Subject 12. Measurement of electrode potentials

1. Importance

Study of mechanisms of formation of the electrode, diffusion, membrane and oxidation-reduction potentials, as well as their responses to various external factors renders it possible to understand mechanisms of most biochemical reactions. Measurement of biopotentials is applied in such important diagnostical methods as electrocardiography, electroencephalography and others. Concentrations of of physiologically active ions (H^+, K^+, Na^+, Ca^+, Cl^-, NO_3^-) in biological fluids and tissues of the organism are measured with EMF values.

Electrochemical methods of analysis (polarography, potentiometric and amperometric titration) are widely applied in medical and biological research. Therefore, doctors need the knowledge of the basics of electrochemistry for professional activities.

Competences

Capacity for abstract thinking, analysis and synthesis, capacity to learn.

Ability to apply knowledge in practical situations.

Know standard methods of physical and chemical (laboratory and instrumental) studies of biological systems of the human and the environment. Be able to analyze and evaluate results of physicochemical (laboratory and instrumental) studies of biological systems in the organism and the environment. Be responsible for decisions taken on the basis of evaluation of results of physicochemical (laboratory and instrumental) studies of biological systems of the organism and the environment.

Ability to assess and ensure quality of work.

Use English language in professional and business communications and preparation of documents.

Ability to choose strategy of communication; ability to work in a team; skills of interpersonal interaction.

Ability to exercise healthy life style.

2. Concrete aims

Explain the mechanism of formation of the electrode potentials.

Analyze the principle of the potentiometry method and make conclusions about its applications in medical and biological research.

Be able to measure oxidation-reduction potentials and predict direction of oxidation-reduction reactions.

Measure electrochemical parameters of solutions.

Calculate electrode and redox potentials.

3. Basic knowledge, skills necessary for studying the subject (interdisciplinary integration)

Previous subjects	Obtained skills

1. Medical and Biological Physics	Describe and apply electrodes. Measure potentials Possess the concept of membrane potentials. Describe electrocardiography.
2. Foreign language by professional orientation	Have basic knowledge of English. Be able to communicate in English. Apply English in professional activities.
3. Latin language and medical terminology	Know medical terminology in Latin language.
4. Safety of life, basics of bioethics and biosafety	Be capable of self-regulation, lead a healthy lifestyle, be able to adapt and act in a new situation.

4. Tasks for independent work during preparation for the class and in class.

4.1. The list of key terms, parameters, characteristics which the student is to learn while preparing for classes:

Term	Definition
1. Electrode.	**Electrode** is a conductor (metal) immersed in a solution of electrolyte.
2. Electrode potential.	**Electrode potential** is the potential difference (potential jump) at the interface between the electrode‒solution phases.
3. The Nernst equation	$\varphi = \varphi^0 + \frac{RT}{nF} \ln a(Me^{n+})$, або $\varphi = \varphi^0 + \frac{0{,}059}{n} \lg a(Me^{n+})$.
4. Redox electrode.	**Redox electrodes** are the elements that consist of an inert conductor (platinum, gold, graphite, etc.) immersed in a solution that contains botn an oxidized and reduced form of the same substance.
5. The Nernst-Peters equation.	$\varphi_{\text{ок}\mid\text{відн}} = \varphi^0_{\text{ок}\mid\text{відн}} + \frac{RT}{nF} \ln \frac{a(\text{ок})}{a(\text{відн})}$.
6. Galvanic element.	**Galvanic element** is a device in which the energy of the chemical reaction is converted into electric energy. It consists of two electrodes.
7. Electrochemical processes in the oral cavity.	If there are dentures made of different metals in the oral cavity, then upon wetting them with oral liquid a galvanic element is formed. The electric current that

	occurs during its operation leads to initiation of a pathological state called galvanosis.

4.2. Theoretical questions to the lesson:

1. Electrode potentials and mechanism of their formation.
2. The Nernst equation. Normal (standard) electrode potential.
3. Normal hydrogen electrode.
4. Measurement of electrode potentials. Measurement and reference electrodes. Chlorine silver electrode. Ion-selective electrodes. Glass electrode.
5. Galvanic elements. Electrochemical processes in the oral cavity.
6. Role of redox reactions in the processes of life.
7. Redox potential as a measure of oxidative and reducing capacity of systems.
8. Peters equation. Standard redox potential.
9. Prediction of direction of redox reactions with the values of redox potentials. Redox potentials in processes of biological oxidation.
10. Method of potentiometry.

4.3. Practical work (task) done by students in class

Measurement of redox potentials

Redox potentials of redox systems are calculated with EMF values, measured by the ionometer EV-74.

