Principle and applications of Ion Selective Electrodes-An overview

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Abstract— **on selective electrodes are used for the detection of a particular ion owing to its selectivity arising from the type of ionophore used. In this paper we propsed the principal, selectivity and applications of ion selective electrodes along with the advantages and limitations.**

I. INTRODUCTION

ELECTROANALYTICAL techniques deal with the measurement of electrical quantities such as current, potential or charge and their relation towards chemical parameters. The birth of bio-electrochemistry took place 200 years ago (1791) in Bologna, Italy, where Luigi Aloisio Galvani was dissecting a frog.1 He discovered that the legs of the dead frog twitched when struck with electricity. Most of this field was concerned with the study of changes in chemical reactions caused by passing electrical current through the reaction mixture and the production of electrical energy by chemical reactions. Electrochemical reactions take place in the liquid-electrode interface in contrast to chemical reactions that occur in bulk solutions. At least two electrodes (conductors) and a sample (electrolyte) solution is required for these techniques, which constitute the electrochemical cell (Fig. 1). The electrode that responds to the target electrode is the indicator (or working) electrode and the other electrode is termed as the reference electrode which is at a constant potential (independent of the properties of the solution).

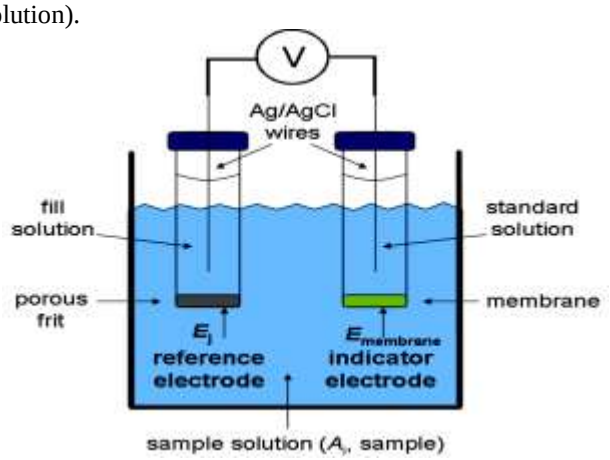

Figure 1: Representation of an electrochemical cell for the measurement of potential.

Potentiometry is an important technique in electroanalysis, which gives information about the sample composition by measuring the potential established across a membrane. Different types of membranes are produced with different ion recognition materials to increase the selectivity and sensitivity. These electrodes are used for decades for the detection of various ionic species like hydrogen, potassium, calcium, and fluoride in complex samples. In contrary, potentiostatic technique deals with the study of charge transfer at the liquidelectrode interface. Here the electrode potential is used to derive an electron transfer reaction, and the resultant current is measured. Electroanalysis can be carried out only when the medium between the two electrodes is conducting.2 These techniques offer low detection limit, high sensitivity, large linear dynamic range, precision and accuracy with a low cost instrumentation. There are a number of important benefits associated with the use of electroanalytical techniques:3

- Selectivity and specificity.
- Low detection limit with high sensitivity.
- Choice of electrode material.
- Results are real time or near real time.
- Miniaturization of the sensors.

ISEs are capable of selectively measuring a particular ionic species. These electrodes are classified as membrane electrodes containing an ion permissible membrane that separates the sample from the internals of the electrode. The main advantage of using ISEs are that they are insensitive to colour, viscosity or suspended solids. They are also tolerant to small changes in pH.4 Response time and reversibility are critical for the performance of this sensor. The problem of reversibility considering all electrochemical processes as equilibrium processes are the contribution of Nernst. Nernst equation states that the change in potential is proportional to the change in ion activity (in logarithmic units) of the system. ISE measurement involves the use of two electrodes, one is the working (indicator) electrode, and the other electrode is the reference electrode whose potential is fixed irrespective of the solution used. The potential that is proportional to the activity of the sample ion is measured across these two electrodes.

Typical calibration curve of a potentiometric sensor determined in this way is shown in figure 2.

