Malaysian Journal of Chemistry, 2023, Vol. 25(4), 99-112

Liquid Polymer Electrolytes: Molar Conductivity Behaviour of Various Lithium Salts in Polyethylene Oxide Systems at Ambient Temperature

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The limiting molar conductivity (Λ_o) value of an electrolyte is an important physical parameter that evaluates its strength. Liquid polymer electrolytes (LPE) based on polyethylene oxide (PEO) with lithium salts in a common organic solvent have been widely studied. In this paper, we determined the Λ_o value for PEO systems in lithium chloride (LiCl) as well as lithium acetate (CH_3COOLi) at room temperature. The molar conductivity (Λ) values of these systems were measured at different salt concentrations (C_{salt}) of 1.0 x 10^{-3} - 2.0 x 10^{-7} mol cm^{-3} in aqueous solution and repeated with methanol (CH_3OH) at PEO concentrations (C_{PEO}) of 1.0 x 10^{-3} - 3.0 x 10^{-3} g cm^{-3}. The compatibility of the experimental data was investigated using the Kohlrausch Law for strong electrolytes and Ostwald's Dilution Law for weak electrolyte systems. However, as these were found to be unsuitable in determining the Λ_o values for PEO-LiCl-CH_3OH and PEO-CH_3COOLi-CH_3OH, the Power Law was used instead. The Λ_o values obtained after calibration deviated only < 2% from the theoretical values.

Keywords: Liquid polymer electrolyte; molar conductivity; limiting molar conductivity; Kohlrausch Law; Ostwald's Dilution Law

Received: February 2023; Accepted: March 2023

The increasing demand for telecommunication devices, computers and hybrid electrical cars has heightened research into rechargeable lithium batteries. Advances in the field of lithium-ion batteries have attracted world-wide attention. To date, different types of polymers, dopants for inorganic salts, and the addition of fillers are considered the most anticipated solutions [1]. There are three major types of polymer electrolytes: liquid polymer electrolytes (LPE), gel polymer electrolytes (GPE), and solid polymer electrolytes (SPE) [2], [3].

An inorganic material such as a salt is often added to the polymer as a dopant that provides free mobile ions for electrical conduction [4]. Normally, the added inorganic salt will dissociate into its individual ions due to the strong electrostatic attraction between the polymer active site, the salt and the solvent. As a result, the salt acts as a charge carrier in the system that coordinates with the backbone of the polymer chain and allows the ions to be transported under the influence of an electric field [5], [6].

A SPE is commonly used nowadays to achieve high energy density and to prevent battery leakage [7], [8]. However, its commercial utility is compromised by limited ion transfers, high emission rates, and low cycle efficiencies [9]. The first SPE system based on PEO exhibited a low ionic conductivity of 10^{-8} S cm^{-1} [10], [11]. This was mainly due to the absence of an organic solvent, thus the PEO itself acts as a solvent in the solid state [12], [13].

SPE systems of PEO doped with inorganic salts have been studied worldwide. The high solubility of a wide range of inorganic salts in PEO is one of the main features of its use in SPE systems [12], [14]. Therefore, practical application of this membrane at room temperature is limited [15], [16].

A LPE is a hybrid system prepared by adding a salt to a polymer solution dissolved in a suitable solvent [17]–[19]. The LPE system has several advantages over SPE. These include high ionic conductivity (κ), high electrical resistance and excellent contact with the electrode. Furthermore, while GPEs have some advantages over LPEs such as enhanced safety and mechanical strength, LPEs have other benefits such as higher ion mobility (making them promising materials for energy storage devices) [20], lower internal resistance [21], simpler manufacturing [22], higher capacitance, and better connection with electrodes [23]. A previous study [24] investigated the Λ_o behaviour of lithium perchlorate ($LiClO_4$) in a PEO-acetonitrile (ACN) electrolyte system at ambient temperature. The study concluded that the presence of PEO enhanced salt dissociation (α) and the coordination of ions at the active site of the ether oxygen of PEO.

Investigating the dependence of the electrolyte solution conductivity on its concentration is important for the evaluation and improvement of the performance of any electrochemical system. In this study, a precise determination of the calibrated limiting molar conductivity (Λ_o) value for electrolytes based on LPE was achieved using a Power Law. A ternary LPE system consisting of PEO-lithium chloride (LiCl)-methanol (CH_3OH) and PEO-lithium acetate (CH_3COOLi)-CH_3OH was prepared. Different concentrations of salt (C_{salt}) ranging from 1.0 x 10^{-3} - 2.0 x 10^{-7} mol cm^{-3} were dissolved in various concentrations of PEO (C_{PEO}) (1.0 x 10^{-3} - 3.0 x 10^{-3} g cm^{-3}) at 25 °C. The salt concentration range was selected to ensure the conductivity measurements for the electrolyte system were in the working sensitivity range of the conductivity probe used in this experiment. The selection of low salt concentrations was important in this study in order to determine the limiting molar conductivity of the electrolyte system under an infinite dilution that has minimum electrostatic attraction between the dissociated salt ions in the system [25].

In the system, LiCl and CH_3COOLi act as charge carriers, providing free-moving ions. In an LPE-based PEO system, the cations of the ionic salts coordinate with ether oxygens at the active sites of the PEO [26]. The results showed that the proposed model fit the experimental data well and deviated very little from the theoretical value, which indicates high potential for these systems in engineering applications.

THEORY

A polymer can have either electrolytic conductivity or ionic conductivity [27], [28]. The higher the value of ionic conductivity, the more charge carriers are present in the electrolyte per unit of time. The conductivity of an electrolyte depends on its ions (Atkins & Paula, 2010). The electrolytic conductivity (κ) depends on the concentration of ions in an electrolyte system and gives the molar conductivity (Λ) when divided by C_{salt}, as shown in Eq. 1.

$$\Lambda = \frac{\kappa}{C_{\text{salt}}} \qquad (1)$$

Λ is defined as the ability to conduct electricity through all ions resulting from complete ion dissociation in the solute. Λ has the units S cm^2 mol^{-1}. As mentioned earlier, a strong electrolyte is one that undergoes complete dissociation. The conductivity of a strong electrolyte obeys the Kohlrausch Law, as shown in Eq. 2 [29].

$$\Lambda = \Lambda_o - \kappa C_{\text{salt}}^{1/2} \qquad (2)$$

For a weak electrolyte system, Λ_o obeys Ostwald’s dilution law (Eq. 3), which applies to an aqueous solution and not an organic solvent. A more accurate way to calculate the value of Λ_o for a weak electrolyte system with an organic solvent is by using Eq. 4, also known as the Power Law, as proposed by a previous study [30].

