar conductivity (Λ_o) after power law (S cm^2 mol^{-1})
0.001	y = 0.7298x + 0.2281	0.9959	115.89
0.002	y = 0.7331x + 0.2374	0.9966	112.69
0.003	y = 0.8124x + 0.7226	0.9959	100.47

Based on the regression analysis, it was observed that the Λ_o values decreased as the C_{poly} increased (showing an inverse relationship). Specifically, C_{poly} of 0.001 and 0.002 g/cm^3 yielded Λ_o values of 115.89 and 112.69 S cm^2 mol^{-1}, respectively. In addition, the highest C_{poly} in the system (0.003 g/cm^3) yielded a Λ_o value of 100.47 S cm^2 mol^{-1}. This trend indicates that as the polymer concentration increases, the limiting molar conductivity decreases, suggesting an enhanced salt dissociation.

These findings are consistent with the reported work by Hanibah *et al.* [16], which proposed that this phenomenon is linked to changes in the solution's viscosity, a factor closely connected to the Walden rule [16]. Lower Λ_o values indicate a higher degree of ion dissociation within the system [17-19]. Increasing the amount of ENR-50 (higher concentration) results in more significant salt dissociation, attributed to the augmented presence of total epoxy groups (C-O-C). Consequently, this enhancement leads to improved $LiClO_4$ dissociation, directly contributing to the improve the conductivity of electrolyte system.

FTIR studies: The FTIR analysis conducted in this study has unveiled a change in peak intensities, attributable to variations in polymer concentration incorporated into the LPE system. Fig. 3 depicts the FTIR spectra spanning from 4000-400 cm^{-1} for pure $LiClO_4$ and ENR-50 mixed with $LiClO_4$ at various concentrations C_{poly} (0.001, 0.002 and 0.003 g/cm^3). In the ENR-50 spectra, absorption peaks were observed at 1375, 1455 and 2961 cm^{-1}, which are attributed to CH_3 groups, while 2929 and 2851 cm^{-1} correspond to CH_2 groups. Additionally, peaks associated with the oxirane group (C-O-C) were detected at 1062, 914 and 834 cm^{-1}. In Fig. 3, the characteristic peaks of $LiClO_4$ were identified at 1618, 1062, 683 and 615 cm^{-1}, which are associated with the internal vibrational modes of the ClO_4^- anion. Notably, the strong absorption peak at 1062 cm^{-1} exhibited the high intensity, potentially indicating an overlap between the vibrations of Li-ClO_4 and C-O-C groups, which coincidently absorb the same wavenumber [28,29].

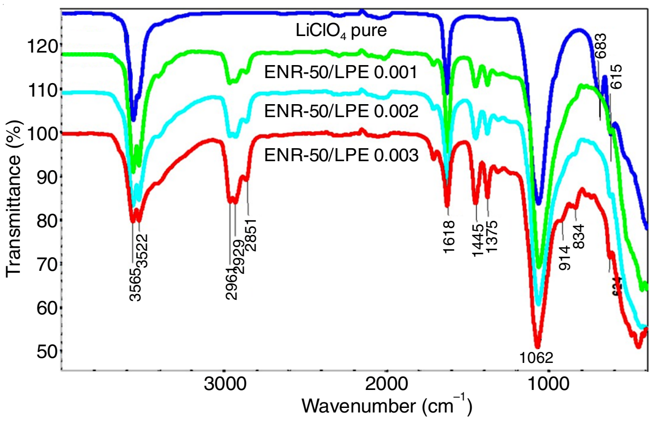

Fig. 3. FTIR spectra (4000-400 cm^{-1}) of ENR-50/$LiClO_4$/THF:ACN at different polymer concentrations (0.001, 0.002 and 0.003 g/cm^3)