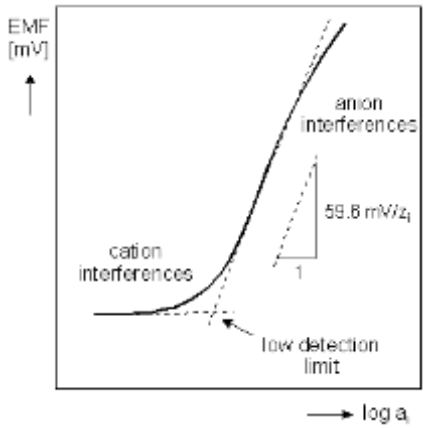

Figure. 2 Typical calibration curve of an ion-selective electrode

Ions, present in the sample, for which the membrane is non-permeable (i.e. non-selective), will have no effect on the mesured potential difference. However, a membrane truly selective for a single type of an ion and completely non-selective for other ions does not exist. For this reason the potential of such a membrane is governed mainly by the activity of the primary (target) ion and also by the activity of other secondary (interfering) ions. The influence of the presence of interfering species in a sample solution on the measured potential difference is taken into consideration in the Nikolski-Eisenman formalism:

$$\mathbf{E = const + S \cdot (\log (a_x) + (z_x/z_y) \cdot \log (K_{xy} \cdot a_y))}$$

where (a_y) is the activity of an interfering ion, (z_y) its charge and (K_{xy}) the selectivity coefficient (determined empirically).

II. General Principle of ISE Analysis

At equilibrium, the membrane potential is mainly dependent on the concentration of the target ion outside the membrane and is described by the Nernst equation. Briefly, the measured voltage is proportional to the Logarithm of the Activity (effective concentration) of the ions in solution. The sensitivity of the electrode is expressed as the electrode Slope - in millivolts per decade of acivity/concentration. Thus the electrodes can be calibrated by measuring the voltage in solutions containing, for example, 10ppm and 100ppm of the target ion, and the Slope will be the slope of the (straight) calibration line drawn on a graph of mV versus Log Activity.

i.e. S = [mV(100ppm) - mV(10ppm)] / [Log100 - Log10]

Thus the slope simply equals the difference in the voltages - since Log100-Log10 = 1.

Unknown samples can then be determined by measuring the voltage and plotting the result on the calibration graph. The measured slope can be used as an indication of the proper functioning of an ISE. The following ranges are acceptable:

Monovalent: Cations +55 ± 5, Anions -55 ± 5.
Divalent: Cations +26 ± 3, Anions -26 ± 3.

III. Ion Transport with an Ionophore

From the basics of ion exchange, let's put a membrane, containing an ionophore, between an "unknown" analyte solution and a "known" reference solution (Figure 3). In this example, the analyte is $\mathbf{A}^+$. The *ionophore* is a neutral "carrier" molecule represented by the blue oval. Figure 4 shows the chemical structure of two ionophores. The ionophore cannot diffuse out of the membrane and but can "trap" the analyte ion (A^+) at the interface between the solution and membrane. Without the ionophore, the analyte would be unable to partition into the organic membrane.

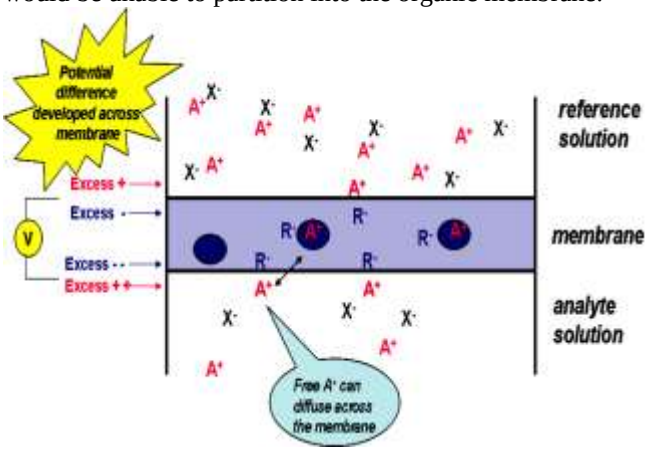

Figure 3. Development of a potential at an ISE.

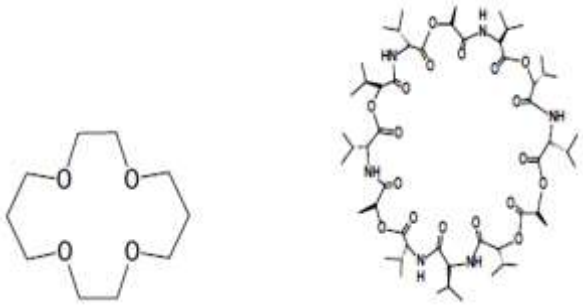

Figure 4. Chemical structures of a crown ether (left) and of valinomycin (right), two ionophores.