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_o} + \frac{\kappa}{K_{eq}(\Lambda_o)^2} \qquad (3)$$

$$log\, \kappa = K' + \gamma\, log\, C_{\text{salt}} \qquad (4)$$

This method is applied to weak electrolyte systems using an organic solvent to accurately determine its Λ_o value. It uses a logarithmic plot of κ versus C_{salt}. Based on Eq. 4, the constant K' represents ion mobility and is expressed as the y-axis, while γ is the slope of the logarithmic plot. The Power Law can be rearranged to give Eq. 5.

$$\kappa = K' \left(\frac{C_{\text{salt}}}{C^{\theta}}\right)^{\gamma} \qquad (5)$$

When the Power Law is compared with equation 1, it results in Eq. 6.

$$\Lambda = K' \left(\frac{C_{\text{salt}}}{C^{\theta}}\right)^{\gamma\text{-}1} \qquad (6)$$

C^{θ} = 1 mol cm^{-3}, and this term is introduced to keep the exponent dimensionless. From Eq. 6, Λ_o can be calculated for an electrolyte system with a referenced salt concentration, denoted as C_{ref}. Therefore, Λ_o can be determined using the Power Law with the electrolytic conductivity data.

EXPERIMENTAL

1. Materials

Polyethylene oxide (PEO) with a molecular weight (M_w) of 4,000 kg mol^{-1} and purity ≥ 99% was purchased from the Sigma-Aldrich Chemical Company and was used only after undergoing a re-precipitation method to purify the PEO. Powdered LiCl (Ajax, 98% purity) and CH_3COOLi (Ajax, 99%) were obtained and dried in a vacuum oven for 48 h at 100 °C to remove any traces of water before dissolution. A high-performance liquid chromatography (HPLC) grade of CH_3OH (Systerm, purity ≥ 99.9%) was used as supplied to dissolve PEO, LiCl and CH_3COOLi.

2. Purification of PEO

The purification of PEO was achieved using a re-precipitation process. A sufficient amount of PEO was dissolved in chloroform (AR grade) to prepare a 2% weight/volume (w/v) solution. The solution was stirred constantly at 50 ℃ for 48 h to achieve complete dissolution. The solution was concentrated to half its original volume using a rotary evaporator. For the re-precipitation of PEO, the viscous PEO solution was added to n-hexane (AR grade). The PEO sample was transferred to a petri dish and dried overnight in a fume hood. The sample was then further dried in the oven for 48 h before being transferred to a vacuum oven at 50 ℃ for an additional 48 h. To prevent the absorption of moisture, the purified PEO was stored in an electronic desiccator under a dry nitrogen atmosphere.

3. Preparation and Measurement of Conductivity

The salt solution and salt-polymer solution system were prepared for conductivity measurements in a controlled environment to minimise errors. The laboratory temperature was controlled at 25 ± 2 ℃. The LiCl stock solution with known concentration was prepared by dissolving LiCl in distilled water. The solution was stirred at 50 ℃ for 24 h. Then, approximately 8-15 dilutions of the stock solution were performed. A similar procedure was followed to prepare the CH_3COOLi stock solution.

The stock solution of PEO in CH_3OH was prepared with a fixed polymer concentration of 2 % (w/v). The PEO solution was stirred at 50 ℃ for 24 h before further use. A series of solutions containing different C_{PEO} in CH_3OH were prepared, as shown in Table 1. These stock solutions were used as solvents for the addition of LiCl and then these procedures were repeated to prepare the CH_3COOLi-polymer solution system.

The stock solution of LiCl in PEO solution was prepared by transferring a known amount of LiCl salt into a solvent of fixed volume (PEO in CH_3OH). The electrolyte solution was stirred at 50 ℃ for 24 h before further use. Then, a series of dilutions of the stock solution was carried out by adding PEO solution. Similar steps were taken to prepare a stock solution of CH_3COOLi in PEO solution.

The κ measurements for the diluted solutions were performed using the SevenCompact S230 Conductivity meter from Mettler-Toledo (Schwerzenbach, Switzerland) with InLab® 731 (measuring range 0.01-1000 mS cm^{-1}) and InLab® 741 (measuring range 0.001-500 μS cm^{-1}) immersion conductivity probes. Both probes had built-in temperature sensors with an accuracy of ± 0.4 ℃. The conductivity meter had an automatic temperature compensation function that provided κ values at a reference temperature of 25 ± 0.4 ℃. The cell constants of the InLab® 731 and InLab® 741 probes were estimated daily by automatic calibration. An aqueous solution of 0.0005 mol dm^{-3} potassium chloride (KCl) (Mettler-Toledo, Schwerzenbach, Switzerland) was used as the primary standard for calibration with the conductivity meter, which had κ values of 1413 and 84 μS cm^{-1} at 25 ℃ when connected to InLab® 731 and InLab® 741, respectively.

RESULTS AND DISCUSSION

1. Limiting Molar Conductivity (Λ_o) Values for Aqueous Salt Solutions

LiCl and CH_3COOLi are known to act as strong electrolytes in the presence of water. However, these inorganic salts are only partially ionized in a non-aqueous system. Therefore, the total number of freely mobile ions in an electrolyte system depends on its salt concentration. Aqueous LiCl and CH_3COOLi will completely dissociate into their individual ions (cations and anions), as shown in Eq. 7 and Eq. 8.

$$LiCl\ (s) \rightarrow Li^+\ (aq.) + Cl^-\ (aq.) \qquad (7)$$

$$CH_3COOLi\ (s) \rightarrow Li^+\ (aq.) + CH_3COO^-\ (aq.) \qquad (8)$$

Table 1. Concentrations of PEO in CH_3OH.

