doi: 10.31674/book.2024ecc.014

Effect of Temperature on Dissociation Constant and Determination of Equivalent Conductance at Infinite Dilution (Λ°) of Two Weak Acids

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Abstract

Dissociation constants of Lactic Acid (2-hydroxy propionic acid) have been studied at four different temperatures (19°C, 25°C, 32°C, 38°C). The change in pKa of lactic acid with temperature has been investigated and found that it increases with the temperature rise. The relationship between temperature and dissociation constant is not linear. In the second section of the experiment, the equivalent conductance of propionic and lactic acids at infinite dilution (Λ°) has been studied using Kohlrausch's Law of independent ion migration. A Python program has been designed to estimate the equivalent conductance of two weak acids. Theoretical calculations support the observed results, providing valuable insights into the behaviour and chemical properties of two weak acids.

Keywords: *Dissociation Constant; Equivalent Conductance at Infinite Dilution (Λ°); Weak Acids*

Introduction

Dissociation of weak acids and bases is the constant that indicates the strength of that acid or base as well as the percentage of various ionic species that are present in the solution at a specific temperature. Temperature and solvent concentration have an impact on the dissociation constant (Albert, 2012). Since the physical and biological characteristics of ionic species vary, it is critical to understand biological substances' dissociation constants in preparative chemistry and spectroscopy (Martin Somer *et al*., 2019; Snyder, Harvey & Wysocki, 2021).

Comparing the pH-metric titration approach to other techniques like conductometric and spectrophotometric techniques, it is more precise and takes less time to determine the dissociation constants of weak acids and bases. It has long been known that one can accurately determine the strength of an acid or its dissociation constant by measuring the changes in pH that occur when a weak acid is neutralized with an alkali (Dasgupta & Nara, 1990; Poplewska, Zimoch & Antos, 2022).

One of the main transport characteristics of electrolyte solutions is conductance, which is important for both their inherent value and for use in technical and industrial settings like plating and batteries. When water samples are taken for chemical analysis, one of the properties of the water's quality that is frequently examined is electrical conductivity. Measurements in the field and the lab can be made quickly, easily, and reliably thanks to modern equipment. Electrical conductivity is frequently used to track the quality of water in streams (Hamid, Bhat & Jehangir, 2020), wastewater treatment plants (Yu *et al*., 2019), and industrial site effluent (Mortadi *et al*., 2020). Natural waters' salinity, ionic strength, main solute concentrations, and total dissolved solids concentrations have all been ascertained by electrical conductivity studies (Corwin & Yemoto, 2020).

Experimental sections

Materials

Propionic Acid (Fig. 1A) and Lactic Acid (2-hydroxy propionic acid) (Fig. 1B), Sodium hydroxide, Potassium hydroxide, Oxalic Acid, Potassium Chloride, and Hydrochloric Acid used in the study were all reagent-grade chemicals purchased from Merck PVT. LTD. Unless otherwise mentioned, these chemicals were used without purification.

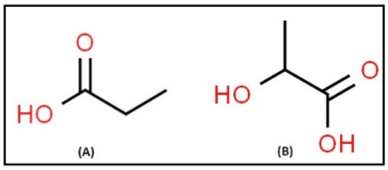

Figure 1: Structure of (A) Propionic Acid and (B) Lactic Acid (Source: Google Image)

Methods

Determination of dissociation constant pH-metrically

When a weak acid, HA, is dissociated in water, the following equilibrium is set up

$$\mathbf{HA\ (aq) \rightleftharpoons H^{+}\ (aq) + A^{-}\ (aq)} \qquad (1)$$

where the conjugated base is A^- (aq), the hydrogen ion is H^+ (aq), and the weak acid is HA (aq). The dissociation constant of the acid HA is the equilibrium constant Ka for this reaction.

$$\mathbf{Ka} = \frac{[\mathbf{H+}]\,[\mathbf{A-}]}{[\mathbf{HA}]} \qquad (2)$$

We need to know $[H^+]$, $[A^-]$, and [HA] to calculate Ka. By taking a pH reading, one can immediately determine the concentration of hydrogen ions $[H^+]$.

$$\mathbf{pH = -log[H^{+}]} \qquad (3)$$

Unfortunately, it is not that simple to calculate [HA] and $[A^-]$. A convenient way for determining K_a, is to determine the pH of the acid solution after a strong base has been added to half neutralize it. At that point, Ka equals to $[H^+]$ as the ratio of $[A^-]/[HA]$ becomes unity.

