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**The manual for laboratory lessons in physical and colloidal
chemistry (Part II):**

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The present manual is intended for pharmaceutical, pediatric, general medicine and medico-biological departments of medical universities, can be used by students of all higher education institutions, as well as teachers and students of colleges and lyceums.

It embraces the topics of chemical kinetics, surface phenomena, adsorption, production and properties of chloride solutions, coagulation of colloidal solutions, laboratory exercises on high molecular weight compounds, problems and exercises, control questions. An appendix with the necessary reference materials for trainings and problem solving is at the end of the manual . The values of the physical measurements, the glossary and the various symbols are in accordance with the accepted recommendations are given in the manual that they are intended to help students to understand.

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P R E F A C E

This manual is intended for second-year students who perform laboratory work on physical and colloid chemistry at the department of Inorganic, physical and colloid chemistry of the Tashkent pharmaceutical institute. A theoretical introduction is given before describing individual experimental works. It gives the amount of knowledge that allows the student to consciously and completely independently do each work.

Unlike most of the existing workshops on physical and colloidal chemistry, the present textbook is interpreted in the light of modern achievements, linking it to pharmacy. In the training of qualified pharmacists, surface phenomena, colloidal chemistry of high-molecular compounds (HMC) and surfactants (surfactants) plays an important role. In pharmaceutical technology, surfactants are widely used as emulsifiers, stabilizers, solubilizers and dispersants. HMC is used as a basis for creating medicines, prolonged action, ointments, candles, and other dosage forms.

Colloidal chemistry, which completes all chemical disciplines, is more of an experimental science. To master it, only theoretical training and knowledge of the laws of this science are not enough. It is also necessary to acquire the skills of experimental research, which requires the development of modern devices, the ability to work out the results of the experiment and make appropriate conclusions and conclusions. The purpose of this training manual is to teach students experimental methods for studying the colloidal-chemical properties of solutions of surfactants and high-molecular compounds, as well as coarse-dispersed systems. HMC and surfactants are widely used in the pharmaceutical industry as emulsifiers, wetting agents, solubilizers, structure-forming agents, stabilizers in the processes of obtaining ointment bases, ointments, candles, etc. the Composition of some drugs, such as cerobrolysin, albumin, casein, polyglucin, reopoliglucin, etc. they consist of peptides and macromolecules of proteins. Therefore, students need knowledge and practical skills on the HMC and surfactants.

Introduction

Physical chemistry is a science that explains chemical and physical phenomena and establishes their regularity on the basis of General principles of physics.

The name of physical chemistry was introduced by M.V.Lomonosov (1752-1753). He first gave it to the definition formulated by the subject and objectives. At the end of the XIX century, physical chemistry became an academic discipline in all universities that trained specialists in natural Sciences and pharmacists. In 1919, the Petrograd chemical and pharmaceutical Institute, the first higher educational institution in Russia, was established. A year later, the Department of physical chemistry was organized at this Institute. The Department was headed by a well-known scientist, honored scientist of N.N.Efremov.

The object of physical chemistry is any system in which chemical transformations occur. Physical chemistry studies the changes occurring in these systems, accompanied by the transition of chemical forms of motion into various physical forms of motion – thermal, electric, radiant, etc. Physical chemistry studies chemical processes in unbroken connection with the accompanying physical phenomena – thermal effects, the occurrence of electric current, radiation energy.

The main task of physical chemistry is to study the mechanism of phenomena, explain the laws that determine the direction of chemical reactions, the speed of their flow, the influence of various factors on them, and establish a relationship between the structure of substances and their reactivity.

At first, the main section was chemical kinetics. Today it includes the doctrine of the structure of the atom, chemical equilibrium, phase equilibria, solutions, electrochemistry, surface phenomena, colloidal chemistry, surfactants, and high-molecular substances. Physical chemistry serves as the theoretical basis for inorganic, organic, pharmaceutical, and analytical chemistry, as well as chemical, physical-chemical, and pharmaceutical technology.

Colloidal chemistry was originally only a branch of physical chemistry. The ever-increasing needs of mankind for new materials, as well as the success of scientists working in this field, have made it an independent science, and a whole scientific direction has been formed – nanotechnology, which is currently a priority path for the development of world science.

The colloidal state of substances is a highly dispersed state of substances. Its individual particles are not molecules, but clusters distributed in the solvent medium and consisting of many molecules. They have a highly developed surface. Due to this, the properties of colloidal systems differ significantly from bulk objects and are largely determined by surface phenomena. Colloidal chemistry deals with the study of colloidal systems and can be considered as the physical chemistry of highly dispersed systems.

SECTION I. CHEMICAL KINETICS. MOLECULARITY AND THE ORDER OF REACTION. METHODS FOR DETERMINING THE REACTION ORDER

Chapter 1. Rate of chemical reactions

Chemical kinetics is a branch of physical chemistry that studies the rate and mechanism of reactions. Studying the mechanism implies a detailed description of all the elementary stages of the reaction. To find out the reaction mechanism, the effect of the concentration of starting substances, reaction products, catalysts and inhibitors, temperature, the nature of the solvent, etc. on the reaction rate is investigated. On the basis of research, a scheme is built that allows you to explain the entire set of experimental facts and allows you to purposefully influence a particular chemical reaction, increase productivity and product yield.

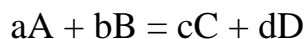
The section of chemical kinetics is also of great importance in pharmacy. The effect of various drugs is explained by the rate of reactions which occur in the body. In addition, various reactions may occur during storage of medicines. The rate of these reactions determines drug expiration dates.

Chemical kinetics consists of two sections:

- 1) formal kinetics-outputs a mathematical description of the reaction rate, ignoring the mechanism of the reaction itself.
- 2) molecular kinetics studies the mechanism of a chemical reaction.

The rate and the rate constant of the reaction

A chemical reaction that occurs in one stage is called an elementary reaction. Consider a simple reaction that occurs in a closed system:



a, b, c, d - stoichiometric coefficients.

