CHAPTER 2

Electrochemical methods

1. Electrochemical methods

1.1. pH métrie

1.1.1. Definition

Analytical methods based on potential measurements are called potentiometric methods**.** Any potentiometric assay including pH measurement is based on a potential difference measurement under zero current conditions, between two electrodes that dip into a sample solution.

Each electrode constitutes a half-cell. We distinguish:

- The external reference electrode, which forms a reference electrochemical half-cell, whose potential is known and constant with respect to that of the sample solution.
- The indicator electrode which comprises an internal reference electrode immersed in a solution of the analyte being assayed and serving as a reference. This electrode is separated from the sample solution by a wall called a membrane, permeable if possible.

The measurement chain thus carried out is as follows:

Reference electrode – Electrolyte junction – Analyte solution – Indicator electrode

The reference electrode is always connected to the negative terminal. In contact with the analyte solution, the indicating electrode develops a potential with respect to the reference electrode which depends on the activity of the analyte. The electrolyte junction prevents the analyte solution components from mixing with those of the reference electrode.

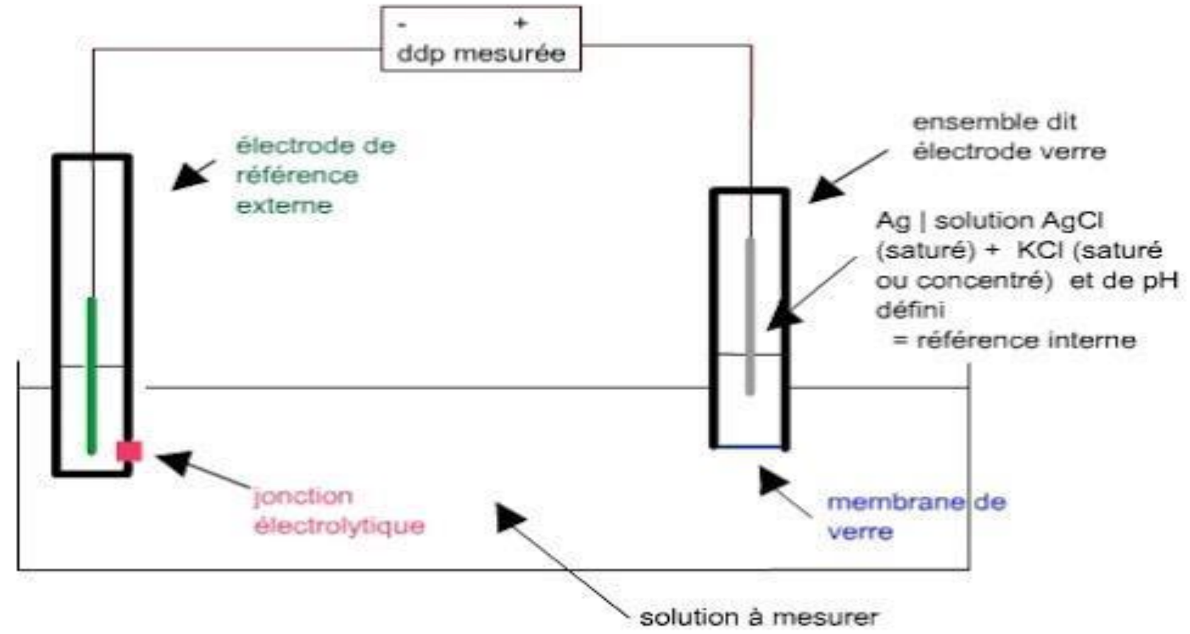

Figure 6.Schamtic structure of an electrometric pH measurement chain using a metric pHè assembly at the glass electrode.

2.1.2. Electrodes

a. Reference electrodes

The ideal reference electrode has a constant potential, known with accuracy and absolutely independent of the composition of the analyte solution.

- **Saturated calomel electrode: the calomel electrode saturated with potassium chloride (KCl) is composed of metallic mercury (Hg) in contact with calomel** Hg_2Cl_2itself in equilibrium with KCl solution.
- **Silver-Ag/AgCl reference electrode:** a silver wire covered with silver chloride immersed in a potassium chloride solution.

b. Indicator electrodes

b.1. Metal electrodes: classified into first-class electrodes (in direct equilibrium with its cation present in solution), second-class electrodes (respond to their own cations as well as anions), inert metal electrodes indicative of redox systems (an inert conductor such as platinum, gold, carbon...).

b.2. Membrane electrodes

pH indicator glass electrode: made of a thin glass membrane responding to H^+ ions . The most used glass is Corning 015 glass, consisting of approximately 22% Na_2O , 6% CaO, and 72% SiO_2.