As with the ion-exchange process, equilibrium is established at both solution-membrane interfaces. The resulting charge separation at each interface leads to a phase-boundary potential. Now that we have developed an electrical potential across the membrane, we need to find a way to measure it. As before, we put an internal reference electrode in the internal reference solution and an external reference electrode in the analyte solution, as shown in Figure 5. The potential difference measured at these two electrodes is the membrane potential.

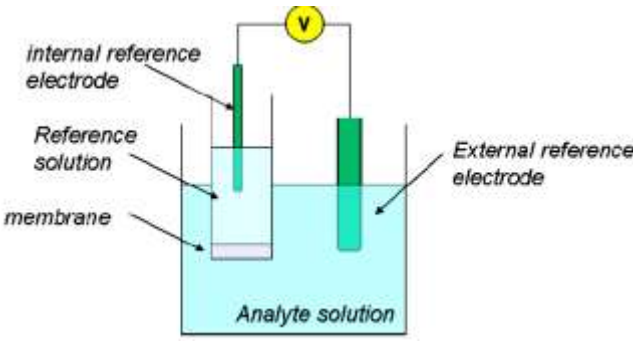

Figure 5. Electrochemical cell for a potentiometric measurement with an ISE.

The Membrane

By now you have learned that the identity of the membrane determines the selectivity of the electrode. In other words the type of membrane used dictates which analyte you can detect. Therefore different electrodes are used for different ions. The membrane should also have low electronic conductivity. The membrane must have low solubility in the analyte solution – we don't want it to dissolve!!

There are three main types of membranes. The electrodes are classified by the membrane material.

1. **Glass membrane electrodes**: The most famous glass electrode determines H^+ activity or pH (*click here for the* pH electrode *section*). The membrane is composed of a silicate glass. Glass electrodes can also be constructed that are sensitive to other cations such as sodium.

2. **Crystalline / solid state membrane electrodes:** The membrane is composed of an insoluble inorganic salt. An ion-exchange process (Figure 2) leads to the formation of a potential at the membrane. Polycrystalline or mixed crystal membranes such as AgCl / Ag_2S can be used to determine Cl^-. This electrode is used in one of the experiments outlined in the Experimental section.

   Single crystal LaF_3 is widely used to determine F^-. The crystal is usually doped with europium to improve the conductivity. At each membrane-solution interface, the following equilibrium takes place:

   $$LaF_3(s) \leftrightharpoons LaF_2^+(s) + F^-(aq)$$

   You can see that the formation of LaF_2^+ creates a charge at the surface. The equilibrium will be shifted to the right for the solution with a smaller F^- concentration, and the potential will become more positive relative to the other side of the membrane. It is this potential difference across the LaF_3 crystal membrane that is measured and related to F^- concentration. The fluoride electrode is extremely selective for F^- but can experience interference from OH^- above pH 8. This electrode is used in one of the experiments listed at the end of this learning module.

3. **Liquid membrane electrodes**: An ion-exchanger or ionophore (neutral macrocyclic ion carrier) is dissolved in a viscous organic liquid membrane. Without the exchanger or ionophore the ion of interest is unable to penetrate the membrane. With the exchanger or ionophore present, the processes described in Figures 2 and 3 transport the ion into the membrane.

   One of the most famous liquid membrane electrodes has been used for calcium determination. Initially, researchers attempted to use glass membrane electrodes (which had been successful for monovalent cations such as H^+ and Na^+) to detect divalent cations, such as Ca^{2+}. When this was determined to be unfeasible, liquid membranes were developed. This electrode works by an ion-exchange process. The cation-exchanger is an aliphatic diester of phosphoric acid, $(RO)_2PO_2^-$, where each R group is an aliphatic hydrocarbon chain containing between 8 and 16 carbons. The phosphate group can be protonated, but has a strong affinity for Ca^{2+}. The cation exchanger is dissolved in an organic solvent and held in a porous compartment between the analyte solution and internal reference calcium chloride solution. The ion-exchanger uptakes Ca^{2+} into the membrane by the following mechanism, forming a complex with the structure shown in Figure 6:

   $$Ca^{2+}(aqueous) + 2(RO)_2PO_2^-(organic) \leftrightharpoons [(RO)_2PO_2]_2Ca(organic)$$

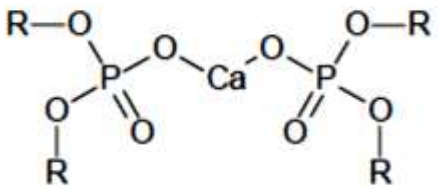

Figure 6. Calcium dialkyl phosphate complex.