10^3 C_{PEO} (g cm^{-3})	**Mass of PEO (g)**	**Volume of CH_3OH (cm^{-3})**
1.0	0.550	550
1.5	0.825	550
2.0	1.100	550
2.5	1.375	550
3.0	1.650	550

As a result of their differential ionization, the concentration of these ions in solution is proportional to the concentration of salt added to the aqueous electrolyte system.

The empirical relationship follows the Kohlrausch equation, as in Eq. 2. Therefore, this equation is used to determine the validity of the conductivity measurement by comparing it with the Λ value of the electrolyte system. Any deviation of this value from Eq. 2 may indicate an error in the conductivity measurement. Λ_o can be estimated by extrapolation at $C_{LiCl}^{1/2} = 0$ and $C_{CH3COOLi}^{1/2} = 0$ from the plots of Λ versus $C_{LiCl}^{1/2}$ and Λ versus $C_{CH3COOLi}$, respectively.

The κ values for the LiCl (aq.) and CH_3COOLi (aq.) solutions were measured using the conductivity meter with the InLab® 731 probe at 25 °C with $C_{LiCl} = 1.0 \times 10^{-3} - 2.0 \times 10^{-7}$ mol cm^{-3} and $C_{CH3COOLi} = 1.0 \times 10^{-3} - 2.0 \times 10^{-7}$ mol cm^{-3}. Tables 2 and 3 show the amounts of κ and Λ for C_{LiCl} and $C_{CH3COOLi}$, respectively. Figure 1 was drawn using Eq. 2 and the data listed in Tables 2 and 3 for LiCl (aq.) and CH_3COOLi (aq.) at 25 °C. Only the data values consistent with a high regression function ($r^2 = 0.98$) in Tables 2 and 3 were adopted for the regression of Eq. 2 in Figure 1, while the highlighted data were excluded.

Table 2. C_{LiCl}, κ and Λ for LiCl aqueous solution at 25 °C.

InLab® 731 Calibration standard: 1413 μS cm^{-1}; Cell constant: 0.510953 cm^{-1}		
10^5 C_{LiCl} (mol cm^{-3})	10^5 κ (S cm^{-1})	Λ (S cm^2 mol^{-1})
0.02	2.96	148.00
0.04	4.37	119.25
0.06	5.76	113.53
0.08	7.69	112.20
0.20	18.80	110.00
0.40	37.60	107.95
0.60	57.60	105.12
0.80	76.90	103.43
2.00	175.90	102.00
4.00	360.00	96.80
6.00	528.00	93.75
8.00	697.00	89.13
10.00	841.00	84.10
12.00	1008.00	84.00
14.00	1155.00	81.50
16.00	1308.00	80.10

Table 3. $C_{CH3COOLi}$, κ and Λ for CH_3COOLi aqueous solution at 25 °C.

InLab® 731 Calibration standard: 1413 μS cm^{-1}; Cell constant: 0.523074 cm^{-1}		
10^5 $C_{CH3COOLi}$ (mol cm^{-3})	10^5 κ (S cm^{-1})	Λ (S cm^2 mol^{-1})
0.02	1.81	90.35
0.04	3.24	80.9
0.06	4.64	77.25
0.08	6.14	76.80
0.20	15.04	75.21
0.40	29.30	73.25
0.60	43.50	72.50
0.80	55.60	69.50
2.00	133.46	66.73
4.00	252.96	63.24
6.00	357.90	59.65
8.00	455.04	56.88
10.00	549.00	54.90
12.00	642.00	53.50
14.00	733.04	52.36
16.00	802.08	50.13

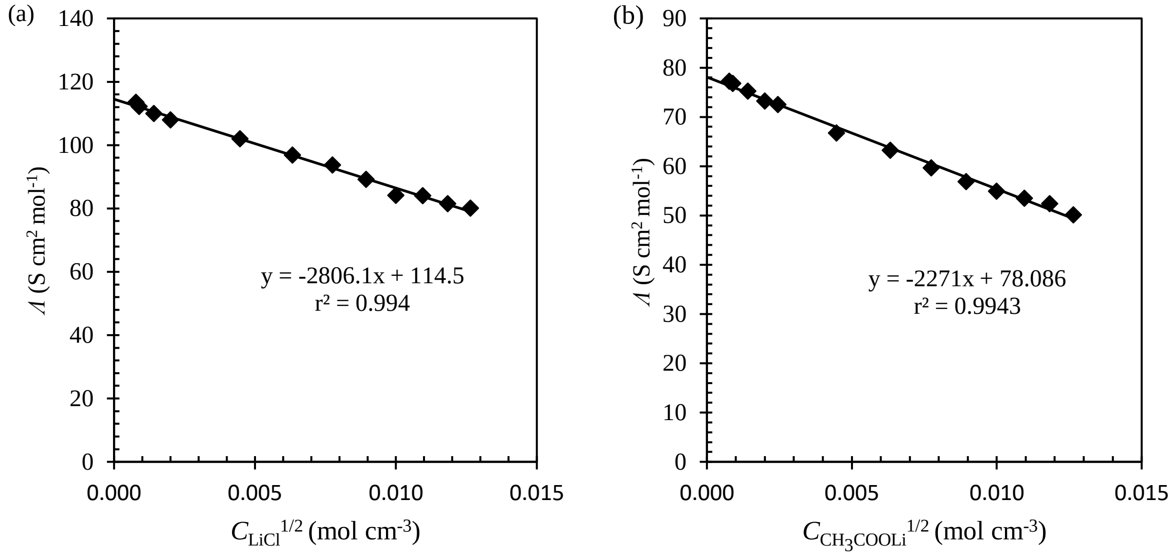

Figure 1. Graphs plotted using Eq. 2 for the data tabulated in (a) Table 2 and (b) Table 3 for the LiCl and CH_3COOLi aqueous solutions at 25 °C.

Regression functions from Figure 1 after Eq. 2.