Upon addition to the ENR-50/$LiCiO_4$ in mixed solvent system, it was observed that the peak at 1618 cm^{-1}, corresponding to the unsaturated ethylene groups (C=C) bonds in ENR, remained unaltered in both frequency and intensity. This observation suggests that Li^+ ions did not exhibit a preference for coordination with the C=C bonds in ENR, despite the fact that this C=C also possesses nucleophilic characteristics [30]. Instead, a significant finding was the disappearance of the peak corresponding to ClO_4^- ion at 683 cm^{-1} across all C_{poly} 0.001, 0.002 and 0.003 g/cm^3 as depicted in Fig. 4. This disappearance suggests the presence of ion dipole interactions occur and this could be attributed to ion-dipole interactions between the active sites of ENR-50, particularly the epoxide groups (C-O-C) and Li^+ ions [28,29]. The electronegativity difference between Li^+ and C=C is 1.57, whereas for Li^+ and C-O-C, the electronegativity difference is 2.46. This suggests that Li^+ ions are more likely to form an ion-dipole interaction with the oxygen atom in the epoxy group of ENR compared to the ethylene groups of ENR [29]. This preference is driven by the greater electronegativity disparity, which results in a stronger attraction between Li^+ ions and the and the lone pair of electrons residing on the oxygen atom of the C-O-C group [28-30].

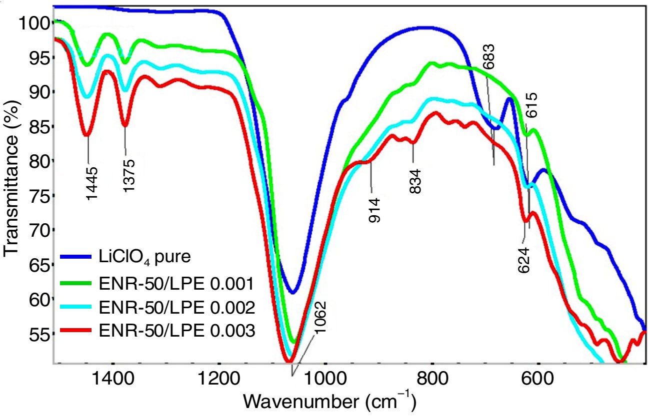

Fig. 4. FTIR spectra (1000-600 cm^{-1}) on ENR-50/$LiClO_4$ at different polymer concentrations (0.001, 0.002 and 0.003 g/cm^3)

In addition, as illustrated in Fig. 4, it is observed that the absorption peak at 914 cm^{-1}, associated with C-O-C, demonstrates an increase in intensity as the polymer concentration (C_{poly}) reaches 0.003 g/cm^3, in contrast to the intensities observed at C_{poly} 0.002 g/cm^3 and 0.001 g/cm^3, respectively. The increasing intensity of this peak with rising C_{poly} suggests an electrostatic interaction occurred between lithium ion and the epoxide group of ENR [28-30]. In summary, these FTIR results provide additional support for the conductivity data.

Conclusion

The utilization of liquid polymer electrolytes has proven to be highly valuable in enhancing our understanding of the fundamental principles of physical chemistry governing salt-polymer systems. The power law comprised of a double-logarithm plot of κ against C_{salt} that serve as an alternative method with acceptable accuracy in the determination of Λ_o at C_{ref}. Interestingly, the value of C_{ref}, which corresponds to Λ_o, is approximately half of the lowest C_{salt} that still adheres to the power law before deviating from the linearity of the regression equation. The introduction of ENR-50 into the $LiClO_4$ system with a mixed solvent of THF:ACN, induces changes in the Λ_o values. In general, as the polymer concentration (C_{poly}) increases, a consistent pattern emerges where the limiting molar conductivity (Λ_o) values decrease. This observation signifies an enhancement in the solution's strength, leading to improved salt dissociation. The FTIR analysis conducted in this study has revealed noteworthy changes, particularly in intensity, as a result of varying polymer concentrations introduced into the LPE system.The ion-dipole interactions between the active sites of ENR-50, especially the epoxide groups (C-O-C) and lithium ion have also been demonstrated in a mixed solvent system (THF:ACN).

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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