Glass indicator electrode for cations other than H^+: such as Na^+, K^+, NH_4^+....

Liquid membrane electrode: the potential develops through the interface between the analyte solution and a liquid ion exchanger.

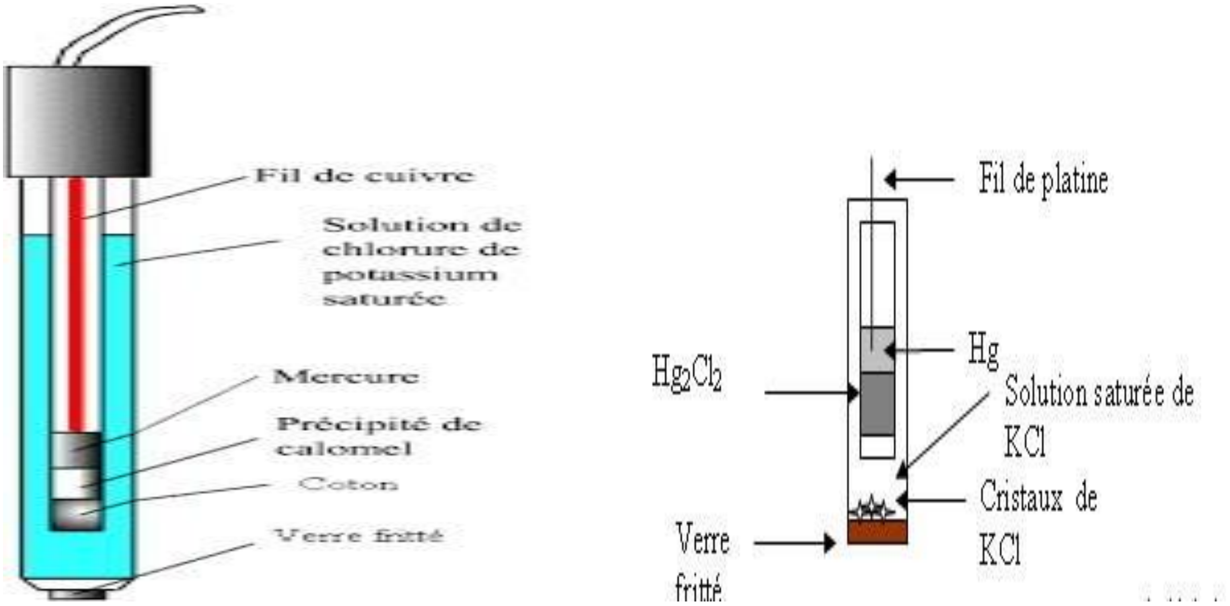

Figure 7.Electrodes used in pH measurement.

Crystalline membrane electrode: a solid electrode. The electrode of the fluoride ion is the best known.

Polymeric membrane electrode: consisting of a polyvinyl chloride (PVC) film in which one or more ion transporters are dispersed.

2.1.3. Potentiometric analysis (pH metry)

a. Equipment

pH-meters are digital voltmeters whose reading scale has been adapted to electrochemical measurements.

Before using the pH meter, check that it is working properly by measuring two solutions of known pH (standard solutions). Note that the electrode has a thin glass membrane which is very fragile. Be careful not to touch the wall of the beaker. It should not remain in the air but be immersed in a KCl-saturated solution.

The pH meter is calibrated with standard solutions of pH = 4 and pH = 7.

b. Analysis

b.1. Direct analysis

This technique only requires the comparison of the voltage of a cell comprising the indicating electrode immersed in the unknown solution, with that taken when the electrode is in contact with a standard analyte solution of known concentration.

b.2. Titration

Any potentiometric titration involves measuring the potential of an indicating electrode based on the volume of titrant added. These titrations provide more reliable data than those obtained using chemical indicators. They are useful if the solution is colored or cloudy.

