Ministry of Health of the Republic of Belarus
Educational institution
"Gomel State Medical University"

Department of General and Bioorganic Chemistry

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METHODOLOGICAL MANUAL
for conducting the laboratory class
in the academic discipline "Medical chemistry"
for students
the first-year of the Faculty of International Students (FIS),
studying in the specialty 7-07-0911-01 "Medical business"

Topic 10: Theories of solutions of weak and strong electrolytes

Time: 2 hours

Approved at the meeting of the Department
of General and Bioorganic Chemistry
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THE TRAINING AND EDUCATIONAL GOAL, TASKS, MOTIVATION TO STUDY THE TOPIC

Training purpose:

– formation of students' basic professional competence for solving diagnostic, research and other tasks of professional activity based on knowledge about theories of weak and strong electrolytes, the role of electrolytes in the human body;

– familiarization with the with the methods of calculating pH in solutions of weak and strong electrolytes.

Educational goal:

– to develop your personal, spiritual potential;

– to form the qualities of a patriot and a citizen who is ready to actively participate in the economic, industrial, socio-cultural and social life of the country;

– learn to observe academic and labor discipline, the norms of medical ethics and deontology;

– to realize the social significance of their future professional activities.

Tasks:

As a result of the training session, the student should

know:

– the main statements of the theories of weak and strong electrolytes;

– features of dissociation of strong, weak and amphoteric electrolytes;

– the concept of the degree of dissociation of the electrolyte, the constants of acidity and basicity;

– the concept of pH, methods for calculating pH in solutions of weak and strong electrolytes;

be able to:

– write equations of electrolytic dissociation of strong and weak electrolytes;

– compare the strength of acids and bases using the acidity and basicity constants;

– calculate the degree of dissociation of weak acids and bases, the concentration of ions in their solutions, pH values;

– calculate the ionic strength in solutions of strong electrolytes, the activity of ions, pH values;

possess:

– skills in experimental determination of pH of solutions using a pH meter with a glass electrode (potentiometric method).

Motivation to study the topic:

Biological fluids and tissues contain many electrolytes, i.e. substances capable to dissociate into ions in an aqueous medium: NaCl, KCl, HCl, $CaCl_2$, NaH_2PO_4, $NaHCO_3$, etc. Electrolytes perform many vital functions in the human body: create a constant osmotic pressure of biological fluids and cause active water transport; affect the solubility of proteins, amino acids and other biologically active compounds, play a key role in maintaining acid-base homeostasis of the body.

Disturbance of electrolyte metabolism leads to pathology and can cause the death of the body. Thus, knowledge of the theory of electrolytic dissociation is an important stage in the formation of a future doctor’s ideology.

NECESSARY EQUIPMENT

1. Methodological manual for students on the topic "Theories of solutions of weak and strong electrolytes".

2. Training tables:

a) Periodic Table of chemical elements by D.I. Mendeleev;

b) table of solubility of acids, bases and salts.

3. Reference materials of basic physico-chemical constants.

4. Chemical reagents and equipment necessary for laboratory work.

CONTROL QUESTIONS ON THE TOPIC OF THE CLASS

1. Elements of the theory of weak electrolytes.

2. Elements of the Debye-Hückel’s theory of strong electrolytes.

3. Calculations of pH in solutions of weak and strong acids and bases. Methods of pH determination.

COURSE OF THE CLASS

The theoretical part

1. ELEMENTS OF THE THEORY OF WEAK ELECTROLYTES

Electrolytes are polar compounds that produce ions when they dissolve in water (acids, bases, salts) and their solutions conduct electricity.

Depending on their ability to dissociate into ions, strong and weak electrolytes are known.

Weak electrolytes are:

a) all organic and most mineral acids: HF, HCN, HNO_2, H_2S, H_2SO_3, H_2CO_3, H_3PO_4 and others;

b) bases with low solubility in water and NH_4OH;

c) some salts, for example, $Fe(CH_3COO)_3$, $Fe(CNS)_3$, $HgCl_2$;

d) water.

