



## Discrepancy in Electrolytic Conductivity Value Using Different Concentrations of KCl (aq.) as Calibrating Standard

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Precise calibration of a conductivity probe in any conductance measurements is an important factor which determines the reliability of further analysis in an experiment. In normal practices standard solution of KCl (aq.) is used for an accurate calibration of the probe to determine the cell constant. Therefore, accurate measurements of electrical conductivity ( $\kappa$ ) for  $\text{LiClO}_4$  (aq.) at 25 °C are reported. A wide range of salt concentrations  $10^{-3}$ - $10^{-8}$  mol  $\text{cm}^{-3}$  have been prepared through a series of dilutions from the stock solution used for the analysis. The conductivity measurement for  $\text{LiClO}_4$  (aq.) is carried out after the conductivity probe has been calibrated using different concentrations of primary standard KCl (aq.) at 25 °C under a controlled environment. Since, the experimental conditions are same in both systems, the same cell constant is adopted in further calculations. The data is analyzed after Kohlrausch's equation and the limiting molar conductivity ( $E_0$ ) values are determined at infinite dilution. It is experimentally shown that molar conductivity ( $E$ ) value for  $\text{LiClO}_4$  (aq.) at 25 °C deviate from the regression function below the  $E$  value of the calibration standard used. This may suggest that the selection of the right concentrations of KCl (aq.) as a calibration standard is an important factor in liquid electrolyte system for a precise conductivity measurement. It is also noticed that the conductivity measurement of the analyte below the calibration value subjected to a large discrepancy in the conductivity measurement.

**Keywords:** Conductivity, Primary standard KCl (aq.), Kohlrausch's equation, Limiting molar conductivity, Liquid electrolyte.

### INTRODUCTION

Electrical conductivity,  $\kappa$  is one of the most intensively studied physical properties for different electrolyte systems<sup>1-3</sup>. Quantity  $\kappa$  of an electrolyte solution is a measure of its ability to conduct electricity that very much depends on the number of ions presented.  $\kappa$  is directly proportional to the total ions in the system. Therefore, it is normal to introduce the molar conductivity ( $E$ ) as defined in eqn. 1 by dividing the electrolytic conductivity with the ionic concentration ( $C$ )<sup>4</sup>.

$$E = \frac{\kappa}{C} \quad (1)$$

Quotient  $E$  as shown in eqn. 1 is normally expressed in siemens centimeter-squared per mole ( $\text{S cm}^2 \text{mol}^{-1}$ ) and is used to analyse the properties of liquid electrolyte for instant measurement of the strength of solvent<sup>3</sup>, ion association<sup>5</sup>, individual ion mobility at a range of salt concentration ( $C_{\text{salt}}$ ) at different analyte temperature<sup>6</sup> and type of solvent used<sup>7</sup>. Therefore, the molar conductivity of the analyte is inversely proportional to the total amount of ions that dissociate in the electrolyte system which greatly depends on the thermodynamic properties

of the solvent used. Other than the ions concentration factor, this value is also considerably dependant on an accurate determination of the cell constant normally calculated after eqn. 2.

$$\kappa = \frac{l}{RA} \quad (2)$$

( $l$ ) length of electrode, cross-sectional surface area ( $A$ ) of the electrode, ( $R$ ) electrical resistance of the solution. From eqn. 2, the  $l/A$  value is known as cell constant for the particular electrode.

Hence, in order to get a precise molar conductivity value a good estimation of the cell constant is important. In normal practice, the electrode used for conductivity measurement will be calibrated using a sample [typically an aqueous solution of potassium chloride, KCl (aq)] of known conductivity and the cell constant is determined by a back calculation of eqn. 2.

However, in any conductivity measurement it is important to precisely calibrate the conductivity probe used for the analysis. The purpose for this calibration is to determine the cell constant of the probe at a given temperature. The accuracy of the latter part of the conductivity measurement is determined by the right choice of the calibration standard to calibrate the probe.