In order to quantify describe the depth occurring of the reaction is entered the degree of transformation ζ . The degree of transformation, i.e. the depth occurring, is determined by the equation:

$$n_i = n_o + v_i \zeta$$

n_o - initial amount of reactants;

n_i – the amount of substance at some point in time from the beginning of the reaction

The rate of reaction is the change in the amount of a reactant or product per unit time and per unit of volume.

This definition of speed is correct if the system is missing in noticeable quantities and the volume of the system does not change. In this case, the concentration is expressed in mol/l, time – in seconds, minutes, etc. To calculate the reaction rate, we need to know how much the concentration of one of the reactant has changed per unit of time. For example, for a certain period of time $\Delta t = t_2 - t_1$ time the concentration of reactants decreases by $-\Delta C = C_1 - C_2$. Then the average reaction rate for a period of time Δt will be:

$$v = - \frac{\Delta C}{\Delta t}$$

The minus sign on the right side of the expression means that the concentration of reactant, and therefore the reaction rate also decreases.

The average rate does not reflect the real rate at each time, so it is defined as a derivative of the concentration of reactants over time at a constant volume of the system.

$$v = \pm \frac{dC}{dt}$$

If a change in the concentration of one of the starting substances is being studied $\frac{dC}{dt} < 0$, and if one of the reaction products $\frac{dC}{dt} > 0$. The reaction rate is always considered positive, and the ratio on the right side of the equation can be positive or negative. The nature of the reactants, temperature, concentration (pressure), catalyst, and other factors influence to the value of the chemical reaction rate.

According to the law of active masses, the rate of chemical reaction is proportional to the concentration of reactants:

$$v = kC_A^a C_B^b \quad (2)$$

k – constant of the reaction rate

C_A, C_B – concentration of reactants

Expression (2) is the main postulate of chemical kinetics.

If $C_A=C_B$, we can obtain $V = k$

This means that the rate constant is the reaction rate at a concentration of reactants equal to one. It, like the rate, depends on the nature of the reactants, temperature, and catalyst, but does not depend on the concentration.

The rate of various reactions are compared by known values of the rate constant K . sometimes K is also called the specific reaction rate. The higher the rate constant, the reaction goes faster.

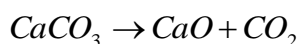
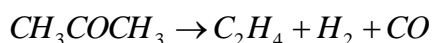
Chapter 2. Molecularity and the order of reaction

All kinetic reactions are classified by their molecularity and reaction order. The molecular nature of a reaction is determined by the number of molecules involved in the elementary act of chemical interaction. On the molecularity of the reaction are divided into three groups: monomolecular, bimolecular and trimolecular.

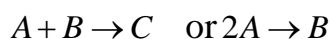
Monomolecular reactions are those in which one molecule participates in one elementary act. Schematically:



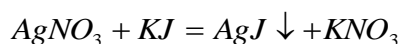
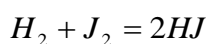
For example:



Bimolecular reactions are those in which two molecules participate in one elementary act. Schematically:

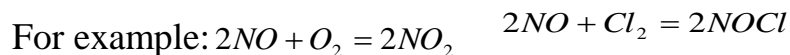
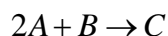


Examples:



Three molecules participate in one elementary act in trimolecular reactions.

Schematically:



Trimolecular reactions are quite rare. Reactions of higher molecular weight are generally unknown. When it follows from the chemical equation that a larger number of molecules participate in the reaction, the process actually occurs through a larger number of intermediate stages of mono - or double-molecular reactions.

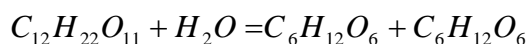
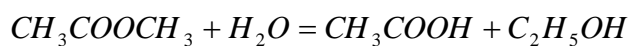
Each type of reaction has its own kinetic equation, which expresses the dependence of the chemical reaction rate on the concentration of reactants. The order of the reaction is determined by the sum of the degree indices at concentrations included in the kinetic equation of the chemical reaction rate. Depending on the rate of concentration, the reactions order are divided of first one ($V = kC$), second ($V = kC^2$) and third ($V = kC^3$), as well as zero and fractional order.

The reaction rate of the first order is proportional to the first degree of concentration. In second-and third-order reactions, the rate depends on the second and third degree of concentration, respectively. In general, for a type reaction:
 $aA + bB = cC + dD$ order $n = a + b$

Zero order is observed in reactions in which the rate does not depend on the concentration. Fractional order occurs in complex reactions that occur through intermediate stages.

The order of the reaction does not always coincide with its molecular structure. Only in the simplest cases is there a coincidence. There are two known reasons for the mismatch of order and molecularity:

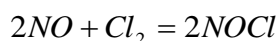
1) when the concentration of one or more participants in the reaction does not change, that is, they are constant. For example:



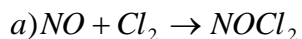
the water concentration is almost constant. Therefore, the reaction rate is

expressed by the equation $V = kC_{\text{reactant}} C_{\text{reactant}} = k' C_{\text{reactant}}$. The reaction is bimolecular, but it is the first order.

2) if the reaction occurs in stages. For example:



Trimolecular reaction, but occurs in two stages:



The first stage proceeds quickly, forming an unstable product. The second stage is slow. The reaction rate is expressed by the equation

$$V = kC_{NOCl_2} C_{NO}$$

The reaction is trimolecular, but it is the second order.

Thus, if the rate of individual stages vary considerably, then the reaction rate as a whole and its order are determined by the rate and order of the slowest stage.

Chapter 3. Kinetic equations of reactions. Methods for determining the reaction order

Chemical reactions are characterized by a kinetic equation and a half-life period. The time in which the concentration of the reactant is reduced to one-half of the initial value is known as the half-life of a reaction. Kinetic reaction equations allow us to calculate the rate constant at any time from its beginning.

