



A New Approach in Determining Limiting Molar Conductivity value for Liquid Electrolyte



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ABSTRACTS

Accurate determination of limiting molar conductivity (Λ_0) value for an electrolyte at infinite dilution is an important physical quantity that reviews the strength of an electrolyte. Therefore, in this study, a power law comprised of a double-logarithmic plot of electrolytic conductivity (κ) and salt concentration (C_{salt}) has been introduced to determine Λ_0 accurately at a corresponding reference salt concentration (C_{ref}). Furthermore, the reliability of the experimental data is verified after Kohlrausch's law for LiClO_4 (aq.) at 25.0 °C which is perfectly identical with the reference data. The workability of the power law is tested for LiClO_4 (aq.) and LiClO_4 in acetonitrile (ACN) at a range of C_{salt} at 25.0 °C. Thus, the Λ_0 for both systems correspond at 106 and 177.4 S cm² mol⁻¹ respectively, after the power law deviated only 2% of the reported value. From the study, it is noted that the corresponding C_{ref} is approximately half of the lowest C_{salt} concentration that obeys the power law at infinite dilution which responds to Λ_0 for an electrolyte system. This alternative method shows a nice linearity for C_{salt} (10^{-5} - 10^{-9} mol cm⁻³) between the experimental and reference data before it deviates from the linearity above $C_{\text{salt}} > 10^{-5}$ mol cm⁻³.

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1. INTRODUCTION

Electrolyte is define as any substance containing free ions (cation and anion) that makes the substance electrically conductive [1]. An electrolyte solution is normally formed when a solute such as inorganic salt is added into a protic or aprotic solvent. The individual components of the solute will dissociate due to thermodynamic interaction with the solvent in a process called solvation [2,3]. A stronger interaction between solute-solvent will enhance the solute dissociation in an electrolyte system [4,5].

The strength of solute dissociation in an electrolyte solution can be monitored by using the electrolytic conductivity (κ) data for a series of conductivity measurement for a wide range of solute concentrations [6,7]. Furthermore, quantity κ of an electrolyte depends a lot on the concentration (C) of the total ions present in the system. Therefore, it is convenient to divide the κ by solute concentration [Eq. (1)] [8].

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

κ = electrolytic conductivity (expressed in siemens per centimeter (S cm⁻¹))
 C_s = solute concentration (example: inorganic salt (C_{salt})) (expressed in mole per centimeter cubic (mol cm⁻³))
 Λ = molar conductivity (expressed in siemens centimeter-squared per mole (S cm² mol⁻¹))

An electrolyte is known as strong if it has a high concentration of ions and dilute if it has a low concentration of ions. This is due to the different dissociation behavior of the solute in a solvent. Again, a strong electrolyte will act as a good conductor of electric current in solution as a result of complete ionization of the solute in the solvent. Therefore, the concentration of solute is to be proportional to the concentration of ions present in the electrolyte system that follows an empirical relation between Λ [Eq. (1)] and C_s that fits the Kohlrausch's equation [Eq. (2)] for a wide range of C_s and temperature [6,8,9].

$$\Lambda = \Lambda_0 - KC_s^{1/2} \quad (2)$$

Unequivocally, Λ_0 denotes molar conductivity at infinite dilution or which is generally known as limiting molar conductivity. Quantity Λ_0 can be estimated by extrapolation at $C_s^{1/2} = 0$ of a Λ

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plot versus $C_s^{1/2}$. At $C_s^{1/2}=0$ the electrolyte is assumed to fully deprotonates, and its molar conductivity is then Λ_0 . Therefore, this quantity is an important parameter for an electrolyte system to indicate solute dissociation behavior (degree of dissociation (α)) for a wide range of C_s as shows in Eq. (3) [8,10]. Quantity K in Eq. (2) is an empirical constant that depends on the type of the electrolyte.

$$\alpha = \frac{\kappa}{C_s}(\Lambda_0)^{-1} \quad (3)$$

However, due to partial dissociation behavior of the weak electrolyte, only a limited number of free ions present in the electrolyte with a lower Λ value is observed at a higher C_s and an exponential increase is noted when $C_s \rightarrow 0$ which deviates from the linearity approach as mentioned in Eq. (2). This indicate that the concentration of total ions in a solution of a weak electrolyte is less than the concentration of the electrolyte itself [6,11]. Hence, for weak electrolytes, the above equation is not valid while approaching $C_s^{1/2}=0$ and will cause a difficulty in determining accurately the Λ_0 value. This is because the extrapolation is unreliable for the asymptotic approach for plot Λ versus $C_s^{1/2}$ to the y-axis [12–14].

Therefore, the Λ_0 of weak electrolyte is normally estimated with Ostwald's dilution law Eq. (4).

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + \frac{\Lambda C}{K_c(\Lambda_0)^2} \quad (4)$$

K_c = equilibrium constant From Eq. (4), a plot of $1/\Lambda$ against ΛC , the values of Λ_0 and K_c can be obtained from the intercept and the slope of the plot. Nevertheless, determination of Λ_0 after the Eq. (4) especially for organic electrolyte solution still could not achieve a good approximation as expected and subjected to numerous assumptions [15–18]. Aprano et al., [12] studied the ion dissociation behavior of LiClO_4 in tetrahydrofuran (THF) by conductivity measurement for the salt concentration below $10^{-6} \text{ mol cm}^{-3}$ at 25°C after Lee-Wheaton equation. However, the estimated value of $\Lambda_0 = 32.1 \pm 0.3 \text{ S cm}^2 \text{ mol}^{-1}$ as compared to that of the expected value of $\Lambda_0 \approx 155.3 \text{ S cm}^2 \text{ mol}^{-1}$. The difference between estimated and expected value was suggested due to inaccuracies in extrapolation of the molar conductivity to the infinite dilution.