For (a):

$$\Lambda = (114.5\ \mathrm{S\ cm^2\ mol^{-1}}) - (2806.1\ \mathrm{S\ cm^2\ mol^{-1}})\ (C_{\mathrm{salt}})^{1/2} \qquad \text{(correlation: 0.9940)} \tag{9}$$

For (b):

$$\Lambda = (78.086\ \mathrm{S\ cm^2\ mol^{-1}}) - (2271\ \mathrm{S\ cm^2\ mol^{-1}})\ (C_{\mathrm{salt}})^{1/2} \qquad \text{(correlation: 0.9943)} \tag{10}$$

Figure 1 shows the regression analysis according to Eqs. 9 and 10. The Λ_o values for LiCl (aq.) and CH_3COOLi (aq.) at 25 °C were 114.5 S cm^2 mol^{-1} and 78.086 S cm^2 mol^{-1}, respectively, which deviated less than 2 % from the theoretical values of 115.03 and 79.59 S cm^2 mol^{-1} [31]. This indicates that the experimental data obtained by the proposed method were acceptable with only a small margin of error. Therefore, using Ostwald's dilution law, the same experimental approach was applied to determine the Λ_o value for a weak electrolyte system (Eq. 3).

2. Limiting Molar Conductivity (Λ_o) Values for Salts in Organic Solution

In the presence of an organic solvent (CH_3OH), the electrolyte system acts as a weak electrolyte due to partial dissociation. Therefore, the Λ_o value of the weak electrolyte cannot be determined directly using the Kohlrausch equation, which is mainly suitable for strong electrolyte systems. Alternatively, Λ_o can be determined using the Ostwald dilution law (Eq. 3). LiCl and CH_3COOLi are examples of weak electrolyte systems in organic solvents. These salts will partially dissociate into their individual ions, as shown in Eqs. 11 and 12.

$$\mathrm{LiCl} \rightleftharpoons \mathrm{Li^+\ (aq.)} + \mathrm{Cl^-\ (aq.)} \tag{11}$$

$$\mathrm{CH_3COOLi} \rightleftharpoons \mathrm{Li^+\ (aq.)} + \mathrm{CH_3COO^-\ (aq.)} \tag{12}$$

It is well known that the concentration of ions is less than the concentration of solutes in a weak electrolyte system. Therefore, the determination of the total free mobile ions in the system is subject to the dissolution of solutes.

The κ values for the LiCl-CH_3OH and CH_3COOLi-CH_3OH systems were measured using a conductivity meter with the InLab® 741 probe at 25 °C in the range of C_{LiCl} and $C_{\mathrm{CH_3COOLi}}$ (1.0 x 10^{-3} - 2.0 x 10^{-7} mol cm^{-3}). Tables 4 and 5 show the Λ, $1/\Lambda$ and κ values for C_{LiCl} and $C_{\mathrm{CH_3COOLi}}$, respectively. Figure 2 was plotted according to Eq. 3 using the data listed in Tables 4 and 5 for the LiCl-CH_3OH and CH_3COOLi-CH_3OH systems at 25 °C. Only the data that fit with a high regression function ($r^2 = 0.98$) in Tables 4 and 5 were adopted for regression of Eq. 3 in Figure 2. The highlighted data in the tables were excluded.

Table 4. C_{LiCl}, Λ, $1/\Lambda$ and κ values for LiCl in CH_3OH at 25 °C.

10^5 C_{LiCl} (mol cm^{-3})	Λ (S cm^2 mol^{-1})	$1/\Lambda$ (mol S^{-1} cm^{-2})	10^4 κ (S cm^{-1})
0.04	100.75	0.0099	0.40
0.08	79.88	0.0125	0.64
0.16	79.19	0.0126	1.27
0.24	77.79	0.0129	1.87
0.32	75.97	0.0132	2.43
0.40	74.68	0.0134	2.99
0.48	73.31	0.0136	3.52
0.56	71.05	0.0141	3.98
0.64	69.88	0.0143	4.47
0.72	69.07	0.0145	4.97
0.80	68.30	0.0146	5.46
0.88	67.16	0.0149	5.910
4.00	56.00	0.0179	22.40
100.00	17.32	0.0577	173.18

Table 5. C_{CH3COOLi}, Λ, $1/\Lambda$ and κ values for CH_3COOLi in CH_3OH at 25 °C.

10^5 C_{CH3COOLi} (mol cm^{-3})	Λ (S cm^2 mol^{-1})	$1/\Lambda$ (mol S^{-1} cm^{-2})	10^4 κ (S cm^{-1})
0.04	77.90	0.0128	0.31
0.08	73.82	0.0135	0.59
0.16	72.98	0.0137	1.17
0.24	72.24	0.0138	1.73
0.32	71.50	0.0140	2.29
0.40	70.25	0.0142	2.81
0.48	69.48	0.0144	3.34
0.56	68.95	0.0145	3.86
0.64	68.13	0.0147	4.36
0.72	67.35	0.0148	4.85
0.80	66.50	0.0150	5.32
0.88	65.93	0.0152	5.80
4.00	60.24	0.0166	24.10
100.00	26.57	0.0376	265.71

Regression functions from Figure 2 after Eq. 3.

For (a):

$$1/\Lambda = (0.0958\ S^{-1}\ cm^{-2}\ mol) + (303.25\ S^{-2}\ cm^{-1}\ mol^{-1})\ \kappa \qquad \text{(correlation: 0.9877)} \tag{13}$$

For (b):

$$1/\Lambda = (0.0133\ S^{-1}\ cm^{-2}\ mol) + (3.2137\ S^{-2}\ cm^{-1}\ mol^{-1})\ \kappa \qquad \text{(correlation: 0.9963)} \tag{14}$$