Zero-order reactions. Since in the equations

$V = -dC/dt$; $V = k_0$ the left side denotes the reaction rate, then equate the right sides of the:

$$-\frac{dC}{dt} = k_0 \quad \text{integrating the resulting equality gives the equation}$$

$$C = -k_0 t + \text{const} \quad \text{on } t=0 \text{ и } C=C_0 \quad \text{const} = C_0 \quad \text{from here}$$

$$C = C_0 - k_0 t$$

$$k_0 = \frac{1}{t}(C_0 - C) \quad \text{unit of measurement } k_0 \quad \text{mole}^{-1}/\text{s}$$

First order reaction. The rate of first order reaction

$$V = -\frac{dC}{dt} = k_1 C \quad \text{equation can be write}$$

$$-\frac{dC}{C} = k_1 dt \quad \text{and integrating it}$$

$$-\ln C = k_1 t + \text{const} \quad \text{on } t=0 \quad C = C_o \quad \text{a } \text{const} = \ln C_o$$

Then $-\ln C = k_1 t + \ln C_o$ and kinetic equation

$$k_1 = \frac{1}{t} \ln \frac{C_o}{C} \quad \text{unit of measurement } s^{-1} \text{ or } \text{min}^{-1};$$

k_1 – the rate constant;

C_o – initial concentration;

C – concentration of the starting substance at time t from the start of the reaction.

Half-life for first order reaction

$$t_{1/2} = \frac{1}{k_1} \ln \frac{C_o}{C_o/2} = \frac{1}{k_1} \ln 2$$

It doesn't depend on initial concentration of reactants.

If the initial concentration of the substance is denoted by a , and the concentration of the reaction product by the time of x , the kinetic equation of the first-order reaction takes the form:

$$k = \frac{1}{t} \ln \frac{a}{a-x}$$

The reaction of the second order. The second-order reaction rate is determined by the equation $V = -\frac{dC}{dt} = k_{II} C_1 C_2$

C_1 and C_2 – concentration of reactants in the moment t . If concentration equals to $C_1 = C_2$ there $-\frac{dC}{dt} = k_{II} C^2$

$$-\frac{dC}{C^2} = k_{II} dt \quad \frac{1}{C} = k_{II} t + \text{const}$$

On $t=0 \quad C = C_o \quad \text{const} = 1/C_o \quad \text{when}$

$$\frac{1}{C} = k_{II} t + \frac{1}{C_o} \quad \text{and} \quad k_{II} = \frac{1}{t} \frac{C_o - C}{C_o C} \quad \text{unit of measurement of the rate constant for}$$

the second order reaction l/mole's.

Half-life $t_{1/2}$ for the first order reaction

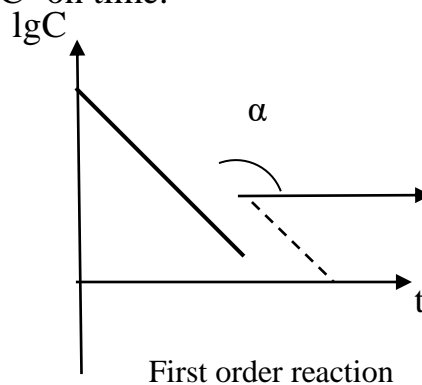
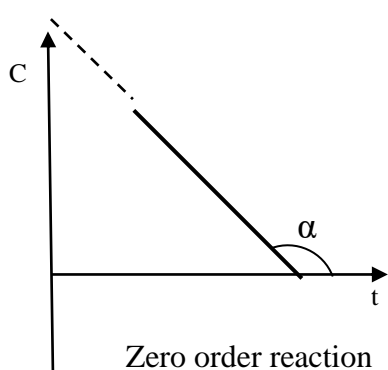
$$t_{1/2} = \frac{1}{k_{II}} \frac{C_o - 1/2C_o}{C_o 1/2C_o} = \frac{1}{k_{II} C_o}$$

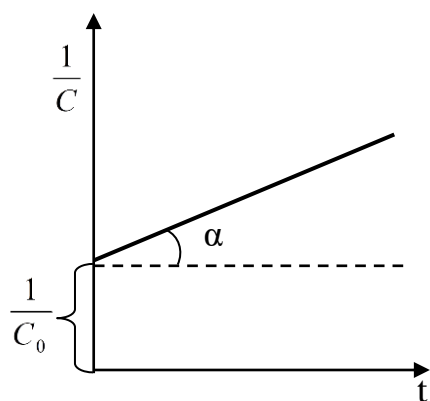
$t_{1/2}$ inversely proportional to the initial concentration of reactants. The higher the initial concentration, the less time it takes for half of the substance to react. If the initial concentrations of two substances are not the same and are equal to a and b, respectively, and the concentration of the reaction product is equal to x, then the second-order rate constant equation takes the form:

$$k = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

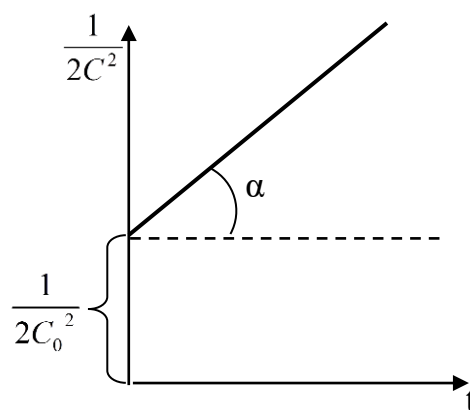
To find out the mechanism of the reaction, you need to determine its order. Distinguish between the private and general order of reaction. The order characterized by a change in the concentration of one of the reactants is a private order. The sum of private order gives the general order of the reaction. The reaction order is determined experimentally. There are four ways to process the results of an experiment. The substitution method. Determine the concentration of the substance at certain points from the beginning of the reaction. According to the obtained data, the rate constant is calculated using equations of the first, second, and third order. Find out what equation the calculation gives an almost constant value. The reaction under study follows this order.