Weak electrolytes are polar covalent compounds that undergo partial (reversible) ionization in water solutions:

$$\mathbf{CatAn \rightleftarrows Cat^+ + An^-} \qquad \boldsymbol{\alpha \ll 1}$$

α is the degree of ionization (ionization percent) of electrolyte, calculated by the formula:

$$\alpha = \frac{n}{N} \times 100\ \%$$

n is the number of ionized solute molecules;

N is the total number of solute molecules in the solution.

In weak electrolytes’ solutions an equilibrium is maintained between ions and molecules of a substance which is characterized by ionization equilibrium constant (K_{ion}):

$$K_{ion} = \frac{[Cat^+] \times [An^-]}{[CatAn]}$$

Several types of ionization constants are known.

Acids ionization constantans are referred as **acidity constants** ($\boldsymbol{K_a}$):

$$CH_3COOH \rightleftarrows H^+ + CH_3COO^-$$

$$K_a = \frac{[H^+] \times [CH_3COO^-]}{[CH_3COOH]}$$

Bases ionization constants are named **basicity constants** (***K$_b$***):

$$NH_4OH \rightleftarrows NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+] \times [OH^-]}{[NH_4OH]}$$

The higher the values of K_a and K_b, the greater the dissociation of acids and bases in aqueous solutions.

Weak electrolytes obey the **Ostwald's Dilution Law**: *the degree of ionization for a weak electrolyte increases with dilution of its solution:*

$$K_{ion} = \frac{C_M \times \alpha^2}{(1-\alpha)}$$

For weak electrolytes α << 1; thus, the equation can be rearranged as: $\alpha \approx \sqrt{\frac{K_{ion}}{C_M}}$

α is the degree of ionization (ionization percent);
C_M is the molar concentration of weak electrolyte, mol/l [1-3].

Problem 1. Calculate the degree of ionization and the concentration of hydroxide ions in 0.45 M ammonium hydroxide solution.

Solution:

$NH_4OH \rightleftarrows NH_4^+ + OH^-$; $\quad K_b = \frac{[NH_4^+] \times [OH^-]}{[NH_4OH]}$

As $[NH_4^+] = [OH^-]$, $K_b = \frac{[OH^-] \times [OH^-]}{[NH_4OH]}$; $\quad K_b = \frac{[OH^-]^2}{[NH_4OH]}$

The concentration of ions is calculated by the formula: $[OH^-] = \sqrt{K_b \times [NH_4OH]}$

The value of basicity constant for ammonium hydroxide is taken from the Reference table "The basicity constants of some electrolytes": $K_b(NH_4OH) = 1.8 \times 10^{-5}$.

Put the values into the formula:

$$[OH^-] = \sqrt{1.8 \times 10^{-5} \times 0.45} = 2.85 \times 10^{-3}\ mol/l$$

To calculate the degree of ionization, we use Ostwald's Dilution Law:

$\alpha = \sqrt{\frac{K_{ion}}{C_M}}$, *where K_{ion} is $K_b(NH_4OH)$;* $\qquad \alpha = \sqrt{\frac{1.8 \times 10^{-5}}{0.45}} = 6.32 \times 10^{-3}$

Answer: $\alpha = 6.32 \times 10^{-3}$; $[OH^-] = 2.85 \times 10^{-3}$ *mol/l*

2. ELEMENTS OF THE DEBYE-HÜCKEL'S THEORY OF STRONG ELECTROLYTES

Strong electrolytes are:

a) some mineral acids: HCl, HBr, HI, $HClO_4$, HNO_3, H_2SO_4 and others;

b) hydroxides of alkali and alkaline earth metals: NaOH, KOH, $Ba(OH)_2$, $Ca(OH)_2$ and others;

c) most salts.

Strong electrolytes are mainly ionic compounds completely dissociated into ions in water solutions:

$$\mathbf{CatAn \rightarrow Cat^{+} + An^{-} \qquad \alpha = 1\ (100\ \%)}$$

Only ions are present in their solutions.

Due to the high concentration of ions an electric field is created in a solution of strong electrolyte; its intensity is estimated by the value of the **ionic strength** (*I*):

$$I = \frac{1}{2} \times \sum C_{M\,i} \times Z_i^2$$

$C_{M\,i}$ – the molarity of ion i, mol/l;

Z_i – the charge number of ion i.