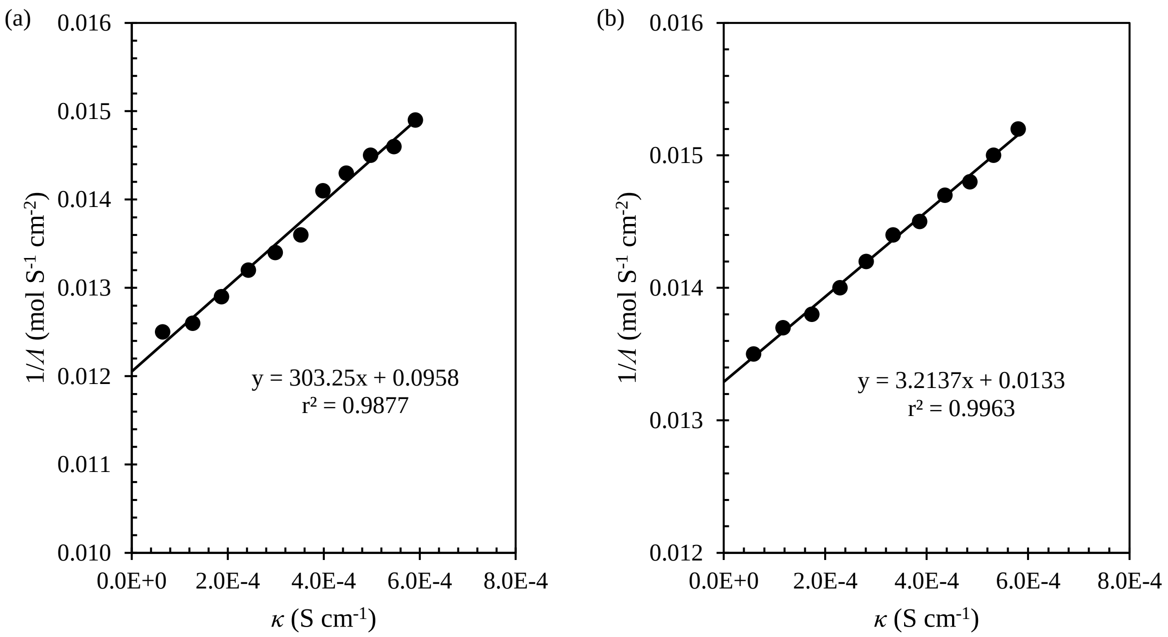

Figure 2. Graphs plotted using Eq. 3 and data tabulated in (a) Table 4 and (b) Table 5 for the LiCl-CH_3OH and CH_3COOLi-CH_3OH systems at 25 °C.

Figure 2 shows the regression analysis according to Eqs. 11 and 12 with the $1/\Lambda_o$ values for the LiCl-CH_3OH and CH_3COOLi-CH_3OH systems at 25 °C, which were 0.0958 mol S^{-1} cm^{-2} and 0.0133 mol S^{-1} cm^{-2}, respectively. From the results, the Λ_o values for the LiCl-CH_3OH and CH_3COOLi-CH_3OH systems were 10.44 S cm^2 mol^{-1} and 75.19 S cm^2 mol^{-1}, respectively. It is observed that the LiCl-CH_3OH and CH_3COOLi-CH_3OH systems had large deviations of more than 5% from the theoretical values reported, which were 91.91 and 81.22 S cm^2 mol^{-1} [32], [33]. This indicates that the experimental data obtained by the proposed method was not suitable for determining the Λ_o value for organic electrolyte systems. Therefore, an alternative method was used, namely the Power Law proposed previously [30].

3. Limiting Molar Conductivity (Λ_o) Values for Aqueous and Non-aqueous Salt Solutions Using the Proposed Power Law

In determining the Λ_o value for an organic electrolyte system, the Power Law was applied, as previously suggested [24]. The Power Law was used because Kohlrausch's equation and the Ostwald dilution law were not suitable to determine the Λ_o value for a complex system. The logarithmic plot of κ versus C_{salt} as in Eq. 4 is the best solution for recalculating Λ_o values for weak electrolyte systems. To test the Power Law, LiCl (aq.) and CH_3COOLi (aq.) at 25 °C were used as reference systems to verify the viability of Eq. 4. Theoretically, the proposed Power Law should be linear for a certain range of C_{salt}. Figure 3 shows the plots obtained from Eq. 4 for the data listed in Tables 2 and 3 for LiCl (aq.) and CH_3COOLi (aq.).

Regression functions from Figure 3 after Eq. 4.

For (a):

$$\log \kappa = 1.8169 + 0.9601 \log C_{salt} \qquad \text{(correlation: 0.9998)} \qquad (15)$$

For (b):

$$\log \kappa = 1.4489 + 0.9256 \log C_{salt} \qquad \text{(correlation: 0.9996)} \qquad (16)$$

By rearranging Eq. 15 and Eq. 16:

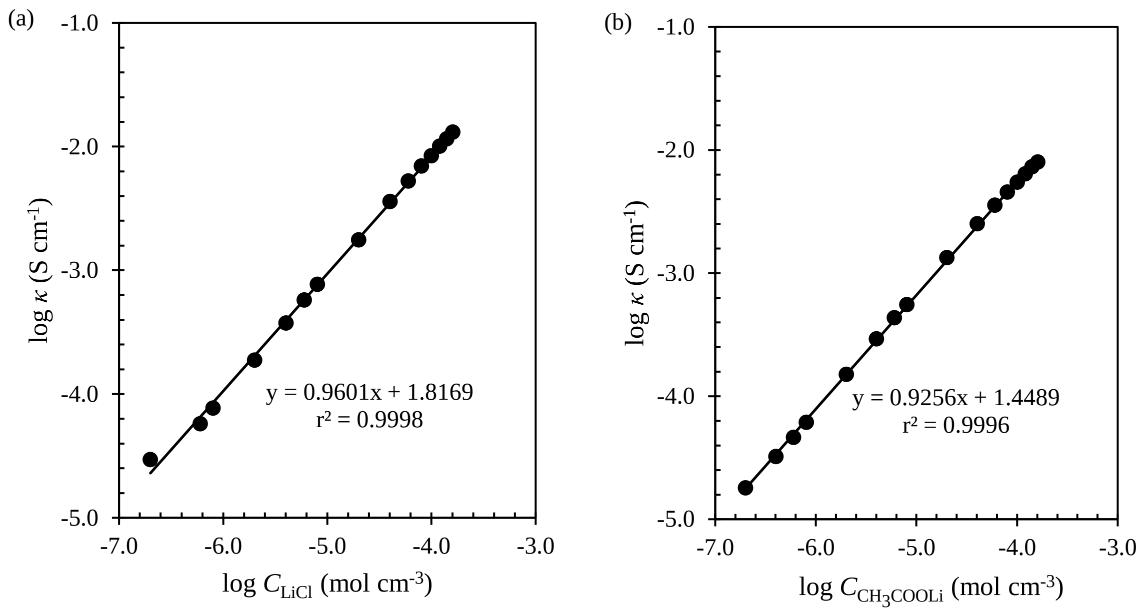

Figure 3. Graphs plotted using Eq. 4 for data tabulated in (a) Table 2 and (b) Table 3 for the aqueous solutions of LiCl and CH_3COOLi at 25 °C.