Graphical method. Experimentally measuring the concentration of the substance at different time intervals from the beginning of the reaction, there are plot of graphs of the dependence of $\ln C$, $1/C$, $1/C^2$ on time.





Second order reaction



Third order reaction

Of that order will be the reaction where this relationship is straightline. By the half-life. The half-life for several initial concentrations is determined experimentally. Based on what relationship exists between them, determine the order of the reaction.

Example: at concentrations of the starting substance $C_0=0.2; 0.1; 0.05$, the half-life is $t_{1/2}=9,45; 18,9; 37,8$. The relationship is obvious from the results $t_{1/2}=1/C_0$. This dependence is for second-order reactions. Hence, a second-order reaction.

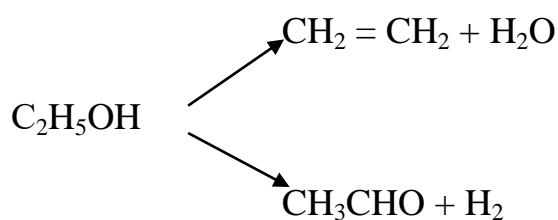
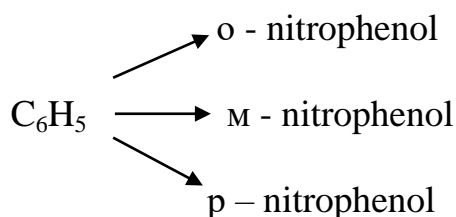
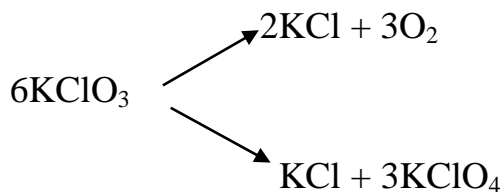
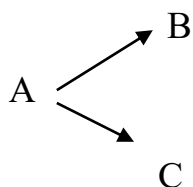
The method of Vant-Goff. The reaction rate is measured at two initial concentrations and the reaction order n is calculated using the formula:

$$n = \frac{\ln V_1 - \ln V_2}{\ln C_1 - \ln C_2}$$

Chapter 4. Simple and complex reactions

Reactions that occur in one stage are called simple. Reactions that consist of two or more simple reactions are called complex reactions. Complex reactions include reversible, parallel, sequential, conjugate, chain, and other reactions. In all of these reactions in the system at the same time there are several simple reactions. Each of these reactions is subject to the law of active masses. The molecular nature of these reactions is determined by the sum of stoichiometric coefficients, and the order is determined experimentally. Parallel reactions are called reactions in which the same starting substances, simultaneously reacting, form different products.

Examples:

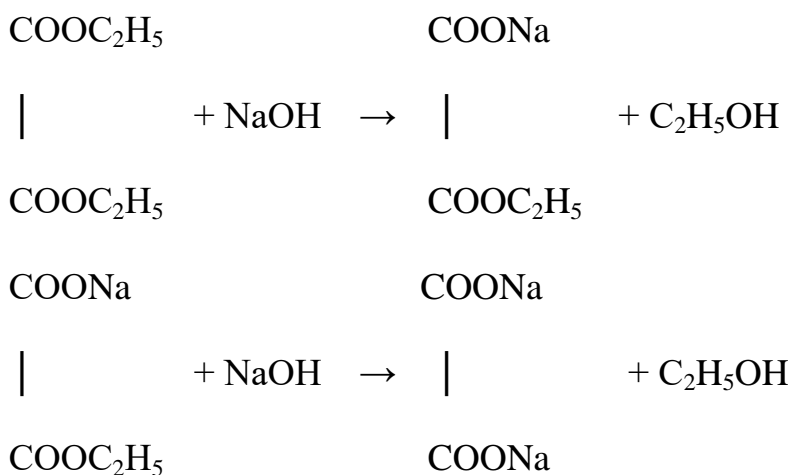


The rate of parallel reactions is determined by the sum of the rates of parallel reactions.

Sequential reactions are reactions that occur through a series of sequential stages in the scheme $A \rightarrow B \rightarrow C \rightarrow D$

Such reactions include hydrolysis of dicarboxylic acid esters, glycol esters or dihalogen derivatives, etc.

Example:



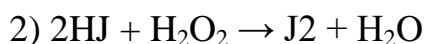
The rate of these reactions is determined by the rate of the slowest stage.

Conjugate reactions are called reactions that proceed according to the

scheme:

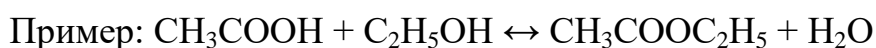
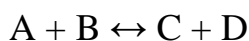


The first reaction can proceed independently. The second reaction occurs only if the first one is present. Example:



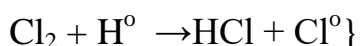
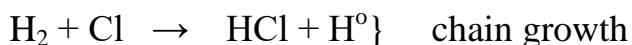
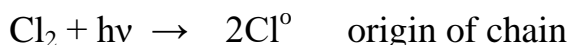
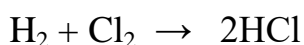
A (FeSO_4) – inductor, B (H_2O_2) – actor, C (HJ) – acceptor. This reaction were studied in 1905 by N.A.Schilov in detail:

Reversible reactions are those that occur simultaneously in both directions. The rate of these reactions is determined by the difference between the forward and reverse reaction rates:



Chain reactions occur in the presence of active particles with unsaturated free radicals. They occur in many stages. The rate of these reactions depends on the concentration of active centers, the length of the chains and the shape of the vessel, the light intensity, and the presence of impurities in the reaction mixture.

Chain reactions proceed until the disappearance of the active centers. Example:



Chapter 5. Kinetics of heterogeneous reactions

Heterogeneous processes are processes that occur at the interface of two phases. These reactions include oxidation of metals under the action of oxygen in the air, decomposition of substances on the electrodes during electrolysis, and others.