Calcium ISEs are commonly used to measure calcium ion activity in biological fluids, as calcium ion is important in many physiological processes, such as bone formation.

4. **Polymer membrane electrodes**: An alternative to wet liquid membrane electrodes is to use a polymeric membrane, which is composed of a polymer such as polyvinylchloride (PVC), a plasticizer, and the ion carrier or exchanger. The response of these electrodes is highly selective and they have replaced many liquid membrane electrodes. Polymer electrodes have been

used to determine ions such as K^+, Ca^{2+}, Cl^- and NO_3^-. Ionophores, or chelating agents, that selectively complex ions include crown ethers and the antibiotic valinomycin (see Figure 4). The important feature of the neutral carrier molecule is its cavity which has dimensions approximately that of a molecule or ion. The valinomycin electrode was one of the first polymer membrane electrodes and is routinely used to determine potassium. The electron-rich center of valinomycin efficiently extracts K^+ ions due to the similarity between the diameter of K^+ and the inner diameter of the valinomycin molecule. The outer lipophilic part of the valinomycin molecule allows it to remain in the polymeric membrane. In the United States alone, nearly 200 million measurements are made annually of blood potassium levels using this electrode.[11]

IV. Selectivity of ISEs

Ion-selective electrodes can experience interferences by responding to the presence of other ions. Although the fluoride electrode comes close, no membrane is 100% specific for only one ion. Equation 4 assumes that all of the electrode response (E_{meas}) is due to one ion. Let's call this analyte ion i and its activity A_i (note that the charge is now z_i). We will call the interfering ion j with corresponding activity A_j and charge z_j. We can account for the lack of 100% specificity by incorporating the activity of j and a ***selectivity coefficient*** (k_{ij}) into equation 4. This new equation is called the Nikolskii-Eisenman equation:

$$E_{meas} = const + \frac{0.05916}{z}\log(A_i + k_{ij}A_j^{z_i/z_j})$$

The selectivity coefficient is a numerical measure of how well the membrane can discriminate against the interfering ion. To put this in perspective, if an electrode has equivalent responses to the two ions, then $k_{ij} = 1.0$. As you can see from the equation, the smaller the k_{ij} values, the less impact the interfering ion will have on the measured potential. When k_{ij} values are less than 1, the ISE is more responsive to the analyte ion and when k_{ij} values are greater than 1, the ISE is more responsive to the interfering ion. For example, a k_{ij} value of 0.01 means that the electrode is 100 times more responsive to ion i over j.

Selectivity coefficients can be experimentally determined. Selectivity coefficients for some of the electrodes previously discussed are listed below.

Analyte ion (i)	Interfering Ion (j)	k_{ij}
K^+ (valinomycin)[a]	Na^+	10^{-4}
	Ca^{2+}, Mg^{2+}	10^{-7}
Ca^{2+} [b]	Mg^{2+}	0.02
	K^+	0.001

V. Application of Ion Selective Electrodes

Enzyme sensor for organophosphorus insecticides- organophosphorus hydrolase in a polymer membrane on a pH sensor is used to catalyse the hydrolysis of compounds with phoshate ester functionality. The detected $[H^+]$ change is proportional to the concentration of the phosphate ester insecticide. This is a good example of the use of an enzyme to give selectivity to a specific class of compounds. Unfortunately, some unknown component of soil interfered.

CHEMFET calcium probe- another example of a simple, mass producible, low cost sensor. This paper stresses the importance of ion-exchange equilibria in the operation of membrane based electrodes. The mechanism of operation in this case is different form that of a normal Ca^{2+} ISE, and leads to a doubling of the sensitivity.

Diagnosis of Cystic Fibrosis using a Potentiometric Array- an example of a clinical application, and the use of multiple sensors in a small, flow-through array. CF can be diagnosed based on elevated levels of Na^+, Cl^+, and K^+ in sweat. Nitrate interference was a problem. You should know the chemical basis for each ISE (Valinomycin for K^+, a crown ether for Na^+, Ag/AgCl for Cl^-).

Determination of Non-Ionic Surfactants by Liquid Membrane Electrodes - Non ionic surfactants (NIS) can increase alkali metal (M^+) interference in alkaline earth (M^{2+}) sensing by partitioning into the membrane and providing sites for M^+ binding. This is an interesting, and unusual, type of interference. The use of this effect to sense NIS is interesting, but doesn't seem very practical. Still it is an example of how potentiometry can be used to sense non-ionic substances, and may be useful in an electrochemical nose.