For (a):

$$\kappa = 65.60\left(\frac{C_{\mathrm{LiCl}}}{C^{\theta}}\right)^{0.9601} \tag{17}$$

For (b):

$$\kappa = 28.11\left(\frac{C_{\mathrm{CH_3COOLi}}}{C^{\theta}}\right)^{0.925} \tag{18}$$

thus,
for (a):

$$\Lambda = 65.60\left(\frac{C_{\mathrm{LiCl}}}{C^{\theta}}\right)^{-0.0399} \tag{19}$$

for (b):

$$\Lambda = 28.11\left(\frac{C_{\mathrm{CH_3COOLi}}}{C^{\theta}}\right)^{-0.0744} \tag{20}$$

From the plotted graph, the Λ_o value for the polymer electrolyte is calculated based on Eq. 21.

$$\Lambda^{o} = K'\gamma\, C_{\mathrm{ref}}^{\gamma-1} \tag{21}$$

The Λ_o value is calculated at a fixed salt concentration which is known as the reference salt concentration (C_{ref}). C_{ref} is needed to accurately calculate the Λ_o value for an electrolyte system. C_{ref} is approximately half of the lowest C_{salt} that obeys the Power Law. It was noted that C_{LiCl} = 6.0 x 10^{-7} mol cm^{-3} and C_{CH3COOLi} = 6.0 x 10^{-7} mol cm^{-3} were data that obeyed the Power Law and were thus used to estimate C_{ref} for the electrolyte system. Therefore, the C_{ref} values for these systems were half of the lowest C_{salt} at C_{ref} = 3.0 x 10^{-7} mol cm^{-3}.

Therefore, the estimated Λ_o values for the electrolyte systems based on Eq. 21 were:

For (a):

$$\Lambda_o = (65.60)(0.9601)(3.0 \text{ x } 10^{-7})^{0.9601-1} \tag{22}$$

$$\Lambda_o = 114.68 \text{ S cm}^2 \text{ mol}^{-1}$$

For (b):

$$\Lambda_o = (28.11)(0.9256)(3.0 \text{ x } 10^{-7})^{0.9256-1} \tag{23}$$

$$\Lambda_o = 79.54 \text{ S cm}^2 \text{ mol}^{-1}$$

In addition to determining the Λ_o values of aqueous salt solutions using the Power Law, non-aqueous salt solutions were also used to verify the workability of Eq. 4. The LiCl-CH_3OH and CH_3COOLi-CH_3OH systems at 25 °C were used as reference systems. Figure 4 shows the graph plotted using Eq. 4 on the data tabulated in Tables 4 and 5 for the LiCl-CH_3OH and CH_3COOLi-CH_3OH systems at 25 °C.

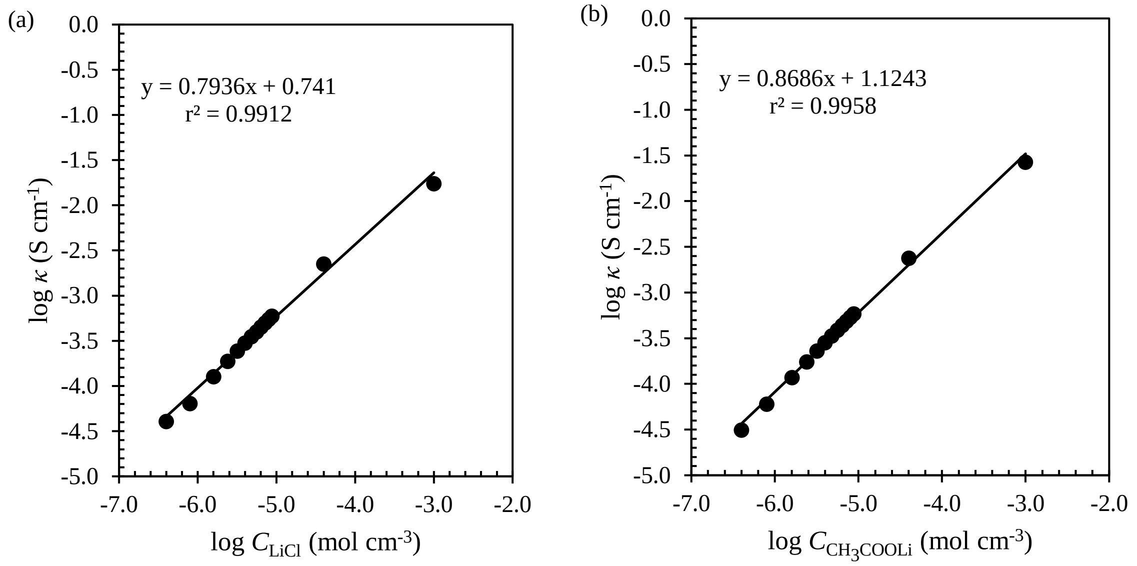

Figure 4. Graphs plotted using Eq. 4 and the data tabulated in (a) Table 4 and (b) Table 5 for the LiCl-CH_3OH and CH_3COOLi-CH_3OH systems at 25 °C.