There are many heterogeneous processes in the pharmaceutical industry. Synthesis of medicinal substances such as phenamine, phenacetin, and benzammon is based on the reduction of solutions of aldehydes and ketones in a saturated alcohol solution of ammonia with hydrogen in the presence of a catalyst. Halogenated derivatives beclamide, oksazil, diazepam, and others get in the presence of solid catalysts iron, Nickel, copper.

All heterogeneous processes consist of 3 stages: 1) transfer of reactants to the phase interface, i.e. to the reaction zone; 2) chemical reaction; 3) removal of reaction products from the reaction zone.

The temperature and concentration of reactants can be adjusted so that the rate of the chemical reaction itself is greater than the rate of transfer of reactants and removal of products. This reaction condition is called the diffusion region, because the diffusion of substances is slow, the speed of the process is determined by the diffusion rate. If the transfer and removal rate is greater than the rate of the chemical reaction, this condition is called the kinetic region of the reaction. The speed of the process depends on the speed of the chemical reaction.

The rate of heterogeneous reactions is affected by mixing, increasing the interface and updating the phase composition.

During mixing, the concentration is equalized throughout the system, but not on the phase interface. Concentration equalization occurs due to diffusion through this layer.

The rate of heterogeneous reaction is quantitatively characterized by the equation: $V = \frac{dC}{dt} = kS(C_o - C)$

κ - solution coefficient; S - surface of phase part

$k = \frac{D}{\delta}$ D –diffusion coefficient; δ - the thickness of the diffuse layer.

Then: $V = \frac{D}{\delta} S dC$ $D = \frac{RT}{6\pi\eta r N_a}$

Increase the rate of heterogeneous reactions by increasing the phase interface. For example: recently, the "boiling layer" method has been used in the pharmaceutical and chemical industries. By this method, the gaseous reagent is passed under pressure through a layer of powdered reagent. The powder particles hang in the volume of the gaseous reagent, the surface increases and the reaction speed increases accordingly.

If the reaction proceeds in the kinetic region, the temperature increase leads to an increase of speed process, because with increasing temperature the rate of chemical reactions increases.

SECTION II. DEPENDENCE OF THE RATE OF REACTION ON TEMPERATURE. THE ENERGY ACTIVATION. DETERMINATION OF STORAGE OF DRUGS. CATALYSIS. THEORY WHICH EXPLAINS CATALYSTS ACTION

Chapter 6. Influence of temperature on the rate of chemical reaction

The rate of a chemical reaction usually increases with increasing temperature. At the same time, with increasing temperature, the value of the velocity constant K increases, therefore, the reaction rate itself increases. This type of temperature dependence of the speed is called normal. This type of dependency is typical for all simple reactions. Currently, well-known reactions, the speed of which decreases with increasing temperature. An example is the reaction of nitrogen (II)-oxide with bromine $2\text{NO} + \text{Br}_2 = 2\text{NOBr}$. This type of temperature dependence of the rate is called anomalous.

The rate of enzymatic reactions occurring in the body, with increasing temperature, first increases, then falls. For example, the rate of decomposition of hydrogen peroxide in the presence of the enzyme catalase in the range 273-320K increases. When the temperature rises above 320, there the rate is a sharp decrease. This pattern is also observed for other enzymatic reactions (Fig.6.1.).

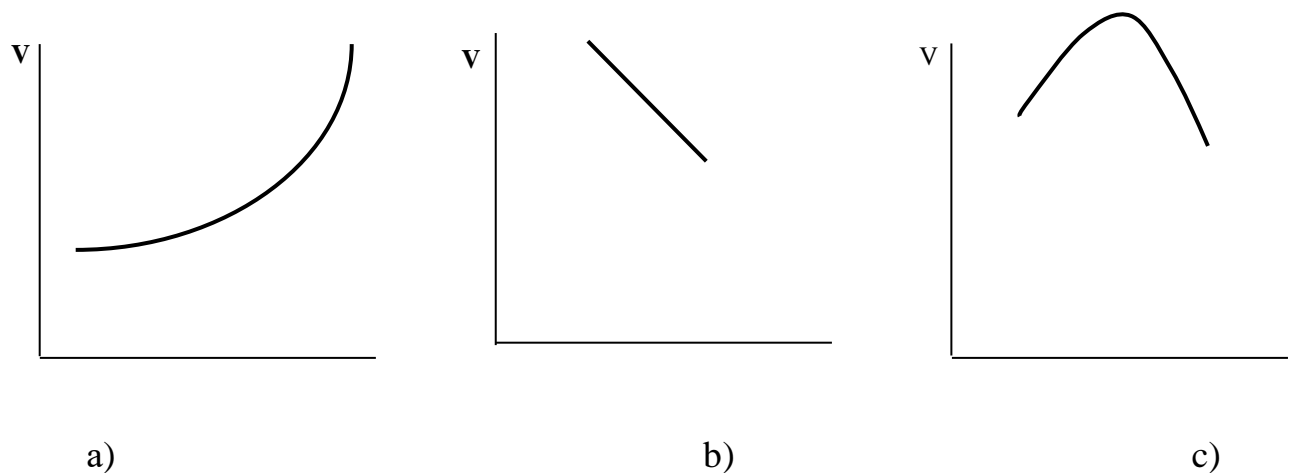


Fig.6.1. Reaction rate dependence on temperature: a) normal dependence; b) the anomalous dependence; c) in enzymatic reactions

For some reactions, this anomaly of temperature dependence is detected even at a temperature below 273.

Consider the reaction with the normal temperature dependence.