1. Preparation for work and measuring EMF.

– press the buttons "t" and "-1-19";

– plug the device in;

– warm up the device for 30 minutes;

– assemble a galvanic cell with the measurement electrode (the platinum electrode EPV-1) and the comparison electrode (the chlorinesilver electrode EVL-IM with the constant potential 0.201± 0.003 V);

– insert the electrodes in their sockets over the turntable and connect them to the device;

– immerse the electrodes in a solution of a redox system in a cup;

– press the button "mV" and the button of the needed measurement range and measure EMF value (E).

2. Calculations and writing a report of the laboratory work

1) Calculate practice values of redox potentials for the three redox systems with the formula:

$$\varphi_{\text{pr}} = E + \varphi_{\text{comp}} ,$$

where: E is EMF value, V (measured); $E = \varphi_{\text{pr}} - \varphi_{\text{comp}}$;

φ_{comp} = 0.201 V – the potential of the chlorinesilver electrode.

2) Calculate theoretical values of the redox potentials for the two redox systems with concentrations of reduced and oxydized forms with the equations:

$$1. \varphi_{\text{I}_2/2^{2-}} = 0.530 - \frac{0.059}{2} \lg \frac{[^2{}_2]}{[\text{I}^-]^2} ;$$

$$2. \varphi_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.771 + 0.059 \lg \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} .$$

Concentrations are given in the table.

3) Fill in Table with the results:

Table

№	Electrode	Composition of solutions	φ^0, V	φ_{pr}, V	φ_{theor}, V	E, V
1	Pt | I_2, $2I^-$	KI (0.1 mol/L) I_2 (0.001 mol/L)	0.530			
2	Pt | Fe^{3+}, Fe^{2+}	Fe^{3+} ($5\cdot10^{-4}$ mol/L) Fe^{2+} ($5\cdot10^{-2}$ mol/L)	0.771			

4) With the standard reduction-oxidation potentials of the systems φ° (in the table) decide, whether the reactions can happen spontaneously:
a) $Fe^{3+} + I^- \rightarrow$
b) $Fe^{2+} + I_2 \rightarrow$
with the formula: $E = \varphi_{ox.} - \varphi_{red.}$ A reduction-oxidation process proceeds spontaneously, if $\varphi_{ox.} > \varphi_{red.}$ and E >0.

Contents of the subject (abstract):

1. Electrode potentials and mechanism of their formation.

Electrode is a conductor (metal) immersed in a solution of electrolyte.

Electrode potential is the potential difference (potential jump) at the interface between the electrode–solution phases.

2. The Nernst equation. Normal (standard) electrode potential

$$\varphi = \varphi^0 + \frac{RT}{nF} \ln a(Me^{n+}), \quad \text{or} \quad \varphi = \varphi^0 + \frac{0,059}{n} \lg a(Me^{n+}).$$

Normal (standard) electrode potential(φ^0) is the electrode potential, which occurs upon an immersion of a metal plate in a solution with the activity of metal ions 1 mol / L.

3. Normal hydrogen electrode

Normal hydrogen electrode is a platinum plate immersed in a solution of sulfuric acid, the activity of H^+ ions in which is equal to 1 mol / L. The solution is saturated with hydrogen at a pressure of 101.3 kPa.

4. Measurement of electrode potentials. Measurement and reference electrodes. Chlorine silver electrode. Ion-selective electrodes. Glass electrode

Measurement electrode is an electrode potential of which is determined. An example of an ion-selective electrode is a glass electrode. When an ion-selective electrode is immersed in a solution, it selectively adsorbs only specific ions on the membrane, and their concentration is determined.

Reference electrode is an electrode with a known value of the electrode potential. For example, a chlorine silver electrode has a constant potential of + 0.2

V. The chlorine silver electrode is a silver wire with a layer of silver chloride deposited on it, and immersed in a KCl solution.

5. Galvanic elements. Electrochemical processes in the oral cavity

Galvanic element is a device in which the energy of a chemical reaction is converted into electrical energy. It consists of two electrodes.

If there are dentures made of different metals in the oral cavity, then upon wetting them with oral liquid a galvanic element is formed. The electric current that occurs during its operation leads to initiation of a pathological state called galvanosis.

6. Role of redox reactions in the processes of life

Protons and the electrons from substrates (carbohydrates or fats) are transferred to oxygen with the formation of the final products of H_2O and CO_2, which promotes the capture of the energy in ATP.

7. Redox potential as a measure of oxidative and reducing capacity of systems

The more negative the value of the redox potential, the stronger reducing agent is the system and vice versa.

8. Peters equation. Standard redox potential

$$\varphi_{\text{ок}|\text{відн}} = \varphi^0_{\text{ок}|\text{відн}} + \frac{RT}{nF}\ln\frac{a(\text{ок})}{a(\text{відн})}.$$

$\varphi^0_{\text{ок}|\text{відн}}$ is the standard redox potential.