In a normal practice, different concentrations of primary standard aqueous potassium chloride, KCl (aq.) are used to calibrate the conductivity probe<sup>8-10</sup>. KCl (aq.), is chosen as a calibrating solvent because it is believed to act as a strong electrolyte that fully dissociates to its individual ions in aqueous medium<sup>8</sup>. KCl (aq.) is also noticed to fit well in the Kohlrausch's equation (eqn. 3) for a wide range of ion concentrations and temperature<sup>4,8,11</sup>.

$$E = E_0 - \kappa C_{\text{salt}}^{1/2} \quad (3)$$

Therefore, in this study, we have used different concentrations of primary standard KCl (aq.) to calibrate the probe used for the conductivity measurement and accurately determine the cell constant at 25 °C. Then, the validity range of the calibration using different concentrations of primary standard KCl (aq.) are tested for different electrolyte systems by calculating E and determining limiting molar conductivity,  $E_0$  value. Hence, aqueous lithium perchlorate, LiClO<sub>4</sub> (aq.) at 25 ± 0.4 °C is chosen for this purpose and has been examined after Kohlrausch's equation (eqn. 3) at diluted salt concentrations,  $C_{\text{salt}}$ . Later, the deviation of the molar conductivity values from eqn. 3 will be an indication of error in conductivity measurement that may be due to the calibration of the probe is no longer valid below that  $C_{\text{salt}}$ .

## EXPERIMENTAL

Anhydrous LiClO<sub>4</sub> with purity > 99 % was obtained from Acros Organic and dried in a vacuum oven at 100 °C for 24 h to eliminate any traces of water before dissolution in the water. Water is used for the preparation of LiClO<sub>4</sub> (aq.) and the rinsing of the glassware in this analysis. The water used in this study was prepared by passing through the double distilled water to water deionizing system Arium<sup>®</sup> 611D1 (Sartorius, Goettingen, Germany) that generally has electrolytic conductivity less than 18 × 10<sup>6</sup> Ω cm at 25 °C. Afterwards, the deionized water was kept in a fluorinated high-density polyethylene (FLPE) container (Nalgene Labwere, Rochester USA) before further use.

Preparation of the LiClO<sub>4</sub> (aq.) as well as the conductivity measurement for the systems was carried out under a controlled environment to minimise error in  $\kappa$  measurements. The temperature of the laboratory was controlled at 25 ± 2 °C. All the glassware used was cleaned with concentrated chromic sulphuric acid. Then, it was further cleaned with Extran<sup>®</sup> 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.

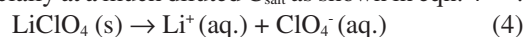
LiClO<sub>4</sub> (aq.) stock solution of known concentration was prepared. Subsequently, the solution was stirred for 24 h at 50 °C. Then, an approximately 8-12 subsequent dilutions were carried out from the stock solution for the analysis. The  $\kappa$  measurement for the diluted solution of LiClO<sub>4</sub> (aq.) solutions were carried out using Mettler-Toledo SevenCompact S230 Conductivity meter (Schwerzenbach, Switzerland) with its dip-type conductivity probes InLab<sup>®</sup> 731 (measuring range 0.01-1,000 mS cm<sup>-1</sup>) and InLab<sup>®</sup> 741 (measuring range 0.001-500 μS cm<sup>-1</sup>). Both probes 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  $\kappa$  from the conductivity meter are the  $\kappa$  at referred temperature of 25 ± 0.4 °C. All the preparation steps of the solution and conductivity measurements are carried out in a glove box under nitrogen gas condition avoid the absorption of carbon dioxide gas into the salt solution that may cause error in conductivity measurement particularly at low salt concentration.