If the rate constant of this reaction at temperature T is denoted by k_T , and the constant at (T+10) by k_{T+10} , the ratio of the second value to the first gives the temperature coefficient of the reaction γ :

$$\gamma = \frac{k_{T+10}}{k_T}$$

According to the Van't Hoff empirical rule: in homogeneous reactions, when the temperature increases by 10 K, the rate of the chemical reaction increases by two to four times. And so the value of the temperature coefficient γ varies between 2-4. For example, if the temperature coefficient γ is equal to two, it can be calculated that when the temperature increases by 100K, the reaction rate will increase by 1024 times, i.e. in General, the temperature coefficient formula:

$$\gamma^n = \frac{k_{T+n10}}{k_T} \quad \gamma = 2 \quad n = 10$$

$$\gamma^n = 2^{10} = 1024$$

According to the Van't-Goff rule, the temperature coefficient of velocity for

each reaction must be a constant value. However, in reality, it is greatly reduced when the temperature increases.

Based on the Van't-Goff rule, a "method for accelerated aging of the dosage form" was developed to determine its shelf life. Increasing the temperature increases the rate of decomposition of the drug by 10 times or more compared to its value at room temperature. This reduces the time to establish the shelf life of medicines and makes it possible to determine the optimal storage temperature.

Determining the shelf life of the dosage form by this method, it is kept in drying cabinets at an elevated temperature T for a certain time t_T . Determine the amount of decomposed drug m and recalculate to a standard temperature of 298 K. the decomposition Process is a first-order reaction. Speed at the selected temperature T and standard 298K:

$$v_T = k_T C_o \quad v_{298} = k_{298} C_o \quad \text{here}$$

$$\frac{v_T}{v_{298}} = \frac{k_T}{k_{298}} \quad (1)$$

Consider the same mass of decomposed drug for standard and real storage conditions, determine the rate of decomposition by equalities: $v_T = \frac{m}{t_T}$ $v_{298} = \frac{m}{t_{298}}$

here $\frac{v_T}{v_{298}} = \frac{t_{298}}{t_T} \quad (2)$

From (1) and (2) get $t_{298} = \frac{k_T}{k_{298}} t_T$

The real temperature is applied $T = 298 + 10n$ $n = 1, 2, 3$ and others

$$\frac{k_{298+10}}{k_{298}} = 2 \quad (3)$$

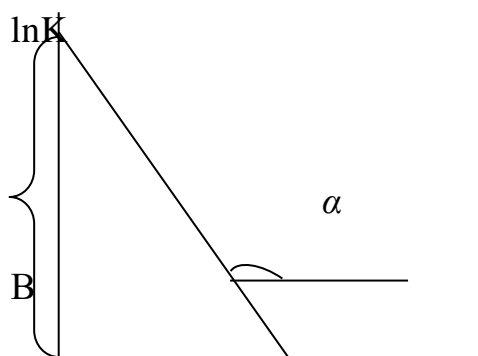
Get the final value of the shelf life under standard conditions 298K $t_{298} = 2^n t_T \quad (4)$

More accuracy of dependence rate constant on temperature was found by Arrhenius $\ln k = B - \frac{A}{T} \quad (5)$ where, k - chemical reaction rate constant

A, B - empirical constant. Their values can be found in the dependency

graph $\ln k = f(1/T)$

The segment intersected by a straight line on the ordinate axis is equal to B, and the tangent of the angle of inclination of the straight line $\operatorname{tg} \alpha = -A$



The Arrhenius equation gives the dependence of the rate constant of a chemical reaction on the absolute temperature, a pre-exponential factor and other constants of the reaction

$$k = z_0 e^{-E/RT} \quad (6)$$

K – the rate constant (frequency of collisions resulting in a reaction)

z_0 – pre-exponential factor

e - base of the natural logarithm

E - activation energy

R - universal gas constant

T – absolute temperature (in kelvins)

Active collision theory

The theory of chemical kinetics is based on two theories applicable to both catalytic and non-catalytic reactions. This is a theory of active collisions (TAC) and the theory of the active complex (TAC).

The theory of active collisions is derived from the kinetic model of gases. Let's consider the basics of the theory of active collisions on the example of a bimolecular gas reaction.

A chemical reaction requires a collision of molecules. Each collision in the theory of active collisions is considered as a single act of interaction or

transformation of particles, which results in the formation of new particles of reaction products or intermediate compounds. This theory assumes that not all collisions lead to interaction.

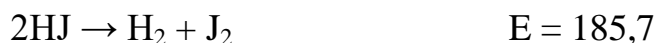
For example: in 1 kmol HJ, located in a volume of 1m^3 at 10^5 PA and 556 K, there are approximately $5,5 \times 10^{37}$ collisions per 1 second. And the amount of iodine that is formed over the same period of time shows that only one collision out of 2×10^{17} possible, accompanied by a chemical reaction: $\text{HJ} + \text{HJ} = \text{H}_2 + \text{J}_2$

The collision may not be effective for two reasons: 1) the collision is not energetic enough to activate the molecules; 2) the colliding molecules come together so that they cannot react with each other.

For an effective collision of particles, they must come together at a distance at which the electrons and atoms of one molecule will fall into the environment of the action of the electric forces of the extension of another or other molecules. But attraction is preceded by repulsion. Only those molecules and atoms that have enough energy can collide effectively. In addition, the formation of a new state requires the destruction of the old one, which is obviously also associated with energy costs. This means that the reaction rate depends not only on the number of collisions, but also on some property of the colliding molecules. Arrhenius explained this phenomenon in his theory of active collisions.

According to this theory, only those molecules that have the energy reserve necessary for a particular reaction to occur, i.e., excess energy compared to the average value of the molecule's energy, are reactive. These molecules are called active molecules. This excess energy of the molecule, due to which the chemical reaction occurs, is called the activation energy. The activation energy is the minimum excess energy compared to the average energy of the reacting substances, which is necessary for the chemical reaction to take place. This energy is expressed in kJ/mol. It is less than the energy of breaking bonds in the molecule, since in order to react, a complete break of bonds is not required, they only need to be weakened.

The amount of activation energy depends on the structure of the molecule and the reaction it enters into. That is, each chemical reaction is characterized by its own amount of activation energy. We give the activation energy values for some reactions in kJ/mol:



The activation energy of molecules can be reduced under the influence of external factors: temperature rise, radiant energy, catalysts, etc. the figure shows the activation energy of the reaction.