Regression functions from Figure 3 after Eq. 4.
For (a):

$$\log \kappa = 0.741 + 0.7936 \log C_{salt} \qquad \text{(correlation: 0.9912)} \qquad (24)$$

For (b):

$$\log \kappa = 1.1243 + 0.8686 \log C_{salt} \qquad \text{(correlation: 0.9958)} \qquad (25)$$

By rearranging Eqs. 24 and 25:

For (a):

$$\kappa = 5.5081\left(\frac{C_{LiCl}}{C^{\theta}}\right)^{0.7936} \qquad (26)$$

For (b):

$$\kappa = 13.3137\left(\frac{C_{CH_3COOLi}}{C^{\theta}}\right)^{0.8686} \qquad (27)$$

thus,
for (a):

$$\Lambda = 5.5081\left(\frac{C_{LiCl}}{C^{\theta}}\right)^{-0.2064} \qquad (28)$$

for (b):

$$\Lambda = 13.3137\left(\frac{C_{CH_3COOLi}}{C^{\theta}}\right)^{-0.1314} \qquad (29)$$

Therefore, the Λ_o values obtained using Eq. 21 were:
For (a):

$$\Lambda_o = (5.5081)(0.7936)(4.0 \text{ x } 10^{-7})^{-0.2064} \qquad (30)$$

$$\Lambda_o = 91.4404 \text{ S cm}^2 \text{ mol}^{-1}$$

For (b):

$$\Lambda_o = (13.3137)(0.8686)(4.0 \text{ x } 10^{-7})^{-0.1314} \qquad (31)$$

$$\Lambda_o = 80.1324 \text{ S cm}^2 \text{ mol}^{-1}$$

The proposed Power Law was used to calculate Λ_o values for both strong and weak electrolyte systems. The calculated Λ_o values had a relatively small percentage deviation from the reported values. Therefore, the same method was used to calculate Λ_o values for the liquid polymer electrolyte systems.

3. *Limiting Molar Conductivity (Λ_o) Values for Liquid Polymer Electrolyte Solutions*

The proposed Power Law is a precise technique for determining Λ_o for a liquid polymer electrolyte-based organic solvent system. Tables 6 and 7 show the κ values for different C_{LiCl} and C_{CH_3COOLi} at various C_{PEO}. Figure 5 was plotted using Eq. 4 with the data tabulated in Tables 6 and 7 for the PEO-LiCl-CH_3OH and PEO-CH_3COOLi-CH_3OH polymer electrolyte systems at 25 °C. Only data consistent with a high regression function (r^2 = 0.98) were adopted for the regression of Eq. 4 in Figure 5, while the highlighted data were excluded.

Table 6. κ values at various C_{LiCl} for a range of C_{PEO} in CH_3OH at 25 °C.

10^5 C_{LiCl} (mol cm^{-3})	C_{PEO}: 0.0010g cm^{-3}	C_{PEO}: 0.0015g cm^{-3}	C_{PEO}: 0.0020g cm^{-3}	C_{PEO}: 0.0025g cm^{-3}	C_{PEO}: 0.0030g cm^{-3}
	10^3 κ (S cm^{-1})	10^3 κ (S cm^{-1})	10^3 κ (S cm^{-1})	10^3 κ (S cm^{-1})	10^3 κ (S cm^{-1})
0.04	0.042	0.035	0.026	0.023	0.021
0.08	0.066	0.057	0.044	0.039	0.035
0.16	0.121	0.105	0.082	0.074	0.066
0.24	0.175	0.154	0.111	0.105	0.101
0.32	0.219	0.182	0.126	0.122	0.117
0.40	0.267	0.227	0.166	0.159	0.149
0.48	0.323	0.278	0.201	0.191	0.185
0.56	0.373	0.324	0.236	0.224	0.213
0.64	0.418	0.368	0.265	0.255	0.245
0.72	0.471	0.398	0.303	0.270	0.255
0.80	0.509	0.440	0.346	0.312	0.287
0.88	0.554	0.503	0.403	0.335	0.316
4.00	1.994	1.752	1.424	1.255	1.192
100.00	16.200	13.600	11.100	10.500	9.700

Table 7. κ values at various $C_{\mathrm{CH_3COOLi}}$ for a range of C_{PEO} in CH_3OH at 25 °C.

10^5 $C_{\mathrm{CH_3COOLi}}$ (mol cm^{-3})	C_{PEO}: 0.0010g cm^{-3}	C_{PEO}: 0.0015g cm^{-3}	C_{PEO}: 0.0020g cm^{-3}	C_{PEO}: 0.0025g cm^{-3}	C_{PEO}: 0.0030g cm^{-3}
	10^3 κ (S cm^{-1})	10^3 κ (S cm^{-1})	10^3 κ (S cm^{-1})	10^3 κ (S cm^{-1})	10^3 κ (S cm^{-1})
0.04	0.035	0.033	0.031	0.028	0.025
0.08	0.066	0.062	0.054	0.050	0.045
0.16	0.119	0.106	0.100	0.098	0.084
0.24	0.169	0.155	0.136	0.130	0.123
0.32	0.208	0.198	0.168	0.153	0.144
0.40	0.255	0.245	0.213	0.192	0.183
0.48	0.297	0.289	0.254	0.237	0.213
0.56	0.342	0.338	0.294	0.278	0.253
0.64	0.397	0.378	0.333	0.313	0.288
0.72	0.446	0.427	0.370	0.353	0.317
0.80	0.495	0.451	0.405	0.373	0.332
0.88	0.642	0.517	0.425	0.390	0.343
4.00	1.695	1.654	1.458	1.413	1.167
100.00	8.000	7.900	7.800	7.700	6.000

From Tables 6 and 7, the logarithmic graphs of κ versus C_{LiCl} and κ versus $C_{\mathrm{CH_3COOLi}}$ were plotted, as shown in Figure 5. From these graphs, the regression functions were calculated based on Eq. 4, while the Λ_o values for the polymer electrolytes were calculated using Eq. 21.