The cell constant of InLab<sup>®</sup> 731 and InLab<sup>®</sup> 741 probes was estimated by automatic calibration on daily basis. The primary standard of aqueous solution of potassium chloride (KCl) (Mettler-Toledo, Schwerzenbach, Switzerland) at concentrations 0.1, 0.01 and 0.0005 mol dm<sup>-3</sup> with the quantities  $\kappa$  at 12.88, 1413 and 84 μS cm<sup>-1</sup>, respectively, at 25 °C were used for the calibration with the conductivity meter attached to InLab<sup>®</sup> 731 and InLab<sup>®</sup> 741, respectively.

## RESULTS AND DISCUSSION

Lithium perchlorate (LiClO<sub>4</sub>) salt is believed to act as a strong electrolyte in the presence of water. Aqueous LiClO<sub>4</sub> will completely dissociate to its individual ions (cation and anion) especially at a much diluted  $C_{\text{salt}}$  as shown in eqn. 4<sup>12,13</sup>.



As a result of their complete ionization, the concentration of ions in the solution is proportional to the concentration of LiClO<sub>4</sub>(s) added into the solvent. Kohlrausch suggested an empirical relationship as shown in eqn. 3. Therefore, this equation can be used to determine the validity of the conductivity measurement by comparing the molar conductivity value of the electrolyte system. Any discrepancy of this value from eqn. 3 may indicate error in the conductivity measurement.

Consequently, the validity of the conductivity measurements of aqueous LiClO<sub>4</sub> using different concentrations of primary standard KCl as calibration standard was carried out at 25 °C at a dilute range of LiClO<sub>4</sub> (aq.) concentrations. Three different concentrations of KCl (aq.) solutions are used to calibrate the conductivity probe and the cell constant is determined accurately. Since, these measurements are performed in the same conductivity probe and in the same condition it is assumed that the value of cell constant remains unchanged for the two sets of measurements. Therefore, the validity of the conductivity measurements can be tested after eqn. 3 at a diluted concentration. E at infinite dilution,  $E_0$  can be estimated for a particular electrolyte system by extrapolation at  $C_{\text{salt}}^{1/2} = 0$  of a plot of E versus  $C_{\text{salt}}^{1/2}$ .

The  $\kappa$  results for LiClO<sub>4</sub> (aq.) solution were measured using conductivity meter coupled with InLab<sup>®</sup> 731 and InLab<sup>®</sup> 741 at 25 °C at  $C_{\text{salt}} = 1 \cdot 10^{-3}$ - $1 \cdot 10^{-8}$  mol cm<sup>-3</sup>. Tables 1 and 2 show quantities of  $\kappa$  and E at respective  $C_{\text{salt}}$  for LiClO<sub>4</sub> (aq.) at 25 °C for the work done in this study using different concentrations of KCl (aq.) as calibration standards.

Tables 1 and 2 quantities of  $\kappa$  and E at respective  $C_{\text{salt}}$  for LiClO<sub>4</sub> (aq.) at 25 °C for the work done in this study using the method discussed above. Fig. 1 is plotted after eqn. 3 for set of data as tabulated in Tables 1 and 2 for aqueous solution of LiClO<sub>4</sub> at 25 °C using different calibration standards. Only the highlighted data in Table-1 and 2 was adopted for linear