On the ordinate axis, the energy of the system's molecules is deposited, and on the abscissa axis, the course of the reaction. If the transition of the system from state I to state II occurs with the release of heat, i.e. the process is exothermic, then the total energy reserve of the products is less than the initial products. The energy difference of state I and II is equal to the thermal effect of the ΔH reaction. The energy level K describes the least amount of energy that the molecules must have in order to react when they collide (Fig.6.2.).

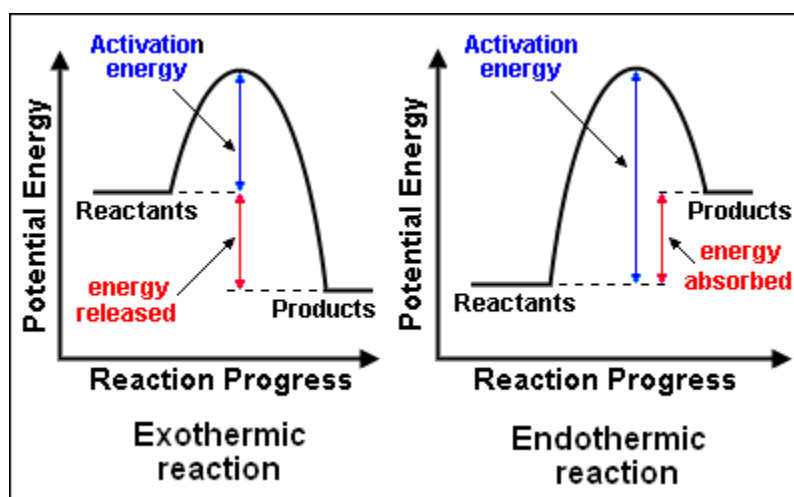


Fig.6.2. Energy level diagram of exothermic and endothermic reaction

During the transition from state I to state II, the system must overcome the energy barrier, i.e. it must have a certain excess of energy to enter into chemical interaction.

The rate of a chemical reaction depends on the amount of activation energy: the higher it is, the slower the reaction will proceed, the lower the energy barrier, the less excess energy and the faster the reaction speed.

The theory of the active complex

The theory of chemical kinetics is based on two theories. One is applied to catalytic reactions, the other is applied to non-catalytic reactions. This is a theory of active collisions (TAC) and the theory of the active complex.

Active collision theory is used for non-catalytic reactions. It is proposed based on the molecular kinetic theory. According to this theory, a chemical reaction requires collisions of molecules. Each collision is considered as a single act of interaction or transformation of particles, resulting in new particles of reaction products or intermediate compounds. The calculated speed constant is much larger than the experimentally found rate constant.

The rate of a chemical reaction ultimately depends on the ratio between the number of active and inactive molecules. The number of active molecules can be calculated using the Maxwell-Boltzmann law:

$$N_a = N_o e^{-E/RT} \quad (7)$$

где, N_a - number of active molecule; N_o - number of total molecule;

e - base of natural logarithm;

R - universal gas constant;

T - absolute temperature.

The equation can be written as: $k = k_o e^{-E/RT}$ (8)

or after taking the logarithm:

$$\ln k = \ln k_o e^{-E/RT} \quad (9)$$

k - the rate constant under normal conditions;

k_o - the rate constant provided that all collisions lead to a reaction.

If we compare equations (5) and (9), we can find out the physical meaning of the Arrhenius equation constants. $A = E/R$ characterizes the activation energy $B = \ln k_0$ i.e. it is equal to the logarithm of the number of collisions per 1 second per unit volume.

If the velocity constants k_1 and k_2 are known at two temperatures T_1 and T_2 , you can find the value E from equation (9):

$$\ln \frac{k_{T_2}}{k_{T_1}} = \frac{E}{T} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{или} \quad \lg k \frac{k_{T_2}}{k_{T_1}} = \frac{E}{2,303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\text{Where: } E = \frac{\lg \frac{k_2}{k_1}}{T_2 - T_1} 2,303.R.T_1.T_2$$

Chapter 7. Homogeneous and heterogeneous catalysis

The rate of the chemical reaction can be controlled using a catalyst. A substance that changes the rate of a chemical reaction and remains in a chemically unchanged state and quantity after the reaction is called a catalyst. The change in the rate of a chemical reaction in the presence of a catalyst is called catalysis.

Catalysts can be a wide variety of substances in any of the three aggregate States: acids, salts, bases, metals, various organic and organomineral compounds, and gaseous substances. In some cases, various impurities have a catalytic effect. For example: dust, the surface of the vessel walls, and reaction products.

Regularities of catalysis:

1. The catalyst is actively involved in the elementary act of reaction. It forms an intermediate compound with one of the reaction participants due to chemical bonds or electrostatic interaction. After each chemical act, he is regenerated and enters into interaction with the new molecules of the reacting substances.

2. The participation of the catalyst does not affect its stoichiometric equation.

3. The catalyst has a selective action, i.e. it can change the speed of one reaction and does not affect the rate of another

4. The catalyst lowers the activation energy.

5. The catalyst does not affect the value of the equilibrium constant, i.e. it changes the rate constants of the forward and reverse reaction to the same extent.

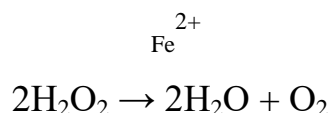
6. With the addition of promoters, the activity of the catalyst increases; the addition of inhibitors reduces the reaction rate.

There are two types of catalysis: 1) positive, when the reaction rate increases; 2) negative, when the reaction rate decreases.

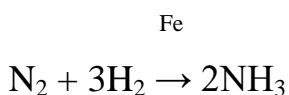
Reactions whose speed changes under the action of the product are called autocatalytic, and the process itself is called autocatalysis.

