

Repercussion of Routine Laboratory Practice in the Determination of Degree of Dissociation of Anion of Weak Electrolyte Using Correlation of Nernst Equation with Equivalent Conductance at Equilibrium

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Abstract— Strong electrolytes are totally ionized at all dilutions; hence the Ostwald's dilution law only applies to weak electrolytes and completely fails in the case of strong electrolytes. Water molecules surround and solvate the ions, weakening the strong electrostatic interactions between them, which causes the ions in the solid to separate and scatter equally throughout the solution when ionic substances dissolve in water. Under normal circumstances, ionic compounds will dissociate almost entirely when dissolved, which is why they are categorised as strong electrolytes. This process represents a physical change known as dissociation.^{1,2} In other words, when dissolved in water, they do not produce a lot of ions.

They create a tiny current with their solutions. As the ions transition from their fixed and ordered positions in the crystal to the mobile and considerably more disordered states in solution, the system becomes more chaotic due to the loss of electrostatic attraction, which allows each hydrated ion in a dilute solution to move independently. Sometimes, the electrostatic interactions between the ions and water molecules are too weak, causing the crystal to become intractable because the increase in disorder cannot offset the energy needed to separate the ions.^{3,4} That is, they produce relatively few ions when dissolved in water. Their solutions produce a small current. Therefore, unlike in a perfect solution, ions are not evenly distributed throughout the solution. In present research paper the study of deviation from the ideal behavior has been proposed through experimental outcomes.

Keywords— Electrolyte, Dissociation, Electrostatic

I. INTRODUCTION

Introduction The degree of ionization (or dissociation) of any weak electrolyte is inversely proportional to the square root of concentration and directly proportional to the square root of dilution. A mathematical expression of the law of mass actions that gives the relationship between equilibrium constant/dissociation constant, the degree of dissociation and concentration at constant temperature is called Ostwald's dilution law^{1,2}.

Kohlrausch law states that at infinite dilution, when dissociation is complete, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the ion with which it is associated and the value of equivalent conductance at infinite dilution for any electrolyte is the sum of the contribution of its constituent ions (cations and anions). Thus, we can say it states that 'conductivity of ions of an electrolyte at infinite dilution is constant and it does not depend on nature of co-ions'.⁹

$$\lambda_{eq}^{\infty} = \lambda_c^{\infty} + \lambda_a^{\infty}$$

Where λ_{eq}^{∞} = Equivalent conductivity at infinite dilution
 λ_c^{∞} = Equivalent conductivity of cation at infinite dilution
 λ_a^{∞} = Equivalent conductivity of anion at infinite dilution

When the concentration of the electrolyte is almost zero, at that point, Equivalent conductivity is called limiting Equivalent conductivity⁹. The Equivalent conductivity of the solution can be defined as the volume of the solution that is conducting that also contains one mole of electrolyte when kept between two electrodes with a unit area of cross-section and one unit length of distance. With the decrease in the concentration, the Equivalent conductivity increases. The increase in the Equivalent conductivity is due to the increase in the volume that comprises one mole of electrolytes^{5,6}.

II. METHODOLOGY

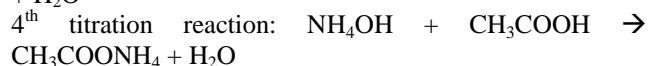
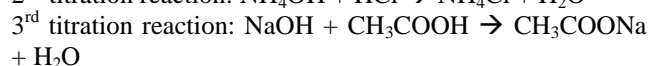
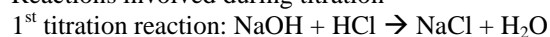
Materials required – Burette, beaker, stand, funnel, conductometer

Chemicals prepared – 0.1N HCl, 0.1N NaOH, 0.1N NH₄OH, 0.1N CH₃COOH

Method used– Conductometric titration: The determination of end point of a titration by the means of conductivity measurements is known as conductometric titration. All the conductometric observations have been made on Digital Conductivity Meter, METZER OPTICAL INSTRUMENT PVT. LTD.