Ions with opposite charges attract each other. As a result, anions are more likely to be detected near cations in solution, and vice versa. In general, the solution is electrically neutral, but there is an excess of ions of the opposite charge near any given ion. The sphere of ions with the opposite charge surrounding each ion in an aqueous solution is defined as the *ionic atmosphere* (Fig. 1):

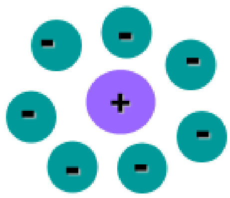

Figure 1 – A model of ionic atmosphere

Ionic atmosphere's density depends upon solutions' concentration.

The presence of an ionic atmosphere has retarding effect, reduces the mobility of ions and reduces the degree of their participation in the processes occurring in the solution.

Quantitatively, the effect of interionic interaction on the behavior of ion is characterized by its activity and activity coefficient.

Activity of ion (*a*) is effective concentration that takes in account the mutual attraction of oppositely charged ions and according to which ion participates in interactions occurring in solutions of strong electrolytes:

$$a(ion) = \gamma(ion) \times C_M(ion)$$

γ – the activity coefficient of an individual ion (cation or anion) which expresses the deviation of a solution from the ideal behavior ($\gamma < 1$) and depends upon the ionic strength of a solution and ions charge numbers.

Activity coefficient shows how many times the ion's activity differs from its true concentration.

Thus, to describe the real properties of strong electrolyte solutions we should use not their true concentration, but their effective concentration or activity [2, 3].

Problem 2. Calculate the ionic strength of the $MgCl_2$ solution, the activity of magnesium and chloride ions in this solution, if the normality of the salt in the solution is 0.2 mol / l.

Solution:

To calculate the ionic strength, it is necessary to know the molar concentrations of ions, so we have to convert the normality of $MgCl_2$ to the molarity according to the formula:

$C_M(X) = C_N(X) \times f_e(X)$, *where* $f_e(MgCl_2) = ½$ *or 0.5*

$C_M(MgCl_2) = 0.2 \times 0.5 = 0.1$ *mol/l*

Let's write down the salt dissociation equation and determine the concentration of each ion in the solution:

$$\underset{0.1\ M}{MgCl_2} \rightarrow \underset{0.1\ M}{Mg^{2+}} + \underset{2\times 0.1 = 0.2\ M}{2Cl^-}$$

The ionic strength of the given solution may be calculated according to the formula:

$$I = \frac{1}{2} \times \sum C_{M\,i} \times Z_i^2$$

Let's insert the calculated values of ion concentrations into the formula; it should be remembered that the charge of the magnesium ion is (+2), and the chlorine ion is (–1):

$$I(MgCl_2) = \frac{1}{2} \times \left[0.1 \times (+2)^2 + 0.2 \times (-1)^2\right] = \frac{1}{2} \times [0.4 + 0.2] = \frac{1}{2} \times 0.6 = 0.3\ mol/l$$

Using the Reference table "Activity coefficients of ions in aqueous solutions", let's find the activity coefficients for each ion: $\gamma(Mg^{2+}) = 0.34$; $\gamma(Cl^-) = 0.62$

Calculate the activity of each ion by the formula: $a = \gamma \times C$

$a(Mg^{2+}) = 0.34 \cdot 0.1 = 0.034$ *mol/l*; $a(Cl^-) = 0.62 \cdot 0.2 = 0.124$ *mol/l*

Answer: $I(MgCl_2) = 0.3$ *mol/l*; $a(Mg^{2+}) = 0.034$ *mol/l*; $a(Cl^-) = 0.124$ *mol/l*

3. CALCULATIONS OF pH IN SOLUTIONS OF WEAK AND STRONG ACIDS AND BASES. METHODS OF pH DETERMINATION

As a rule, the acidity (basicity) in dilute aqueous solutions and biological fluids is expressed in pH units (pOH) and can be calculated as:

- **for weak electrolytes:** $pH = -\log[H^+]$; $pOH = -\log[OH^-]$
- **for strong electrolytes:** $pH = -\log a(H^+)$; $pOH = -\log a(OH^-)$

The acidity or basicity of an aqueous solution is described quantitatively using a **pH scale:**