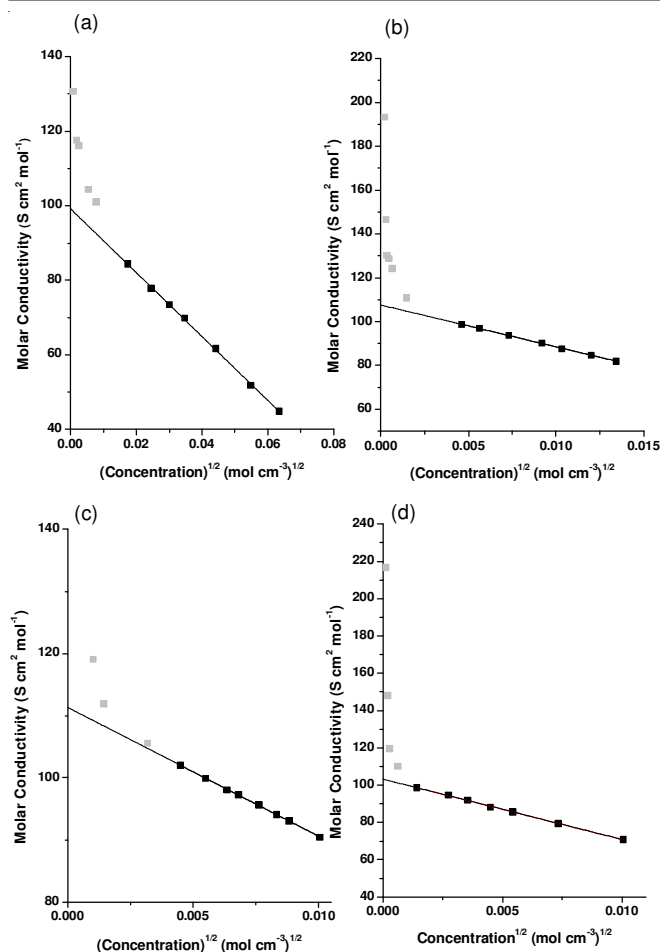


Fig. 1. Plotted after eqn. 3 for set of data as tabulated in Tables 1(a) and (b) and 2(c) and (d) for aqueous solution of  $\text{LiClO}_4$  at 25 °C. Experiment data: (■) data included; (□) data excluded in the regression. Solid curve represents the linear regression after eqn. 3

regression of eqn. 3 in Fig. 1. Only  $\kappa$  value of  $\text{LiClO}_4$  (aq.) above the  $\kappa$  value of the calibration standard is used in this analysis. It was also noted the  $\kappa$  values for  $\text{LiClO}_4$  (aq.) below  $\kappa$  value of the calibration standard deviated from the linear approach after eqn. 3 and this data was excluded from the analysis.

Regression function from Fig. 1 after eqn. 3.

For (a):

$$E = (99.16 \text{ S cm}^2 \text{ mol}^{-1}) - (856.5 \text{ S cm}^{7/2} \text{ mol}^{-3/2}) (C_{\text{salt}})^{1/2} \quad (5)$$

(correlation. 0.9994)

For (b):

$$E = (107.60 \text{ S cm}^2 \text{ mol}^{-1}) - (1.90 \times 10^3 \text{ S cm}^{7/2} \text{ mol}^{-3/2}) (C_{\text{salt}})^{1/2} \quad (6)$$

(correlation. 0.9995)

For (c):

$$E = (111.31 \text{ S cm}^2 \text{ mol}^{-1}) - (2.07 \times 10^3 \text{ S cm}^{7/2} \text{ mol}^{-3/2}) (C_{\text{salt}})^{1/2} \quad (7)$$

(correlation. 0.9997)

For (d):

$$E = (103.76 \text{ S cm}^2 \text{ mol}^{-1}) - (3.33 \times 10^3 \text{ S cm}^{7/2} \text{ mol}^{-3/2}) (C_{\text{salt}})^{1/2} \quad (8)$$

(correlation. 0.9991)

Fig. 1 indicates the regression analysis using eqns. 5-8 showing  $E_0$  values for  $\text{LiClO}_4$  (aq.) at 25 °C using different concentration of KCl (aq.). It is noticed that whenever the conductivity measurement of  $\text{LiClO}_4$  (aq.) is measured below the  $\kappa$  value of the calibration standard used the molar conductivity data starts to deviate from eqn. 3. This has been observed for all the studied systems using different concentrations of KCl (aq.).

This indicated a positive connection between the conductivity measurements of the sample with the standard used for the calibration for a particular probe. From the experimental data, it is noted the conductivity measurement below the conductivity data of the calibration standard resulted in a discrepancy in molar conductivity measurement which deviated from the ideal electrolyte behaviour even though all the conductivity measurements in this study were measured within the sensitivity of the probes used. This indicates that a careful selection of the KCl (aq.) solution for the calibration purpose is an important factor.