Electrolytic conductivity is measured using the electroanalytical technique of conductometry, and its value changes as the concentration of ions in a solution changes. The solution's electrolytic conductivity results from cations (positive ions) and anions (negative ions) transferring electric charges while being affected by an external electric field. The foundation of conductometric titration is the observation of changes in the titrated solution's conductivity.¹⁰ The mobility of ions other than the ones that were initially present in the solution, which is what causes these modifications, is converted. As a result, when we plot the conductance against the volume of the titrant added, we obtain two branches of straight lines, and the point at which the lines intersect is the equivalence point.¹¹

Reactions involved during titration –



III. RESULTS AND DISCUSSION

Before the alkali is added, the acid solution has a high conductance due to the highly mobile hydrogen ions. When alkali is added to a strong acid, the highly mobile hydrogen ions are replaced by less mobile metallic ions; the conductance will, therefore decrease. When neutralization is complete, further addition of alkali will cause the conductance to increase owing to the excess of highly mobile OH⁻ ions; the conductance will thus be minimum at the equivalence point. A plot of conductance versus the volume of titrant added will consist of two almost straight-line branches intersecting at the neutral point. When both acid and base are strong, the titration can be carried out from either side, i.e., alkali can be added to the acid or vice versa. When a weak base like NH₄OH, is added to a strong acid, the conductivity falls initially due to the replacement of H⁺; after the neutral point conductance, remains practically constant, since the excess of weak base is not appreciably ionized in presence of its salt^{13,14}.

In case of weak acid, like CH₃COOH, against a strong base, the conductivity first decreases owing to the creation of the salt that prevents weak acid from ionization but it soon commences to be increased as a result of the highly ionized salt's increased conductivity that of the weak acid which it replaces. At once following the neutral point, the conductance rises more quickly. due to the excess of OH⁻. When the acid is very weak, the conductance increases

from the beginning of neutralization. In the titration of a weak base versus weak acid gave the conductance in first decreasing manner but it soon begins to increase due to the salt formation, and finally becomes constant after the neutral point.

The theory given by Debye and Huckel explains that why on dilution, Equivalent conductance increases if the electrolyte is strong. Electrolytes dissociate in solutions state to give positive and negative ions. Each ion is surrounded by an ionic atmosphere of opposite charge. This ionic atmosphere is spherically symmetrical. When current is passed through the solution, the center of ion of the ionic atmosphere moves towards the oppositely charged electrode. During this movement it has to rebuild an ionic atmosphere of opposite charge around it. At this time the old ionic atmosphere dies out. These two processes do not take place simultaneously.¹² There is some time lag which is called time of relaxation.

Old ionic environment drags the travelling ion backward for slowing velocity. Due to this the effect is called relaxation effect. As the solvent is polar so the ion-solvent interaction causes solvent molecules to travel along the ionic atmosphere as well. Further restrictions are placed on the central ion's ability to migrate towards the opposite electrode. It is called the electrophoretic effect. By decreasing the electrophoretic action, dilution raises the equivalent conductance of a strong electrolyte

Table 1: For NaOH vs HCl –

| S.No. | Volume of base (ml) | Conductance (s/m) |
|-------|---------------------|-------------------|
| 1 | 0 | 0.94 |
| 2 | 2 | 0.80 |
| 3 | 4 | 0.52 |
| 4 | 6 | 0.39 |
| 5 | 8 | 0.40 |
| 6 | 10 | 0.47 |
| 7 | 12 | 0.60 |
| 8 | 14 | 0.69 |
| 9 | 16 | 0.72 |
| 10 | 18 | 0.79 |
| 11 | 20 | 0.86 |
| 12 | 22 | 0.90 |
| 13 | 24 | 0.95 |
| 14 | 26 | 0.99 |
| 15 | 28 | 1.02 |

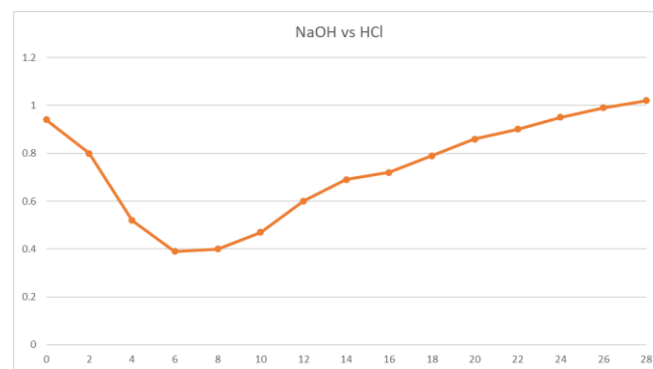


Figure 1

Table 2: For NH₄OH vs HCl –

| S.No. | Volume of base (ml) | Conductance (s/m) |
|-------|---------------------|-------------------|
| 1 | 0 | 0.86 |
| 2 | 2 | 0.79 |
| 3 | 4 | 0.72 |
| 4 | 6 | 0.59 |
| 5 | 8 | 0.54 |
| 6 | 10 | 0.48 |
| 7 | 12 | 0.39 |
| 8 | 14 | 0.36 |
| 9 | 16 | 0.32 |
| 10 | 18 | 0.32 |
| 11 | 20 | 0.32 |
| 12 | 22 | 0.32 |
| 13 | 24 | 0.32 |
| 14 | 26 | 0.32 |
| 15 | 28 | 0.32 |

