

Institute of Natural and Life Sciences

Department of Biotechnology

Practical work N° 1: conductimetric titration

The main objective of this lab work is to carry out and understand all the steps involved in a titration by conductometry. However, before presenting the experimental part, we will first review some essential basic concepts necessary to grasp the principles of the electrical phenomena occurring within electrolytes.

Theoretical Background

1.1 Ionic Molar Conductivity

Under the influence of an electric field, the ions in an electrolyte move more or less easily. This mobility depends, among other factors, on the size of the ion, its charge, the temperature, and the solvent used. The conductivity of the solution is expressed as the sum of the conductivities of each ionic species, as follows:

$$\sigma = \sum_{i=1}^n |z_i| \times \lambda_i \times c_i$$

This is the Kohlrausch law. The ionic molar conductivity, λ_i (S m²/mol), varies with temperature, the solvent used, and the concentration of the ionic species. This makes it very difficult to utilize the measurement results. However, when working with dilute solutions, λ_i is assumed to be similar to its value extrapolated to infinite dilution:

$$\lambda_i^0 = \lim_{c_i \rightarrow 0} \lambda_i \implies \sigma \approx \sum_{i=1}^n |z_i| \times \lambda_i^0 \times c_i$$

Here, λ_i^0 is the ionic molar conductivity at infinite dilution of the ionic species. It is important to note that in the Kohlrausch law, concentrations are expressed in mol/m³ and not in mol/L, as is usually the case. However, the conversion is simple; one just needs to know that 1 m³ = 10³

L. Thus, we can remember: $1 \text{ mol/L} = 10^3 \text{ mol/m}^3$ or $1 \text{ mol/m}^3 = 10^{-3} \text{ mol/L}$, leading to the formula:

$$\sigma \approx 10^3 \sum_{i=1}^n |z_i| \times \lambda_i^0 \times c_i$$

The values of λ_i^0 are tabulated; here are some values listed at 25 °C.

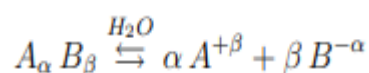
Table 1: Values of λ_i^0 for some ionic species at 25 °C

Cations	λ_i^0 (mSm ² /mol)	Anions	λ_i^0 (mSm ² /mol)
H_3O^+	34.98	OH^-	19.92
Na^+	5.01	Cl^-	7.63
NH_4^+	7.34	HSO_4^-	7.90
Ba^{2+}	6.36	CH_3COO^-	4.09
Li^+	3.87	$HC_2O_4^-$	7.42
K^+	7.35	$C_2O_4^{2-}$	4.00
Ca^{2+}	5.90	SO_4^{2-}	8.00

The basic principle of conductivity measurements involves applying a constant voltage (in Volts, using alternating current) across the terminals of two electrodes. The conductimeter then measures the variations in the intensity of the electric current (in Amperes) flowing between the two electrodes and calculates the conductivity accordingly (see the previous lab session).

To illustrate this, let's consider a solution of an electrolyte with the general formula

$A^\alpha B^\beta$. Each ion is characterized by an ionic molar conductivity λ , given in S·m²/mol, such that...



$$\sigma = \beta \lambda_A^0 [A^{+\beta}] + \alpha \lambda_B^0 [B^{-\alpha}]$$

It is noted that the absolute value of the charge number of an ionic species appears as a factor in front of the conductivity of that ionic species. In the case of a titration, such as an acid-base titration, the conductivity of the solution as a function of the volume of the titrant takes the form:

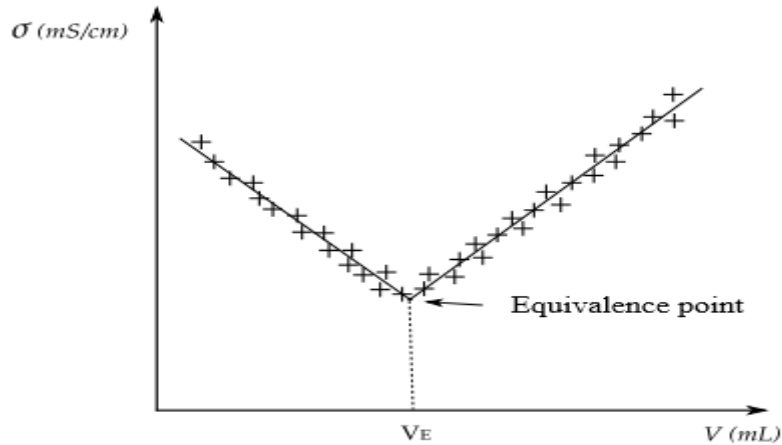


Figure 1: Shape of the conductivity as a function of the volume added during a titration.