Metalloporphyrin-Based Ion Selective Membranes (two presentations) - the most important point from these papers is that ion complexation can be used as a quite specific means of detecting ions. Selectivity is very different from that for ion-exchange and solubility based electrodes. A gallium(III) tetraphenylporphyrin has good specificity for valproate (an anti-epileptic drug) over salicylate and Cl^-. However, the detection limit was not good enough (this is a common limitation of ISEs). Other metalloporphyrins are more selective for other anions, such as salicylate and Cl^-. Cl^- selectivity is important because the relatively high solubility of AgCl leads to interference from Br^-, I^- etc. with AgCl based ISEs. Dimerization of some metalloporphyrins

can lead to enhanced sensitivity (not the same a detection limit).

Nitrate-selective electrodes- the main point of this paper was to illustrate that the mode of operation of many ISEs is not well understood. In this case, as in glass pH electrodes, the sensing is due to ion-exchange that is confined to a thin layer at the surface of the membrane. This may be true in many other cases. Another important aspect of this paper is that the ionophore (ion-exchanger) was covalently bound to the polymer membrane. In most other cases, the ionophore is simply dissolved in the membrane.

Modified Electrodes and Applications of Voltammetry

Boron doped diamond modified electrode for ASV of Pb and Cu - the main point here is that AVS can be done at the 10^{-6}M level without the use of Hg. However, Hg drops (detection limit ~ 10^{-6}M for Cu, 10^{-8}M for Pb) or Hg films are better.

Carbon nanotube + Nafion + "poly-phenol" modified electrode for phenol oxidation- Carbon nanotubes increase the current by speeding up the electron transfer kinetics (they can't speed-up diffusion in the solution). This is probably due to an increase in active electrode area, with the ends of the tubes acting as electrocatalytic sites. Oxidative pretreatment in the phenol solution almost eliminates passivation of the electrode by phenol polymerization. Electrocatalytic benzoquinone sites are formed, probably at the tube ends.

Microelectrodes for antioxidants in engine oil - the key advantage is that the low current allows voltammetry to be performed in highly resistive media.

Microelectrodes for field use- advantages are low currents (two electrode cell, simple electronics), insensitivity to oxygen (need to be able to explain this for final exam, but not mid-term). Derivative staircase works better than DP or SW voltammetry. Pulses are not needed because of high Faradaic/charging current ratio at a microelectrode.

"CuCl" modified Pt(III)- use of a well defined electrode surface (i.e. atomically flat with a single crystallographic face exposed) and "atomic" microscopy to understand the structure of electrode surfaces at the atomic level. This is an important part of understanding electrode processes at a fundamental level, and particularly importing to understanding/developing electrocatalysts. Cu underpotential deposition (UPD) on Pt is an important model system.

Electrochemical "taste/smell" sensors- the important concept here is that an array of sensors with different responses to the same sample can be used to "recognise" complex mixtures. Electrochemical sensors are well suited for this type of device because it is easy to build small arrays with large numbers of different sensing elements. Sensing elements can differ in the type of response (e.g. potentimetric, amperometric, voltammetric), applied stimulus (e.g. potential or waveform), material (e.g. Pt, Au, C), coating.

Ultrasonic cleaning of the electrode - another example of an electrode activation/prevention of passivation method. Other methods include laser activation, electrochemical activation, and exposure of a clean/active surface by physical means (e.g. Hg drop, cutting, grinding/polishing). This paper also provides an example of a coupled separation-electrochemical analysis, and ASV without Hg. The detection limit for Cu(II) was ca. 10^{-8}M, so better than the diamond modified electrode (above), and better than Hg.

VI. Advantages and limitations of I.S.E.

Advantages:

1. Linear response: over 4 to 6 orders of magnitude of A.
2. Non-destructive: no consumption of analyte.
3. Non-contaminating.
4. Short response time: in sec. or min. useful in indus. applications.
5. Unaffected by color or turbidity.

Limitations:

1. Precision is rarely better than 1%.
2. Electrodes can be fouled by proteins or other organic solutes.
3. Interference by other ions.
4. Electrodes are fragile and have limited shelf life.
5. Electrodes respond to the activity of uncomplexed ion. So ligands must be absent or masked. μ must be kept constant.

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