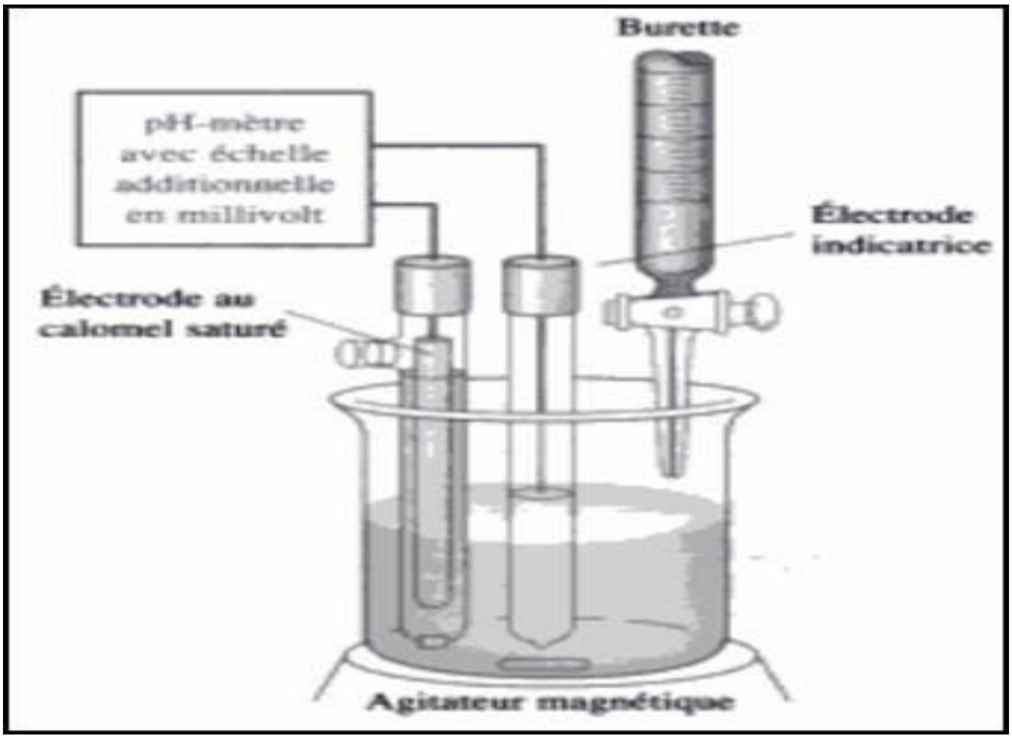

Figure 8.Titration method

There are several methods to determine the end point of titration. The most immediate is simply to plot the potential graph as a function of reagent volume. The inflection point of the curve is visually estimated and taken as the end point of titration.

2.2. Conductimetry

2.2.1. Definition

Conductimetry is a quantitative analysis technique, allowing access to the concentrations of ions in solution. This technique is based on the knowledge of the conductivity σ **of** the solution, a quantity directly related to the conductance **G** , measured with a device called a **conductimeter.**

2.2.2. Principle

a. Passage of the current within a solution

When an electric field is **applied between two electrodes immersed in an ionic solution, the ions migrate respectively towards the electrode of opposite sign, driving their molecules of hydration water. Cations migrate in the direction of the field, anions in the opposite direction. It is recalled that an electric current can only flow in a solution if it contains ions. These solutions are called electrolytic** solutions **or** electrolyte. b. Conductivity of a solution

In electrolytic solution, electrical conductivity is the quantity that characterizes the ease with which charge carriers move under the effect of a potential difference. The conductivity **of** a solution is written in the form:

$$\sigma = \sum_{i} \lambda_i c_i$$

in siemens per meter (S/m or $\Omega^{-1.m}$-1). the siemens S being the name of the unit Ω^{-1}.

where **ciest** the concentration of ion i (expressed in mol/L) and **λ iest its molar ionic conductivity (expressed in S.m2** $^{/mol).}$

c. Ionic molar conductivity

The ion molar conductivity **λ irend takes into account the ability of the ion i in particular to move when subjected to a potential difference. It depends on the temperature and the solvent but also varies with the concentration of the species i.**

$$\lambda_i = z_i \mu_i F$$

***z*ile** number of charges (arithmetic quantity without a sign), and **μila** mobility (in m2 /S.V); F is the Faraday constant (F = 96485 C/mol 96500 C/mol).

At high dilution, the ions are sufficiently far apart from each other not to have mutual interactions. The molar conductivity then has, for a given ion, its maximum value, called **infinite dilution molar conductivity**, and symbolized by λ^0. When the solution is no longer an infinitely diluted solution, but a real solution, the molar conductivity of the ions decreases.

d. Resistance and conductance

We consider the column of liquid between the two plates of the cell. It is possible to measure the electrical resistance of this portion of liquid. We measure the intensity of the current flowing between the two plates and the voltage between the two plates, and we access: $\mathbf{R = U/I}$ measured in Ohm (Ω)

I: ampere current intensity (A).

U: Voltage between plates in volt (V).

