

EXPERIMENT 5

MOLAR CONDUCTIVITIES OF AQUEOUS ELECTROLYTES

Objective: To determine the conductivity of various acid and the dissociation constant, K_a for acetic acid

1 Theory

1.1 Electrical conductivity in solutions

An electric current in solution is the result of the net movement of free ions in a specific direction. The current may be determined by measuring the resistance R between two similar inert electrodes immersed in the solution, as in the figure below where the oval region represents the solution; A represents the electrode area and l is the normal distance between the electrode planes. In actual practice an A.C. current with a low frequency of the order of approximately 1000 Hertz is used (to prevent electrolysis) in the measurement, and the components representing the resistance R in the complex impedance Z for the circuit is determined. We will always refer to this component (the real portion of the complex impedance) for what follows. The resistance is also dependent on the frequency (Debye-Falkenhagen effect). The theory and measurement here concentrates on low frequency measurements where the Onsager equation is meaningful. The fully automated measuring apparatus has been configured for low frequency measurement in accordance with the theory of electrolytes.

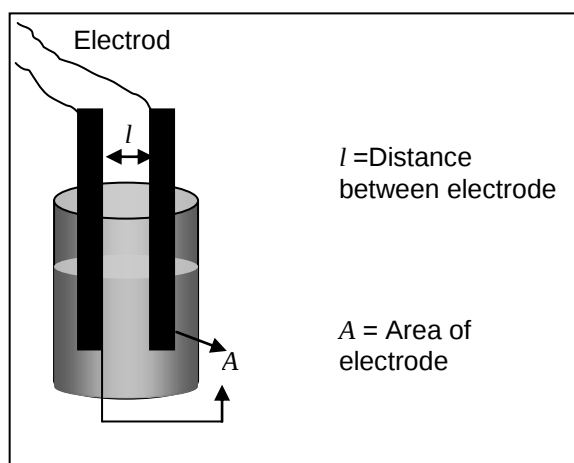


Figure of conductivity circuit

According to Ohm's law, the resistance R (unit Ohm, symbol Ω) for the above circuit

$$\text{is given by } R = \rho \frac{l}{A} \quad (1)$$

where ρ is the resistivity of the solution. The cell constant refers to $\frac{l}{A}$ but there is no need to refer to this quantity here. The electrical conductivity of the solution κ is defined as $\kappa = \frac{1}{\rho}$ where the current density, j , is given by $j = \kappa E$. The conductance

of the solution, L , is defined as $L = \frac{1}{R}$ and has units Siemen, where $\frac{1}{\Omega} = 1 \text{ S}$ (1 Siemen). On the other hand, from (1), κ has the units (S.I) $[\text{S}][\text{M}^{-1}]$. This is the quantity that the conductivity apparatus measures. Normally, (such as the ones currently used in the laboratory), the units of $\kappa = \frac{1}{\rho}$ is $\text{mS cm}^{-1} \equiv 10^{-1} \text{ S cm}^{-1} \equiv 10^{-1}$

S m^{-1} . Because the conductivity is dependent on the concentration of the electrolytes, Kohlrausch defined the molar conductivity, Λ_m , so that comparisons can be made at any concentration as follows

$$\Lambda_m = \frac{\kappa}{c} = \frac{\Lambda}{c}; \kappa = \frac{1}{RA} \quad (2)$$

where c is the concentration of the electrolyte concerned. Clearly, Λ_m has S.I. units $\text{S m}^2 \text{ mol}^{-1}$. Normally Λ_m drops in value as the concentration of the electrolyte increases. This observation can be explained by the Debye-Huckel theory where an ionic atmosphere of opposite charge to the ion is formed which retards the motion of the ion by inducing a force in the opposite direction to the motion of the ion. This dynamic asymmetry effect (also a relaxation effect) reduces the value of the molar conductivity compared to that when $c \rightarrow 0 (\Lambda_0)$ by a factor of form $BA \Lambda_0 \sqrt{c}$; there is another effect called the “electrophoretic effect” which refers to the retardation due to the movement of solvent molecules dragged by the ion and the ionic atmosphere and this effect has the form $A \sqrt{c}$ for univalent ions. Thus the total effect due to the two separate effects has the form

$$\Lambda = \Lambda_0 + B\Lambda_0 \sqrt{c} + A\sqrt{c} = \Lambda_0 - \beta c^{1/2} \quad (3)$$

for any one solvent at any one temperature for a univalent system. If the conductivity of the solution is $\Lambda (\text{c.g.s}) = x \text{ mS cm}^{-1}$ as given in most readouts, and the concentration is $c \text{ mol dm}^{-3}$ (as is the case in most machine readouts), then the molar conductivity in S.I. units will be $\Lambda = \frac{x}{c} \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$. We recommend that you plot

the values using c.g.s units. Plotting Λ vs $\sqrt{c}$ linearizes the curve and determines Λ_0 as the intercept and $-\beta$ as the gradient for “strong” electrolytes that are essentially fully dissociated at all concentrations. This plot does not work well for “weak” electrolytes because the steep gradient in the vicinity of low concentrations does not yield accurate values of the intercept. This is what will be discovered in the course of the experimentation according to the procedure below. The steep slopes are due to the constant dissociation of the electrolyte. For such cases, the following law is required.

1.2 Kohlrausch's Law

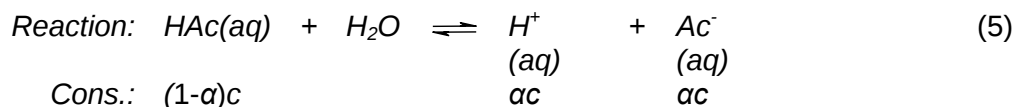
This law states that the molar conductivity at infinite dilution Λ_0 for an ionic salt is the sum of the molar conductivities at infinite dilution of its separate ions λ_0^+, λ_0^- , the signs referring to charge, i.e.,

$$\Lambda_0 = \lambda_0^+ + \lambda_0^- \quad (4)$$

Note that at infinite dilution, even weak electrolytes are fully dissociated and cannot be distinguished from strong electrolytes.