Determination of equivalent conductance at infinite dilution (Λ°)

The equivalent conductance of a strong electrolyte rises linearly with dilution. The linear relationship between Λ and √C can be extended to the Λ-axis, where the intercept corresponds to Λ°.

In the case of weak electrolytes, the equivalent conductance increases gradually initially and then rapidly when the concentration gets very low. This is due to (i) the larger degree of dissociation with dilution as per Ostwald's dilution law and (ii) growing distances between oppositely charged ions by increasing the volume of the solution. Therefore, extrapolation to have the Λ° value of a weak electrolyte is not feasible due to the slope's fluctuating nature.

The Λ° values of weak electrolytes can be effectively determined using Kohlrausch's law of independent migration of ions at infinite dilution. Three strong electrolytes are selected, and the algebraic combination of their Λ° values provides the required Λ° value (Picálek & Kolafa, 2007). For instance, the calculation of Λ° for CH_3COOH is:

$$\Lambda^\circ_{CH3COOH} = \Lambda^\circ_{CH3COOK} + \Lambda^\circ_{HCl} - \Lambda^\circ_{KCl} \quad (4)$$

All three electrolytes, viz., CH_3COOK, KCl, and HCl are strong electrolytes (the first two being salts), and their Λ° values are estimated by the extrapolation method. Thus Λ° of CH_3COOH is determined.

Instrumentations

The pH of all the solutions is recorded by Systronics Digital pH Meter 335, with 0 to 14 pH Range, 0 to +1999 mV Range, and 0.01 pH, 1 mV resolution. The temperature during the experiment was maintained by a thermostatic bath and monitored by the thermometer. The conductance of all the solutions was measured by Systronics Digital Conductivity Meter 304, with 0 µS to 200 mS range, 0.1µS resolution, 0^0C to 100^0C temperature range.

Theoretical confirmation for determination of equivalent conductance

A Python program has been devised to link to the graphs of λ_{eqv} vs √Concentration in cases of KCl, HCl, Potassium Lactate, and Potassium Propionate to cross-calculate the equivalent conductance λ at infinite dilution. Python software was created by Google Collaboratory, a Google Research offering. Anyone can write and run Python programs with it; installing various library packages is not a burden. It is simple to use and doesn't require setup, and the apps automatically save to Google Drive.

This Excel-linked application provides great results when calculating the equivalent conductance at infinite dilution using the Linear Regression approach. Because of its connectivity to the Excel sheet, the application uses the updated data whenever any changes are made to the sheet.

This software will help to cross-check our data and findings because Excel tends to store junk numbers and generate incorrect results. Additionally, this application uses LINEAR REGRESSION to provide findings after creating tables and graphs to calculate the equivalent conductance at infinite dilution.

Results and Discussion

Determination of dissociation constant at different temperatures pH-metrically

Results summarized in Table 1 show the effect of temperature on pKa values of Lactic acid using the pH-metric method. As temperature increases from 19°C to 38°C, pKa values increase from 3.63 to 4.11 and the total increase is 0.48 units. When weak acid dissociation occurs, a temperature rise gives the system more energy. In response, the system moves the equilibrium in the direction of the endothermic dissociation reaction, which absorbs the additional energy. Because of this, the weak acid's dissociation is encouraged, which increases the dissociation constant (pKa) as temperature rises.

Table 1: *Effect of temperature on pKa values of lactic Acid*

Temperature(°C)	pKa
19	3.63
25	3.87
32	3.98
38	4.11

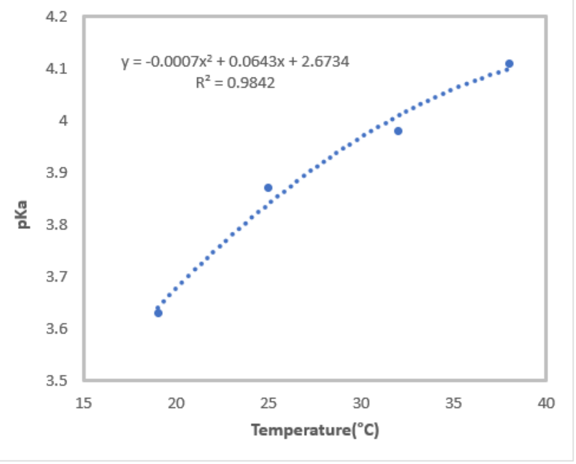

Figure 2: pKa vs Temperature plot of Lactic acid *(Source: Primary Source)*

It is important to note that the relationship between temperature and the dissociation constant (pKa) of Lactic acid is not linear. pKa of Lactic acid shows a parabolic curve (Figure 2, Equation 5) when the temperature increases. The equation is as follows:

$$\mathbf{y = -0.0007x^2 + 0.0643x + 2.6734} \qquad (5)$$

Where y = pKa and x is the temperature in °C.