In addition, the validity of this set of experimental data was also confirmed by comparing the limiting molar conductivity value by extrapolating the  $\text{LiClO}_4$  (aq.) concentration to zero after eqn. 3. In our opinion if the calibration is valid for a range of concentrations the  $E_0$  for  $\text{LiClO}_4$  (aq.) should be same as reported at similar experimental conditions.

Fig. 2 is plotted after eqn. 3 for the set of data as tabulated in Tables 1 and 2 for aqueous solution of  $\text{LiClO}_4$  at 25 °C.

TABLE-1  
ELECTROLYTIC CONDUCTIVITY ( $\kappa$ ), MOLAR CONDUCTIVITY (E) AND  $C_{\text{salt}}$  FOR  $\text{LiClO}_4$  (aq.) OF EXPERIMENTAL RESULTS IN THIS STUDY USING DIFFERENT KCl (aq.) CALIBRATION STANDARD AT 25 °C

InLab® 731 Calibration standard: 12.88 mS cm <sup>-1</sup> ; Cell constant: 0.551048 cm <sup>-1</sup>			InLab® 731 Calibration standard: 1413 μS cm <sup>-1</sup> ; Cell constant: 0.548753 cm <sup>-1</sup>		
10 <sup>4</sup> C <sub>salt</sub> (mol cm <sup>-3</sup> )	10 <sup>3</sup> κ (S cm <sup>-1</sup> )	E (S cm <sup>2</sup> mol <sup>-1</sup> )	10 <sup>4</sup> C <sub>salt</sub> (mol cm <sup>-3</sup> )	10 <sup>3</sup> κ (S cm <sup>-1</sup> )	E (S cm <sup>2</sup> mol <sup>-1</sup> )
40.2	188.4	44.861	1.81	14.88	81.976
30.0	155.6	51.861	1.44	12.21	84.761
19.5	122.6	61.735	1.06	9.330	87.680
12.0	83.80	69.833	0.845	7.623	90.207
9.00	66.10	73.444	0.532	4.984	93.687
6.00	46.70	77.833	0.316	3.062	96.953
3.00	25.30	84.333	0.213	2.100	98.675
0.600	6.060	100.99	0.0213	0.2360	110.89
0.300	3.130	104.32	0.00426	0.05290	124.28
0.0600	0.6970	116.16	0.00213	0.02740	128.75
0.0300	0.3530	117.66	0.00128	0.01663	130.24
0.00600	0.0784	130.65	0.000851	0.01248	146.60
-	-	-	0.000426	0.008230	193.36

TABLE-2  
ELECTROLYTIC CONDUCTIVITY ( $\kappa$ ), MOLAR CONDUCTIVITY (E) AND  $C_{\text{salt}}$  FOR  $\text{LiClO}_4$  (aq.) OF EXPERIMENTAL RESULTS IN THIS STUDY USING DIFFERENT KCl (aq.) CALIBRATION STANDARD AT 25 °C