The conductance is given by the inverse of this resistance:

$$G = 1/R = I/U$$

Conductivity is related to conductance by the geometric parameters defining the volume of solution contained between the plates:

$$\sigma = G \times L/S$$

S: surface of the plates in m2 l: distance between the plates in m

We therefore relate **σ to G by a constant** Kcalled the **cell constant** (expressed in m-1) and whose value should be determined experimentally: σ =K G

2.2.3. Conductimetric dosing

a. Conductivity meter

A conductivity meter is an **ohmmeter** that determines the resistance R**of the** volume of solution contained between the two plates. For this, it imposes a potential difference between the plates. This imposed voltage is alternating (with a frequency of a few hundred Hz) to avoid the polarization of the plates. It must, moreover, be weak to avoid electrolyzing the species contained in the solution.

b. Cellule conductimétrique

A conductometric cell consists of two parallel plates coated with platinum black, which is finely divided metallic platinum in order to increase the active surface of the plates. These two plates have a surface **S** (about 1 cm2) and are separated by a distance **L** (about 1 cm).

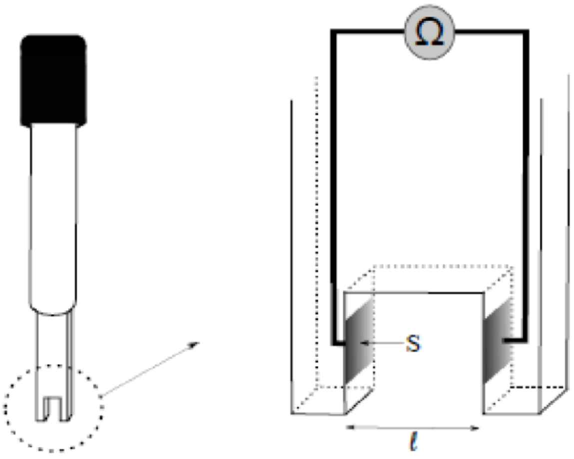

Figure 9. Diagram of a conductimetric cell (left) and zoom on the plates (right).

c. Steps of the measurement

Calibration of the conductivity cell

The calibration operation of the conductivity meter consists in determining the value of the cell constant **Kqui** connecting **σ** to G**. For this, the conductance of a potassium chloride solution KCl of known concentration is measured.**

Direct measurement

✓ Gently remove the plastic sleeve protecting the conductometric cell.

✓ Rinse the cell with distilled water.

✓ Using a piece of absorbent paper, remove as best as possible the water contained between the two plates in order not to pollute the other solutions.

✓ Immerse the conductometric cell in the solution to be analyzed which is left at rest without agitation so as not to disturb the electric field lines by forced convection movements.

✓ Place the cell in the center of the container to avoid distortion of field lines near the walls. Also ensure that no air bubbles are trapped between the plates.

✓ Once the value displayed by the conductivity meter has stabilized, note it then remove the cell from the solution, rinse with distilled water and replace the protective sleeve.

Conductimetric titration

During conductimetric titration, the solution is homogenized after each addition of titrant reagent. The agitation is however switched off before each conductimetric measurement. For each addition, record the volume V of titrant solution added and the conductivity in a table.

Plot the change σ = f(V) on a graph. The graph consists of two straight lines: their intersection determines the equivalence point.

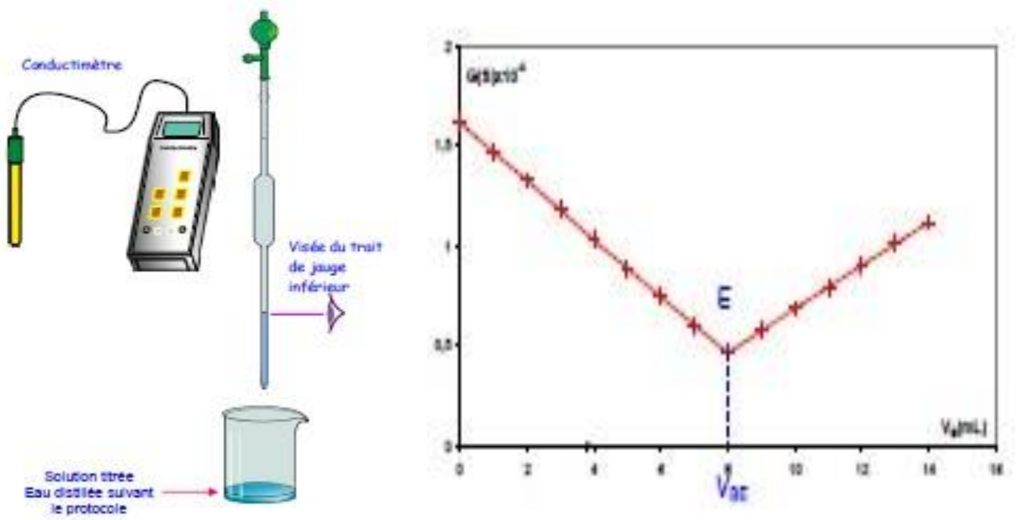

Figure 10. Conductometric titration