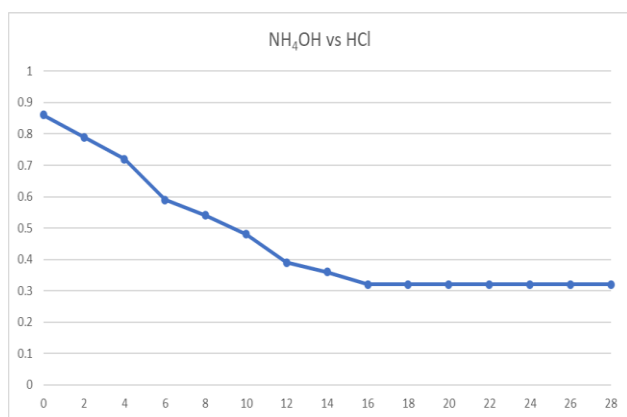


Figure 2

Table 3: For NaOH vs CH₃COOH

| S.No. | Volume of base (ml) | Conductance (s/m) |
|-------|---------------------|-------------------|
| 1 | 0 | 0.16 |
| 2 | 2 | 0.28 |
| 3 | 4 | 0.31 |
| 4 | 6 | 0.34 |
| 5 | 8 | 0.36 |
| 6 | 10 | 0.38 |
| 7 | 12 | 0.42 |
| 8 | 14 | 0.45 |
| 9 | 16 | 0.47 |
| 10 | 18 | 0.54 |
| 11 | 20 | 0.56 |
| 12 | 22 | 0.58 |
| 13 | 24 | 0.61 |
| 14 | 26 | 0.67 |
| 15 | 28 | 0.71 |

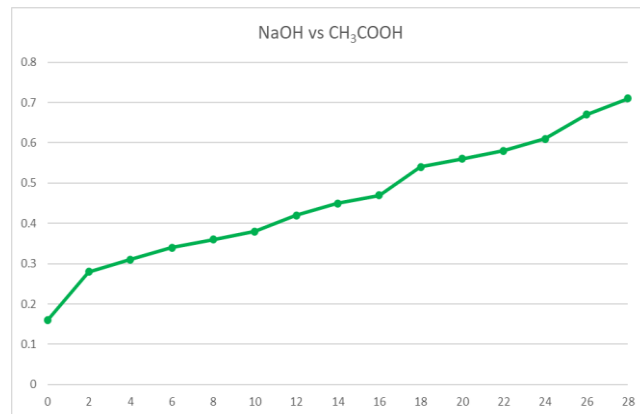


Figure 3

Table 4: For NH₄OH vs CH₃COOH –

| S.No. | Volume of base (ml) | Conductance (s/m) |
|-------|---------------------|-------------------|
| 1 | 0 | 0.15 |
| 2 | 2 | 0.16 |
| 3 | 4 | 0.17 |
| 4 | 6 | 0.19 |
| 5 | 8 | 0.20 |
| 6 | 10 | 0.20 |
| 7 | 12 | 0.20 |
| 8 | 14 | 0.22 |
| 9 | 16 | 0.22 |
| 10 | 18 | 0.23 |
| 11 | 20 | 0.21 |
| 12 | 22 | 0.20 |
| 13 | 24 | 0.19 |
| 14 | 26 | 0.18 |
| 15 | 28 | 0.18 |
| 16 | 30 | 0.18 |
| 17 | 32 | 0.18 |
| 18 | 34 | 0.18 |

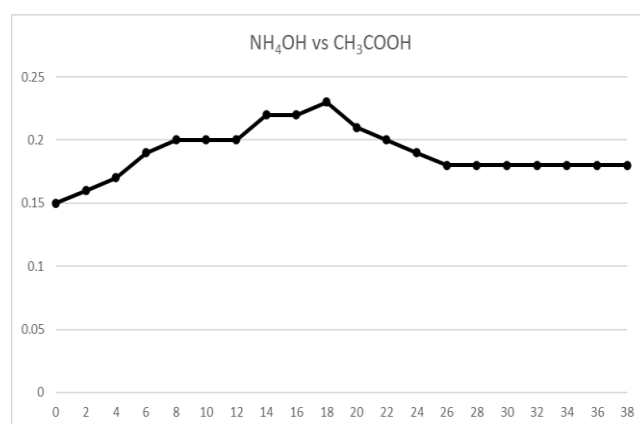


Figure 4

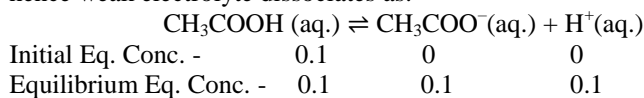
In all the graphs in figures 1 to 4, on x-axis – volume of base and on y-axis – conductance has been taken.