1.3 Dilution Effects of Weak Electrolytes

For any one temperature and concentration, the degree of dissociation α implies the following for a weak electrolyte such as acetic acid HAc, where the weak acid has the following equilibrium relative to its total concentration, c .



From the above equilibrium (5), ignoring activity coefficients, the acid dissociation constant K_a is given by

$$K_a = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]} = \frac{\alpha^2 c}{1-\alpha} \quad (6)$$

where, according to Arrhenius, α is given as

$$\alpha = \frac{\Lambda_m}{\Lambda_o} \quad (7)$$

for all concentrations (and $\alpha \rightarrow 1$, when $\Lambda_m \rightarrow \Lambda_o$). The normal procedure is to measure Λ_m and do the above extrapolation to determine Λ_o for some related strong salt of the above acid and then to use the Kohlrausch law to determine Λ_o for this acid, rather than to do a direct extrapolation, which is used only for strong electrolytes. In this experiment, you will determine Λ_o for the related salts CH_3COONa , HCl and NaCl and then use some linear subtractions to yield Λ_o for CH_3COOH .

2 Experimental procedure

2.1 Variation of molar conductivities with different electrolytes

An already calibrated machine is available, which consists of a rod-like electrode connected by an electrical lead to a box housing the read-out display and the electronics. Please ensure that you NEVER use the electrode as a stirrer. Instead, please agitate or shake the beaker in which the test solution is placed; the electrode must remain vertical and stationary at all times, clamped to its stand. Electrodes are very expensive and damage to them must be minimized. The reading for the conductivity is the one for the test solutions K_s less the conductivity of distilled H_2O $\kappa_{\text{H}_2\text{O}}$ used for the preparation of the solutions. (Ask the technician for samples of distilled water used for the preparation), so that $\Lambda_M = (\kappa_s - \kappa_{\text{H}_2\text{O}}) / c_M$. Normally, $\kappa_{\text{H}_2\text{O}}$ is not significant and may be neglected, but check to be sure and decide for yourself. You will be briefed on the usage of the device. The range of measurement is approximately 0-19.99 mS.

- (i) Prepare the following solutions with the indicated concentrations by using the 100ml volumetric flasks and the 5, 10, 25 and 50 ml pipettes (either bulb or graduated pipettes). In each case (1)-(4) below, the first value in the series is the stock solution, and the rest are prepared from it by successive dilution. Normally 100 ml is sufficient for each solution volume, but your situation may differ.
- (1) 0.1, 0.05, 0.025, 0.01 mol L⁻¹ for NaCl,
 (2) 0.1, 0.05, 0.025, 0.01, 0.005 mol L⁻¹ for CH₃COONa,
 (3) 0.02, 0.01, 0.005, 0.0025, 0.001 mol L⁻¹ for HCl, and
 (4) 0.1, 0.05, 0.025, 0.01, 0.005, 0.0025 mol L⁻¹ for CH₃COOH.
- (ii) Measure the conductivity of each of the solutions at least three (3) times, and take the average value and determine the mean **temperature** of your solutions for which the conductivities apply. Tabulate the solution concentration c , $c^{1/2}$, the conductivity and the molar conductivity for each of the preparations using the **table 1(a) -1(d)** on the handout sheets provided.
- (iii) Draw a graph Λ_m vs. $c^{1/2}$ for each of the electrolytes using your experimental data and determine Λ_o (using (3)) by extrapolating to $\sqrt{c} = 0$ for each of the electrolytes and compare the values of Λ_o derived from experiment to the ones from literature (**table 2**). The method fails for one of the electrolytes. Identify the electrode and why?

2.2 Determination of the degree of dissociation index α of acetic acid

- (iv) From the determinations in (iii) above, use Kohlrausch's law to determine the degree of dissociation index, α for acetic acid.
- (v) For each of the concentrations given in (i) (4), calculate the required constant; α may be determined from (7) with the experimental values of Λ_m and Λ_o for each electrolyte. K_a is determined from α which was derived previously and (6), where the concentration of the acid is known (Ask technician on duty). Since these measurements are at constant temperature, the K_a values should not vary much and the average gives an indication of the absolute K_a value. Compare the literature value of $K_a = 1.8 \times 10^{-5}$ (mol dm⁻³) at 298.15K with your own. Record your calculation into **table 3**.

3 Discussion

- Relative to your error bounds, are the values for Λ_o and K_a derived from these experiments close to the literature values?
- The degree of dissociation is given by $\alpha = \Lambda_m/\Lambda_o$. Why is this expression not very accurate? How can it be corrected so that it becomes exact? [Hint: refer to the Onsager equation]

4 References

1. Barrow, G. M. (1996). *Physical Chemistry*, 6th edn. McGraw-Hill.
2. Moore, W. J. (1972). *Physical Chemistry*, 5th edn. Longmans.
3. Levine, I.N. (2002). *Physical Chemistry*, 5th edn. McGraw-Hill.

Plagiarism Warning!

Some of these experiments are carried out in groups of usually a pair of students. Therefore expectedly, each member of a group followed an identical procedure in the laboratory and has the same set of raw data. Members of a group are allowed to discuss the analysis of data with one another. However, preparation of the report including data analysis, interpretation and discussion must be prepared by the individual student submitting the report.

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nb: Please quote experimental error estimates for all your data presented.