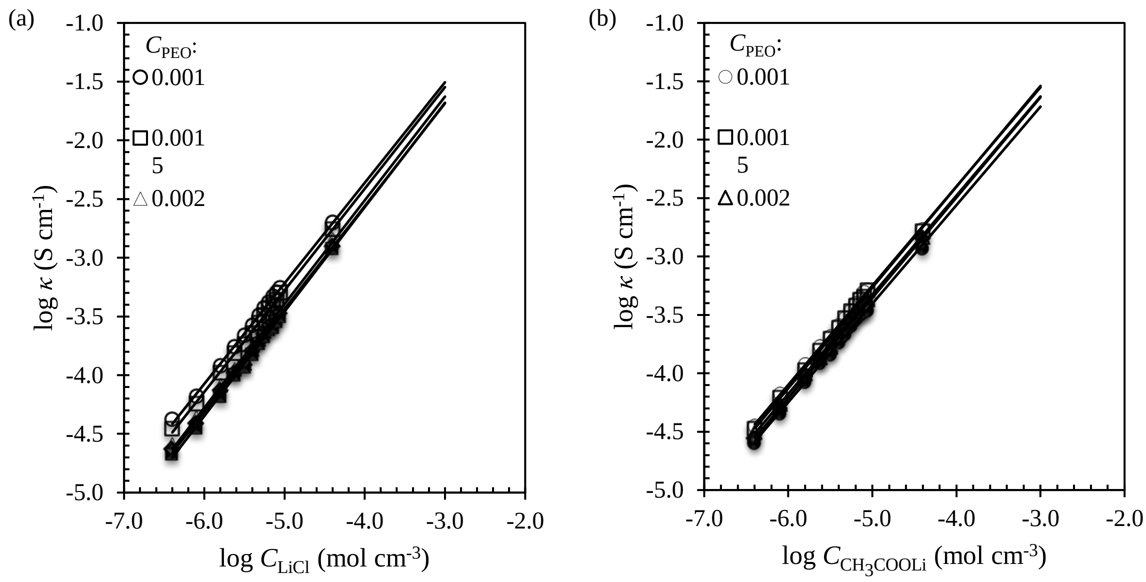

Figure 5. Graphs plotted using Eq. 4 for the data tabulated in (a) Table 6 and (b) Table 7 for the LiCl-PEO-CH_3OH and CH_3COOLi-PEO-CH_3OH polymer electrolyte systems at 25 °C.

Regression functions from Figure 5 after Eq. 4.
For (a):

C_{PEO}: 0.0010g cm^{-3}

$$\log \kappa = 1.0628 + 0.8562 \log C_{salt} \quad \text{(correlation: 0.9985)} \tag{32}$$

or

$$\Lambda = 11.5558\left(\frac{C_{LiCl}}{C^{\theta}}\right)^{-0.1438} \tag{33}$$

For (b):

C_{PEO}: 0.0010g cm^{-3}

$$\log \kappa = 0.9967 + 0.8492 \log C_{salt} \quad \text{(correlation: 0.9986)} \tag{34}$$

or

$$\Lambda = 9.9243\left(\frac{C_{LiCl}}{C^{\theta}}\right)^{-0.1508} \tag{35}$$

Therefore, Λ_o values could be derived from the plotted graphs using Eq. 21 with C_{ref} = 4.0 x 10^{-7} mol cm^{-3}. The C_{ref} value used to calculate the Λ_o value for LPE system was taken from the LiCl-CH_3OH and CH_3COOLi-CH_3OH electrolyte systems, with the assumption that the C_{ref} value did not change with the addition of PEO in the system.

For (a):

C_{PEO}: 0.0010g cm^{-3}

$$\begin{aligned}\Lambda_o &= (11.5558)\,(0.8562)\,(4.0 \times 10^{-7})^{-0.1438} \\ &= 82.2998 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned} \tag{36}$$

For (b):

C_{PEO}: 0.0010g cm^{-3}

$$\begin{aligned}\Lambda_o &= (9.9243)\,(0.8492)\,(4.0 \times 10^{-7})^{-0.1508} \\ &= 77.7176 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned} \tag{37}$$

Table 8. Λ_o values at different C_{PEO} for the PEO-LiCl-CH_3OH and PEO-CH_3COOLi-CH_3OH polymer electrolyte systems at 25 °C.

10^3 C_{PEO} (g cm^{-3})	PEO-LiCl-CH_3OH	PEO-CH_3COOLi-CH_3OH
	Λ_o (S cm^2 mol^{-1})	Λ_o (S cm^2 mol^{-1})
0	91.44	80.13
1.0	82.30	77.72
1.5	70.39	72.77
2.0	51.72	64.94
2.5	47.88	59.92
3.0	44.20	55.05

The limiting conductivity was inversely proportional to the degree of salt dissociation. Therefore, the total salt dissociation of both salts was different mainly due to their electrostatic attraction to the backbone of the PEO chain, which was very much dependent on the elements present.

The electronegativity difference between Li and Cl is 2, while for Li and O it is 2.5. Therefore, the degree of salt dissociation in the LiCl electrolyte system is expected to be higher compared to the LiO system.

The Λ_o values at different C_{PEO} for PEO-LiCl-CH_3OH and PEO-CH_3COOLi- in Table 8. From the table, it can be seen that Λ_o CH_3OH are summarized decreased with increasing C_{PEO}. This indicates that the degree of salt dissociation increased, which is due to the presence of polar groups which increased with C_{PEO}. The electrostatic attraction between the salt ions and the polar groups of the PEO thus becomes stronger. The Λ_o value was higher for the LiCl system compared to the CH_3COOLi system. The CH_3COO^- ion is larger than the Cl^- ion, thus CH_3COOLi has a higher degree of dissociation due to its lower lattice energy. This indicates that a salt with low lattice energy increases the degree of dissociation and hence improves the conductivity of the system.

CONCLUSION

The Power Law was applied to determine the Λ_o value of LiCl and CH_3COOLi in PEO-CH_3OH solutions for a range of PEO concentrations (0.0010-0.0030 g cm^{-3}) at 25 °C due to the unsuitability of the Kohlrausch Law and Ostwald's Dilution Law in determining Λ_o values for weak polymer electrolyte systems based on organic solvents. As the C_{PEO} value increased, the Λ_o value showed a decreasing trend. This indicates that the addition of PEO in weak electrolyte systems increased the dissociation of LiCl and CH_3COOLi and thus increased conductivity values.

ACKNOWLEDGEMENT

The authors thank Universiti Teknologi MARA (UiTM) for granting funds for this project through letter No. 600-IRMI/FRGS-RACER 5/3 (098/2019) and 600-RMC/MyRA 5/3/LESTARI (011/2020).

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