The equivalent volume is estimated by noting the x-coordinate of the intersection point (breakpoint) of the straight sections. Experimentally, the linearity of $\sigma=(V)$ is not always verified, particularly due to the dilution of the titrated solution as the titrant is added. This dilution effect is corrected by taking:

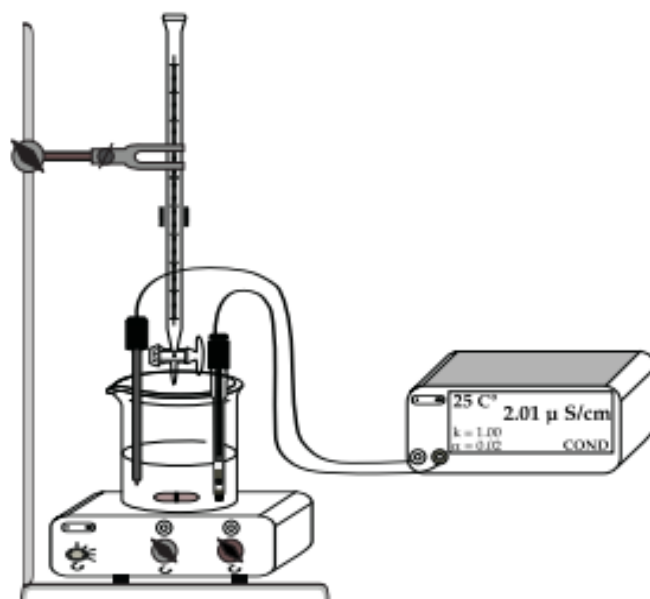
$$\sigma_{cor} = \sigma \times \frac{V + V_0}{V_0}$$

The quantity σ_{cor} is referred to as the corrected conductivity for the dilution factor.

2. Experimental Protocol

We propose to carry out a titration by conductometry of a hydrochloric acid (HCl) solution ($V_0=10.00\text{mL}$) with a sodium hydroxide (NaOH) solution of concentration $c=0.10\pm 0.002\text{mol/L}$. Use a burette graduated in 0.1 mL with a maximum delivered volume of 25 mL. Place the beaker on the magnetic stirrer. Then, introduce into the beaker: the magnetic stir bar, the conductivity cell, the temperature probe, and the pH meter electrode. Position the burette above this setup, ensuring that the magnetic stir bar does not touch the conductivity cell. Maintain moderate stirring to avoid disrupting the transport of ions between the two platinum electrodes. Start the conductimeter. Record the conductivity values for each milliliter of sodium hydroxide added in the table below.

$V_{\text{NaOH}}(\text{ml})$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
$\delta(\mu\text{S}/\text{cm})$																			
$\delta_{\text{cor}}(\mu\text{S}/\text{cm})$																			



Important: For each milliliter of sodium hydroxide added, maintain stirring to homogenize the solution. However, stirring should be stopped before each conductivity measurement. Once the value displayed by the conductimeter is stabilized, record it. After each measurement, rinse the conductivity cell with distilled water and wipe it externally with absorbent paper. **It is strongly advised against touching the platinum electrodes, as this may alter the platinum black.**

3. Required Questions:

1. Complete the previous table.
2. Write the titration reaction.
3. Plot the curves of $\sigma=f(V)$ and $\sigma_{\text{cor}}=f(V)$. Comment on the shapes of the two curves. Determine V_{eq} graphically.
4. Determine the concentration of the hydrochloric acid (HCl) solution.
5. Provide an explanation regarding the high conductivity values of hydronium ions (H_3O^+) and hydroxide ions (OH^-).