Explanation and Calculations –

If α is the degree of dissociation of a weak electrolyte, C is its concentration and V is the dilution. Then

$$\alpha \propto 1/\sqrt{C} \text{ or } \alpha \propto \sqrt{V}$$

Strong electrolytes such as NaCl, NaOH, HCl etc. do not obey Ostwald's Dilution Law because their chemical reaction on dissociation is irreversible in nature. Weak Electrolytes obey Ostwald's Dilution Law. To understand this phenomenon, assume one mole of an electrolyte which is binary in nature is dissolved in water hence the volume of the solution become 'V' dm³. At equilibrium assume that a be the degree of dissociation of this weak electrolyte hence weak electrolyte dissociates as: -



Implementing the law of mass action and using K_{eq} as equilibrium constant-

$$K_{eq} = [\text{H}^+] [\text{CH}_3\text{COO}^-] / [\text{CH}_3\text{COOH}] \dots\dots\dots (1)$$

$$K_{eq} = \alpha^2 C / (1 - \alpha) \dots\dots\dots (2)$$

Putting the values obtained, we get

$$0.1 \times 0.1 \times 0.1 = 0.001 \dots\dots\dots (3)$$

1 - α = 1 (since α is very small for weak electrolytes)

On comparing equilibrium constant with Nernst equation

$$E = E^0 - \frac{2.303RT}{nF} \log_{10} \dots\dots\dots (4)$$

at which ΔG = 0. At equilibrium, the reaction quotient Q = K_{eq} Therefore, substituting Q = K_{eq}

Equation 4 indicates about electrical potential of any cell varies according to the variation observed in reaction quotient Q of the reaction. Reactants get consumed as redox reaction proceeds. Because of consumption of reactant, concentration of the reacting species decreases. On the other hand, as the product formation starts, the concentration of the product species increases. Consequently, cell potential gradually decreases until the both side equation reaches to the equilibrium.

$$E = E^0 - \frac{0.059}{1} \log_{10} K_{eq} \dots\dots\dots (5)$$

$$\log_{10} K_{eq} = E - E^0 + 0.059$$

putting the values from eq. (1) and also the values of electrode potentials

$$\frac{\log_{10}[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1 - 0.39 + 0.059 \dots\dots\dots (6)$$

Using equivalent conductance of the reactant in eq. (6)

$$\frac{\log_{10}[\lambda\text{H}^+][\lambda\text{CH}_3\text{COO}^-]}{[\lambda\text{CH}_3\text{COOH}]} = 1 - 0.39 + 0.059 \dots\dots\dots (7)$$

putting the values of Equivalent conductivity of above reactants from observation tables

$$\frac{\log_{10}[0.01][\text{CH}_3\text{COO}^-]}{[0.16]} = 1 - 0.39 + 0.059 \dots\dots\dots (8)$$

$$[\log 0.01 - \log 0.16] + (\log (\lambda\text{CH}_3\text{COO}^-) - \log 0.16) = 1 - 0.39 + 0.059$$

$$[\log (\lambda\text{CH}_3\text{COO}^-) - \log 0.16] = 0.551 - (\log 0.01 - \log 0.16)$$

$$\log \lambda\text{CH}_3\text{COO}^- = 0.551 - \log 0.01$$

$$\log \lambda\text{CH}_3\text{COO}^- = 0.551 - (-2)$$

$$\log \lambda\text{CH}_3\text{COO}^- = 2.551$$

$$\lambda\text{CH}_3\text{COO}^- = \text{Antilog } 2.551$$

$$\lambda\text{CH}_3\text{COO}^- = 0.936$$

(Since degree of dissociation)

$$\alpha = \frac{\lambda\text{CH}_3\text{COOH}}{\lambda\text{CH}_3\text{COO}^-}$$

$$\alpha = 0.16 / 0.936$$

$$\alpha = 0.17$$

IV. CONCLUSION

Present research paper proves that the study of deviation from the ideal behaviour has been certainly reached at high extent through experimental outcomes. The cell potential of an electrochemical cell can be determined using the Nernst equation for any temperature, pressure, or reactant concentration. The standard cell potential, temperature, reaction quotient, and the cell potential of an electrochemical cell are all related by the Nernst equation. The Nernst equation can be used to calculate the cell potentials of electrochemical cells even in unusual circumstances. From the above experiments and arguments for the Anion dissociation level in the weak electrolyte, using routine laboratory practice, it has been found that the degree of dissociation of anion of weak electrolyte using correlation of Nernst equation with equivalent conductance at equilibrium has been proved through calculative outcomes.

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