InLab® 731 Calibration standard: 1413 $\mu\text{S cm}^{-1}$ ; Cell constant: 0.564230 $\text{cm}^{-1}$			InLab® 741 Calibration standard: 84 $\mu\text{S cm}^{-1}$ ; Cell constant: 0.094718 $\text{cm}^{-1}$		
$10^4 C_{\text{salt}}$ ( $\text{mol cm}^{-3}$ )	$10^3 \kappa$ ( $\text{S cm}^{-1}$ )	E ( $\text{S cm}^2 \text{mol}^{-1}$ )	$10^4 C_{\text{salt}}$ ( $\text{mol cm}^{-3}$ )	$10^3 \kappa$ ( $\text{S cm}^{-1}$ )	E ( $\text{S cm}^2 \text{mol}^{-1}$ )
1.01	9.130	90.444	1.01	7.150	70.828
0.780	7.258	93.092	0.539	4.273	79.318
0.696	6.546	94.106	0.296	2.534	85.645
0.581	5.551	95.597	0.202	1.781	88.172
0.464	4.511	97.273	0.126	1.162	91.939
0.404	4.960	98.060	0.0745	0.7056	94.669
0.303	3.030	99.898	0.0202	0.1990	98.550
0.202	2.060	102.03	0.00404	0.04450	110.20
0.101	1.066	105.60	0.000806	0.009660	119.61
0.0202	0.2260	111.94	0.000404	0.005980	148.09
0.0101	0.1202	119.07	0.000162	0.003500	216.69

However, only experimental data using InLab® 731 with the calibration standard 1413  $\mu\text{S cm}^{-1}$  is used and only this system match the expected experimental conditions from the expected value at 106  $\text{S cm}^2 \text{mol}^{-1}$  [Ref. 14].

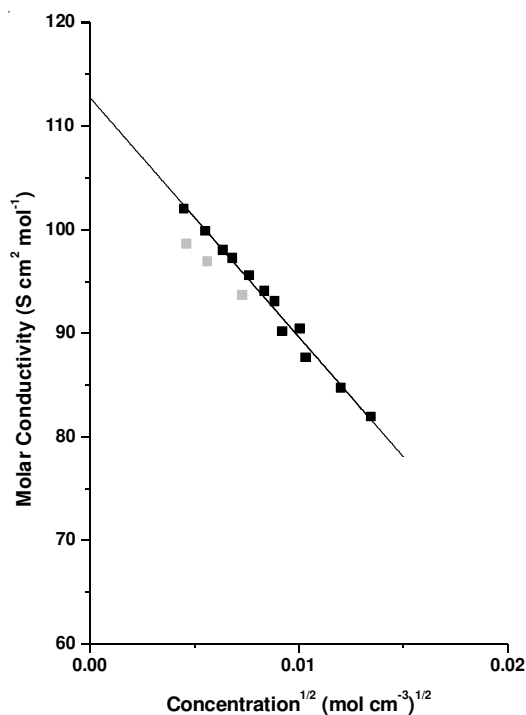


Fig. 2. Plotted after eqn. 3 for the set of data as tabulated in Table-1 and 2 for aqueous solution of  $\text{LiClO}_4$  at 25 °C. Experiment data: (■) data included (above the calibration standard value); (□) data excluded (below the calibration standard value) in the regression. Solid curve represents the linear regression after eqn. 3

Regression function for  $\text{LiClO}_4$  (aq.) in Fig. 2 reads:

$$E = (112.77 \text{ S cm}^2 \text{mol}^{-1}) - (2.31 \times 10^3 \text{ S cm}^7/2 \text{mol}^{-3/2}) C_{\text{salt}}^{1/2} \quad (9)$$

(correlation. 0.9852)

The  $E_0$  value after eqn. 9 obeys the expectant value for the same system at similar experimental conditions and the difference in limiting molar conductivity value from this study and ref.<sup>14</sup> is less than 5 %. This agrees that the measurement of the electrolytic conductivity data in this study is reliable and can be suggested.

## Conclusion

Accurate calibration of a conductivity probe for the determination of the cell constant is a predominant factor for an accurate conductivity measurement for the later part of the experiment. The conductivity measurement for an electrolyte system with a range of concentrations must be calibrated with appropriate calibration standards. Conductivity measurement below the calibration value of the primary standard KCl (aq) may cause deviation in the conductivity measurement from the real value even though the conductivity measurement is still within the range of the sensitivity of the probe used. As shown in this study, measurement of conductivity of  $\text{LiClO}_4$  (aq.) below the  $\kappa$  value of the standard used causes a deviation in the measurement. This has been established after Kohlrausch's equation.

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