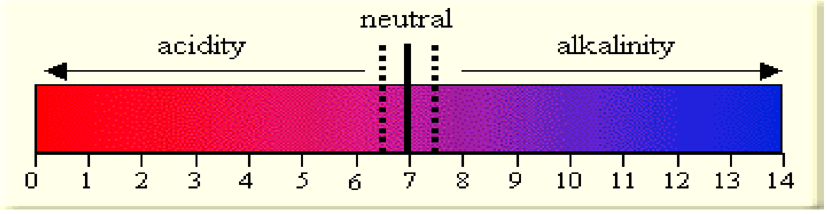

Figure 2 – pH scale

The logarithmic pH scale provides a convenient way to express the concentration of hydrogen ions (H^+) in solution and avoids the use of exponential notation. For practical purposes, the pH scale varies from pH = 0 (corresponds to 1 M H^+) to pH 14 (corresponds to 1 M OH^-), although pH values less than 0 or greater than 14 are possible [1-4].

Ways of measuring the pH of solutions:

▪ use of acid-base indicators, which are weak organic acids or bases, whose ionic and molecular forms have different colors indicating the pH of the medium;

▪ use of pH paper; pH paper is a strip of special paper that is prepared by placing the strip in one or more acid-base state indicators and then drying it; to determine pH, the pH paper is immersed in a test solution, the color of the paper is compared with a color chart, and the approximate pH of the solution can be determined;

▪ using a pH meter with a glass electrode (potentiometric method of analysis), a device whose voltage depends on the H^+ ion concentration:

Figure 3 – pH meter

It gives more precise values than the pH papers. For very precise measurement, the pH meter should be calibrated before each measurement with at least two buffer solutions with known pH values [2,3].

Problem 3. Calculate pH and the degree of ionization in 0.1 M nitrous acid solution.

Solution:

HNO_2 is a weak acid whose ionization is a reversible process:

$$HNO_2 \rightleftarrows H^+ + NO_2^-; \quad K_a = \frac{[H^+]\times[NO_2^-]}{[HNO_2]} = 7.1\times10^{-4}$$

As $[H^+] = [NO_2^-]$, $[H^+] = \sqrt{K_a \times C_M(HNO_2)} = \sqrt{7.1\times10^{-4}\times0.1} = 0.0084\ M;$

$pH = -\log[H^+] = -\log 0.0084 = 2.08$

To calculate the degree of ionization, we use Ostwald's Dilution Law:

$$\alpha = \sqrt{\frac{K_a}{C_M(HNO_2)}} = \sqrt{\frac{7.1\times10^{-4}}{0.1}} = 0.084$$

Answer: *pH =2.08; α = 8.4×10*$^{-2}$

Problem 4. Calculate the ionic strength, the activity of hydroxide ions and the pH in a 0.1 M KOH solution.

Solution:

KOH is a strong base whose ionization is irreversible:

$$\overset{0.1\,M}{KOH} \rightarrow \overset{0.1\,M}{K^+} + \overset{0.1\,M}{OH^-}$$

The ionic strength of the given solution may be calculated according to the formula:

$$I = \frac{1}{2}\times\sum C_{M\,i}\times Z_i^2$$

$$I\,(KOH) = \frac{1}{2}\times\left[0.1\times(+1)^2 + 0.1\times(-1)^2\right] = 0.1\ M$$

Using the Reference table "Activity coefficients of ions in aqueous solutions", let's find the activity coefficients for hydroxide ions: if I = 0.1 M, then $\gamma(OH^-) = 0.76$;

$a\,(OH^-) = \gamma(OH^-)\times[OH^-] = 0.76\times0.1 = 0.076$ *mol/l;*

$pOH = -\log a\,(OH^-) = -\log 0.076 = 1.12$;

$pH = 14 - pOH = 14 - 1.12 = 12.88$

Answer: *I (KOH) = 0.1 mol/l; a* (OH^-) *= 0.076 mol/l; pH = 12.88*

The practical part

Safety instructions before laboratory work.

LABORATORY WORK

Determination of the pH in aqueous solutions by potentiometric method

1. Determination of approximate pH values of the proposed solutions using universal indicator paper by immersing a strip of indicator paper in the test solution and comparing the color with the standard scale.