9. Prediction of direction of redox reactions with the values of redox potentials. Redox potentials in processes of biological oxidation.

The greater the negative value of the redox potential, the more vigorously the system loses electrons and vice versa.

Systems involved in the transport of protons H^+ and electrons in the process of biological oxidation are characterized by a change in the potential from -0.42 to +0.81 V.

10. Method of potentiometry

To determine pH with the potentiometric method, a galvanic element of two electrodes is composed. The electromotive force of the galvanic element is measured using a potentiometer.

Materials for self control:

A. Tasks for self control:

1. The Nernst equation for the nickel electrode at 298 K is:

a) $\varphi = \varphi^0 + \frac{0.059}{n}\lg[Ni^{2+}]$; c) $\varphi = \varphi^0 - 0.059\lg[Ni^{2+}]$;

b) $\varphi = \varphi^0 - \frac{0.059}{n}\lg[Ni^{2+}]$; d) $\varphi = \varphi^0 + 0.059\lg[Ni^{2+}]$.

2. The potential of a metal electrode is standard, if:
a) concentrations of all the substances taking part in the electrode process is one mole per liter;
b) concentrations of all the substances are equal;
c) the concentration of the metal cations equals one mole per liter, and temperature and pressure are standard;
d) it is measured against the standard hydrogen electrode.

3. Choose one best characteristic of the redox electrode:
a) metal immersed in an electrolyte solution and exchanging ions and electrons with it;
b) inert metal immersed in an electrolyte solution and exchanging electrons with it;
c) inert metal immersed in a reduction-oxidation system and conducting electrons only;
d) inert metal immersed in a reduction-oxidation system and exchanging ions and electrons with it.

4. Choose a redox system, which oxidized form is the strongest oxidizing agent at standard conditions:
a) $HBrO + H^+ + 2e^- = Br^- + H_2O$; φ° = 1.34V
b) $CrO_4^{2-} + 4H_2O + 3e^- = Cr(OH)_3 + 5OH$; φ° = - 0.13V
c) $2IO_3^- + 12H^+ + 10e^- = I_2 + 6H_2O$; φ° = 0.19V
d) $H_2O_2 + 2H^+ + 2e^- = 2H_2O$; φ° = 1.78V

5. Choose the best oxidizing agent to transform the Fe^{2+}ion into Fe^{3+}ion at standard conditions< if the standard potential $\varphi_{Fe^{3+}/Fe^{2+}}$ is 0.771V and the standard potentials of the oxidizing agents are given in brackets.
a) $KMnO_4$ (φ° = 1.51V)
b) $KMnO_4$ in neutral medium (φ° = 0.58V)
c) HNO_2 (φ^0 = 1.0V)
d) $CuSO_4$ (φ^0 = 0.153V)

6. The pairs of electrodes that can be used in the galvanic cell for pH measurement are:
1) glass – quinhydrone;
2) hydrogen – normal hydrogen;
3) glass – chlorine silver;
4) calomel – quinhydrone.
a) 2, 3, 4; b) 1, 3; c) 1, 2, 3; d) 1, 4.

B. Practical tasks for self control:

1. Choose a direction of the spontaneous reaction at standard conditions:
$2NaCl + Fe_2(SO_4)_3 \rightleftarrows 2FeSO_4 + Cl_2 + Na_2SO_4$, if
$\varphi^0_{Cl_2|2Cl^-}$ = 1.36V, and $\varphi^0_{Fe^{3+}|Fe^{2+}}$ = 0.771V:
a) from left to right; c) the reaction will not take place;
b) from right to left; d) the reaction will go both ways.

2. Use the series of the standard electrode potentials and tell which of the reactions can take place at standard conditions:

1) $Zn^{2+} + Cu \rightarrow Cu^{2+} + Zn$; 3) $Cd + Co^{2+} \rightarrow Cd^{2+} + Co$;

2) $Mg + Sn^{2+} \rightarrow Sn + Mg^{2+}$; 4) $2Ag + Pb^{2+} \rightarrow Pb + 2Ag^{+}$.

a) 1, 2, 3; b) 2, 3; c) 4; d) 2.

3. Calculate the potential of the hydrogen electrode, immersed in a hydrochloric acid solution. 14.50mL 0.1 *M* NaOH solution is used to titrate10 mL of the hydrochloric acid solution.

a) 0.0685V; b) –0.0435V; c) 0.0495V; d) –0.00985V.

Literature

Main:

1. Medical Chemistry: textbook / V.O. Kalibabchuk, V.I. Halynska, V.I. Hryshchenko et al.; edited by Prof. V.O. Kalibabchuk – Kyiv: “Medicine”, 2010 – 224 p. (P. 80 – 86).

Informational resources:

2. www. pdmu, edu.ua
https://med-chemistry.pdmu.edu.ua/

(Web page of Poltava State Medical University).