Determination of equivalent conductance at infinite dilution (Λ°)

Exact solutions of KCl, HCl, Lactic Acid, Propionic Acid, and KOH were prepared and conductance of KCl, and HCl were measured at (N/10), (N/20), (N/40), (N/80), (N/160) concentrations and that of Potassium lactate and Potassium Propionate were measured at (N/20), (N/40), (N/80), (N/160) concentrations. Graphs were plotted by λ_{eqv} vs √Concentration in each case (Figure 3).

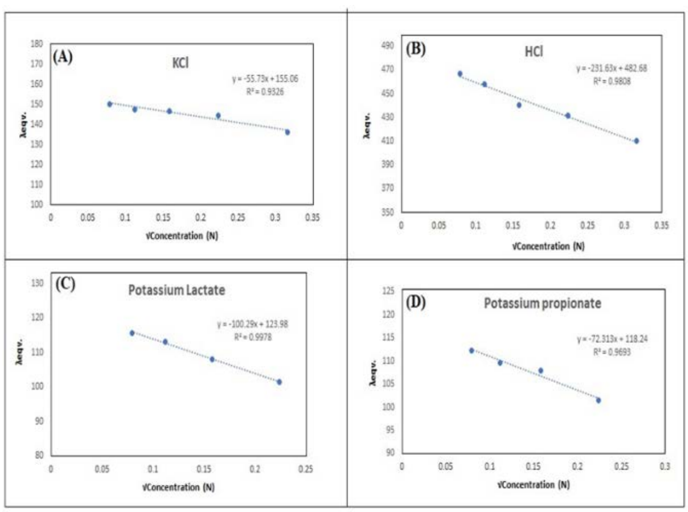

Figure 3: λeqv. Vs. √Concentration plots of (A) KCl (B) HCl (C) Potassium Lactate (D) Potassium Propionate at room temperature (*Source: Primary Source)*

Results summarized in Table 2 show equivalent conductance at infinite dilution of KCl, HCl, Potassium Lactate, and Potassium Propionate. The equivalent conductance at infinite dilution of Lactic acid and Propionic acid has been calculated using the Kohlrausch Law as follows:

$$\mathbf{\Lambda^{\circ}_{Lactic\ acid} = \Lambda^{\circ}_{Potassium\ Lactate} + \Lambda^{\circ}_{HCl} - \Lambda^{\circ}_{KCl}} \qquad (6)$$

$$\mathbf{\Lambda^{\circ}_{Lactic\ acid}} = 123.98 + 482.68 - 155.06 = 451.6\ Ohm^{-1}Cm^{2}Eqv^{-1} \qquad (7)$$

Similarly,

$\mathbf{\Lambda^{\circ}_{Propionic\ acid}}$ = 118.24 + 482.68 - 155.06 = 445.86 $Ohm^{-1}Cm^{2}Eqv^{-1}$ (8)

Table 2: *Equivalent conductance at infinite dilution of different electrolytes*

Electrolyte	**Λ°eqv.($Ohm^{-1}cm^{2}eqv^{-1}$)**
KCl	155.06
HCl	482.68
Potassium Lactate	123.98
Potassium Propionate	118.24
Lactic Acid	451.60
Propionic Acid	445.86