Das et al., [15] estimated quantity Λ_0 for LiClO_4 in THF at the salt concentration range of 10^{-6} – $10^{-4} \text{ mol cm}^{-3}$ at 25°C using conductivity measurement. The Λ_0 of the system was determined though an extrapolation of a double logarithmic plot of Λ as a function of salt concentrations to infinite dilution. The estimated Λ_0 for this electrolyte is $140.8 \text{ S cm}^2 \text{ mol}^{-1}$, the authors highlight the uncertainties up to 3% in estimation of Λ_0 as a result from the formation of ion-pair that predominate in the system.

Chagnes et al., [17,19] studied the conductivity behavior of LiClO_4 in γ -butyrolactone at 25°C after a cube root law by modifying Kohlrausch's equation for the salt concentration between 3.5×10^{-4} – $1.3 \times 10^{-3} \text{ mol cm}^{-3}$. The Λ_0 of this electrolyte is estimated though the extrapolation of plot of Λ against the cube root of LiClO_4 concentrations. The estimated Λ_0 for this electrolyte is a good fit for the expected value. However, the proposed model is only valid for limited organic electrolyte system at a range of temperatures.

Therefore, important theoretical progress was made in recent years by developing empirical and chemical models for electrolyte solution. The low-concentration chemical model is used to improve the accuracy of the determination of Λ_0 for a weak electrolyte system which is produced by modifying Kohlrausch's equation or Ostwald's dilution law [12,15,20,21]. Thus, in this study a new approach known as power law is used to determine the Λ_0 . This model might serve as a general model for the estimation of Λ_0 for different weak organic electrolyte systems with a better

accuracy that might be valid for a large range of salt concentrations. The critical point is the accurate determination of electrolytic conductivity (κ) at a sufficiently low solute concentration at constant temperature (25.0°C). It is important since this is a prerequisite for extrapolation of molar conductivity to zero solute concentration.

Therefore, in an attempt to choose an adequate system to test the power law, lithium perchlorate (LiClO_4) acts as an inorganic salt (C_{salt}) and is used to prepare the aqueous (aq.) solution. Thus, a series of conductivity measurements were carried out at $25.0 \pm 0.4^\circ\text{C}$ for this system. LiClO_4 (aq.) is chosen as a strong electrolyte as a reference system for power law. Hence, the same approach is further adapted for an organic weak electrolyte system, which consists of LiClO_4 in acetonitrile (ACN) to test the validity and the workability of the power law proposed in the determination of Λ_0 . Theoretically, the power law proposed should be linear for a certain range of salt concentrations (C_{salt}).

2. THEORETICAL BACKGROUND: POWER LAW

The power law introduced in this study is due to the inadequate adaptation of Eq. (4) in the estimation of molar conductivity at infinite dilution (Λ_0) for organic weak electrolyte systems. It is a double-logarithmic plot of κ versus salt concentrations (C_{salt}). Power law is proposed because electrolytic conductivity's (κ) of the electrolyte became almost constant below a certain concentration. However, the quantity Λ does not tend under these circumstances to a limiting value for $C_{\text{salt}} \approx 0$. The constancy of κ over a certain salt concentration is a physically relevant effect, such as limits of the measurement of the instrument used [22].

This double-logarithmic plot of κ versus C_{salt} in Eq. (5) may be the best solution to recalculate the Λ_0 value for organic electrolyte systems.

$$\log \kappa = K' + \gamma \log C_{\text{salt}} \quad (5)$$

K' is the intercept and γ is the slope of the double-logarithmic plot Upon rearranging Eq. (5),

$$\kappa = K' \left(\frac{C_{\text{salt}}}{C^\theta} \right)^\gamma \quad (6)$$

Which yields immediately after Eq. (5) and Eq. (1),

$$\Lambda = K' \left(\frac{C_{\text{salt}}}{C^\theta} \right)^{\gamma-1} \quad (7)$$

$C^\theta = 1 \text{ mol cm}^{-3}$, it is introduced to keep the exponential expression dimension-less. K' denotes ion mobility is a constant.

From Eq. (7), the molar conductivity of the electrolyte system is calculated. Hence, the Λ_0 for the system is also calculated after Eq. (7) at a selected salt concentration known as reference salt concentration (C_{ref}). This will be discussed later in details.

Thus, by using the electrolytic conductivity data, quantity Λ_0 can be determined using the power law. For the first part of this study the Λ_0 value for LiClO_4 (aq.) at 25.0°C is determined by a set of reference system that can serve as a strong electrolyte. Then, this value is further compared with the reference data to test the workability of the power law. From the proposed method, this might contribute to a simple alternative yet with an acceptable accuracy in the determination of quantity Λ_0 , for both strong and weak electrolyte systems.

3. EXPERIMENTAL

3.1. Chemical

The inorganic salt anhydrous LiClO_4 with purity $\geq 99\%$ was obtained from Acrōs Organic. It was kept in the electronic

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