2. Determination of pH values of the same solutions using a pH meter with a glass electrode (potentiometric method of analyses).

Table 1 – Experimental data and results of calculations

Test solution	Tap water	Acidic solution	Basic solution	Buffer solution
pH determined using indicator paper				
pH determined by the potentiometric method				
molar concentration of protons, mol/l				

3. Calculation of the molar concentration of hydrogen cations in the studied solutions using the formula: $[H^+] = 10^{-pH}$.

Control over the assimilation of the topic

It is conducted in the form of an oral conversation with students.

METHODOLOGICAL RECOMMENDATIONS FOR THE ORGANIZATION AND PERFORMING OF INDEPENDENT WORK OF STUDENT (IWS)

The time allotted for independent work can be used by students for:

– preparation for laboratory classes;
– taking notes of educational literature;
– performing tasks for self-control of knowledge;
– preparation of thematic reports, abstracts, presentations.

The main methods of organizing independent work:

– studying topics and problems that are not covered in the classroom;
– writing an abstract and making a presentation;
– performing tasks for self-control of knowledge.

List of tasks of IWS:

1. Write the equations of multi-step dissociation of carbonic acid. At what step does dissociation mainly occur?

2. Specify the parameters that characterize the solutions of weak electrolytes:
a) degree of ionization (α);
b) acid ionization constant (K_a);
c) ionic strength (I);
d) base ionization constant (K_b).

3. Specify the parameters that characterize the solutions of strong electrolytes:
a) ionic strength (I);
b) activity coefficient (γ);
c) base ionization constant (K_b);
d) activity of ion (a_{ion}).

4. The ionization constant of monoprotic acid at 25 °C is 1.47×10^{-3}. Calculate the degree of ionization if concentration of the acid is 0.010 M.

Answer: 38.3 %

5. Calculate the pH and the degree of ionization (α) for each of the following solutions: a) 0.375 M HCN ($K_a = 6.2\times10^{-10}$); b) 0.200 M NH_3 ($K_b = 1.8\times10^{-5}$).

Answers: a) 4.82, 4.1×10^{-3} %; b) 11.23, 0.95 %

6. Calculate the ionic strength of 0.0025 M $Ca(NO_3)_2$ solution. What is the activity of nitrate anions in this solution? The activity coefficients of NO_3^- ions for a given ionic strength of the solution is considered equal to 0.9125.

Answer: 0.0075 M; 4.56×10^{-3} M

7. Calculate the ionic strength, the activity of ions and the pH in 0.1 N solution of KOH. The activity coefficients of K^+ and OH^- ions for a given ionic strength of the solution is considered, respectively, equal to 0.75 and 0.76.

Answer: 0.1 M, 0.075 M, 0.076 M, 12.88

The control of the IWS is carried out in the form of:

– evaluation of an oral answer to a question, message, report or presentation;

– individual conversation.

LIST OF SOURCES USED

1. Medical chemistry : textbook for students of higher education establishments – med. univ., inst. and acad. / V.O. Kalibabchuk, V.I. Halynska, L.I. Hryshchenko et al. ; ed. by V.O. Kalibabchuk. – 6th ed., corr. – Kyiv : AUS Medicine Publishing, 2018. – P. 70-76.

2. Основы химии для иностранных студентов = Essential chemistry for foreign students : учебно-методическое пособие / С. В. Ткачёв [и др.]. – 5-е изд. – Минск : БГМУ, 2018. – С. 93-99. – Режим доступа: http://rep.bsmu.by:8080/handle/BSMU/21054.

3. Филиппова, В. А. Общая химия : учеб. пособие для студентов лечеб. фак-та, обуч. на англ. яз. : в 2 ч. = General Chemistry : Educational guaidance for students medical department in English medium / В. А. Филиппова, А. В. Лысенкова, Л. В. Чернышева. – Гомель : ГомГМУ, 2009. – Ч. 1. – 192 с. URI: https://elib.gsmu.by/handle/GomSMU/2679.

4. Chang, Raymond. Chemistry / R. Chang. – 4th ed. – USA : University Science Books, 1991. – 1065 p.