Theoretical Results for calculation of Equivalent Conductance at infinite dilution:

```
import pandas as pd
import numpy as np

# Read the Excel file into a DataFrame
df=pd.read_excel('/dissertation2.xls', sheet_name='KCL')

# Extract the concentration (c) and molar conductance (Λ) values from the DataFrame
c_values_KCl = df['Conc.(N)'].values
Λ_values_KCl = df['λ=1000k/Conc'].values

# Perform linear regression to obtain the slope and intercept
slope, intercept = np.polyfit(np.sqrt(c_values_KCl), Λ_values_KCl, 1)

# Calculate the equivalent conductance at infinite dilution (Λ0)
Λ_infinite_KCl = intercept

# Print the calculated Λ0 value
print("Equivalent Conductance at Infinite Dilution (Λ0) of KCl:",Λ_infinite_KCl,
"S/cm^2/mol")

# Read the Excel file into a DataFrame
df1=pd.read_excel('/dissertation2.xls', sheet_name='HCl')

# Extract the concentration (c) and molar conductance (Λ) values from the DataFrame
c_values_HCl = df1['Conc.(N)'].values
Λ_values_HCl = df1['λ=1000k/Conc'].values

# Perform linear regression to obtain the slope and intercept
slope, intercept = np.polyfit(np.sqrt(c_values_HCl), Λ_values_HCl, 1)

# Calculate the equivalent conductance at infinite dilution (Λ0)
Λ_infinite_HCl = intercept
```

```
# Print the calculated Λ0 value
print("Equivalent Conductance at Infinite Dilution (Λ0) of HCl:",Λ_infinite_HCl,
"S/cm^2/mol")

# Read the Excel file into a DataFrame
df1=pd.read_excel('/dissertation2.xls', sheet_name='LK')

# Extract the concentration (c) and molar conductance (Λ) values from the DataFrame
c_values_LK = df1['Conc.(N)'].values
Λ_values_LK = df1['λ=1000k/Conc'].values

# Perform linear regression to obtain the slope and intercept
slope, intercept = np.polyfit(np.sqrt(c_values_LK), Λ_values_LK, 1)

# Calculate the equivalent conductance at infinite dilution (Λ0)
Λ_infinite_LK = intercept

# Print the calculated Λ0 value
print("Equivalent Conductance at Infinite Dilution (Λ0) of POTASSIUM
LACTATE:",Λ_infinite_LK, "S/cm^2/mol")

# Read the Excel file into a DataFrame
df1=pd.read_excel('/dissertation2.xls', sheet_name='PA')

# Extract the concentration (c) and molar conductance (Λ) values from the DataFrame
c_values_PA = df1['Conc.(N)'].values
Λ_values_PA = df1['λ=1000k/Conc'].values

# Perform linear regression to obtain the slope and intercept
slope, intercept = np.polyfit(np.sqrt(c_values_PA), Λ_values_PA, 1)

# Calculate the equivalent conductance at infinite dilution (Λ0)
Λ_infinite_PA = intercept


# Print the calculated Λ0 value
print("Equivalent Conductance at Infinite Dilution (Λ0) of POTASSIUM
PROPIONATE:",Λ_infinite_PA, "S/cm^2/mol")
LA=(Λ_infinite_LK)+(Λ_infinite_HCl)-(Λ_infinite_KCl)
PA=(Λ_infinite_PA)+(Λ_infinite_HCl)-(Λ_infinite_KCl)
print("Equivalent Conductance at Infinite Dilution (Λ0) of LACTIC ACID:",LA,
"S/cm^2/mol")
print("Equivalent Conductance at Infinite Dilution (Λ0) of PROPIONIC ACID:",PA,
"S/cm^2/mol")
```

OUTPUT

Equivalent Conductance at Infinite Dilution (Λ_0) of KCl: 155.05871962722784 S/cm^2/mol

Equivalent Conductance at Infinite Dilution (Λ_0) of HCl: 482.6782230454404 S/cm^2/mol

Equivalent Conductance at Infinite Dilution (Λ_0) of POTASSIUM LACTATE: 123.97634009166136 S/cm^2/mol

Equivalent Conductance at Infinite Dilution (Λ_0) of POTASSIUM PROPIONATE: 118.24331067469753 S/cm^2/mol

Equivalent Conductance at Infinite Dilution (Λ_0) of LACTIC ACID: 451.5958435098739 S/cm^2/mol

Equivalent Conductance at Infinite Dilution (Λ_0) of PROPIONIC ACID: 445.8628140929101 S/cm^2/mol

Equivalent Conductance at infinite dilution (Λ_0) from the theoretical calculations of Lactic acid and Propionic acid is found to be 451.596 and 445.863 $Ohm^{-1}cm^2eqv^{-1}$ respectively. The output obtained from the theoretical calculations is almost similar to our experimental results. So, the theoretical calculation agrees well with the experimental values.

Conclusion

The pKa value of Lactic acid increases with an increase in temperature and the graph of pKa vs Temperature gives a parabolic curve. The equivalent conductance at infinite dilution for KCl, HCl, Potassium Lactate, and Potassium Propionate was determined and found to be 155.06, 482.68, 123.98, and 118.24 $Ohm^{-1}cm^2eqv^{-1}$ respectively. Using these values, the equivalent conductances of Lactic Acid and Propionic Acid were calculated and found to be 451.60 and 445.86 $Ohm^{-1}cm^2eqv^{-1}$ respectively. These data were well supported by the Python program.

Acknowledgment

The authors would like to express Warmest thanks to the supervisor Dr. Sanjib Ghosh and special thanks given to the Management, The Bhawanipur Education Society College, Kolkata, India for providing the research facilities.

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