All catalytic reactions are divided into homogeneous and heterogeneous.

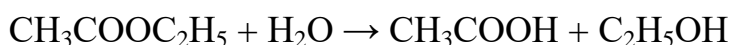
If the reactants and the catalyst are in the same phase, the catalysis is called homogeneous. Example: decomposition of hydrogen peroxide in the presence of Fe (II) salts in aqueous solutions. The solution of hydrogen peroxide in the absence of impurities persists for a long time without decomposition. However, when a small amount of solution is added, FeSO_4 results in an intense release of oxygen:



If the reactants and the catalyst are in different phases, the catalysis is called heterogeneous. Example:



An example of an autocatalytic reaction is saponification of acetic ethyl ether in a neutral medium:



In that reaction, the catalyst is acetic acid, or rather hydrogen ions.

In homogeneous catalysis, the mechanism of action of the catalyst is explained by the formation of intermediate compounds. In general, this can be

represented as follows:



Catalyst forms non-stable intermediate compound of AK. The rate of this reaction depends on how quickly this compound is formed and decomposed.

In heterogeneous catalysis, most often the catalyst is a solid, and the reacting substances are in a liquid or gaseous state. In this case, the reaction occurs on the interface of the two phases, i.e. on the surface of the catalyst. To explain the mechanism of heterogeneous catalysis, there are two positions:

1) catalysis is associated with the adsorption of reactants on the surface of the catalyst.

2) the catalytic reaction involves not the entire surface of the catalyst, but individual areas called active centers.

Currently, there are a number of theories that explain the mechanism of heterogeneous catalysis.

The multiplet theory of A.A. Balandin. The theory is based on the structural correspondence between the arrangement of atoms on the active sites of the catalyst surface and the structure of molecules of reacting substances. According to this theory, the active centers on the surface of the catalyst are separate sections – multiplets of the crystal lattice of the catalyst. A molecule of the reacting substance is adsorbed to sit on such a multiplet so that its different groups are bound by different atoms of the multiplet. In this case, the bonds of the adsorbed molecule are deformed, with increasing distance, the chemical bonds become loose and can easily break and interact faster.

Theory of active ensembles. According to this theory, amorphous formations of several atoms on the catalytic inactive surface of the carrier have catalytic activity. These atoms gather in small groups-ensembles of 2-3 atoms, forming active centers.

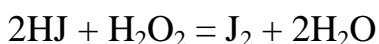
For example, in the synthesis of ammonia, iron applied to coal, asbestos, or alumogel is used as a catalyst. On the surface of the carrier, ensembles of several

iron atoms are formed. For the synthesis of ammonia, ensembles of three atoms are necessary. According to the theory of ensembles, iron atoms move freely on the surface of the carrier. The activity of the catalyst is determined by the number of ensembles and their mutual location.

Laboratory work 1.

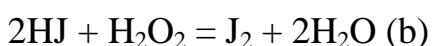
Determination of hydrogen iodide with hydrogen peroxide by the rate of constant of oxidation reaction.

Task: determine the reaction rate constant:



Equipment and reagents : 200 conical flask, burette 25 ml, 0,4% NaJ, 1 mole/l H_2SO_4 , 0,025 mole/l $\text{Na}_2\text{S}_2\text{O}_3$, 0,5% starch solution.

Theoretical explanation. The following processes occur:



The rate of this reaction depends on the concentration of hydrogen peroxide. The change in its concentration is determined by the equivalent amount of released iodine, which is titrated with a solution of sodium thiosulfate. Reactions (a) and (c) proceed instantly, so the speed of the total process is determined by the rate of a slower reaction (b).

Since sodium iodide is regenerated during the titration of iodine with sodium thiosulfate, the concentration of Na and HI are practically constant and, therefore, reaction rate (b) is determined only by the concentration of H_2O_2 .

The oxidation of iodic acid with hydrogen peroxide proceeds according to the kinetic equation of the first order reaction.

The kinetic equation of the first order reaction:

$$k = \frac{2,303}{t} \lg \frac{a}{a-x}$$

Work performance: 25 ml of a solution of 0.4% NaJ solution and 2.5 ml of a H_2SO_4 solution with a concentration of 1 mol/l are poured into a 200 ml conical flask.

A burette with a capacity of 25 ml is filled with a solution of $\text{Na}_2\text{S}_3\text{O}_3$ with a concentration of 0.025 mol/l.

Add 1 ml of $\text{Na}_2\text{S}_3\text{O}_3$ solution and 5 drops of 0.5% starch solution to the flask with the solution from the burette. Then 5 ml of a H_2O_2 solution are added and the mixture is stirred. When blue staining appears, turn on the stopwatch and mark the time. This is considered the beginning of the reaction (t_0). 0.5 ml of $\text{Na}_2\text{S}_3\text{O}_3$ are quickly added from the burette, the solution is stirred. The color of the solution disappears. After some time, a blue color appears again and the stopwatch is recorded (t_1). Without turning off the stopwatch, the operation of adding a 0.5 ml $\text{Na}_2\text{S}_3\text{O}_3$ solution is repeated 5 more times and each time the stopwatch is recorded. 1-2 drops of a solution of ammonium molybdate are added to the reaction mixture to quickly bring the reaction to completion. The liberated iodine is titrated with thiosulfate from the same burette until the solution becomes discolored. The total volume of sodium thiosulfate consumed is equivalent to the volume taken up of the H_2O_2 solution to complete the reaction.

The data obtained are entered into the table and the reaction constant for each time is calculated according to the above formula. The average value of the rate constant is calculated.

No	Volume of $\text{Na}_2\text{S}_2\text{O}_3$ which is added at this moment, ml	Volume of $\text{Na}_2\text{S}_2\text{O}_3$ which is added at this moment of stain, ml	The time of every stain, t in sec	k c^{-1}
1.				
2.				
3.				
4.				
5.				

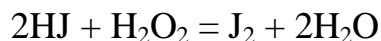
The half-life of the reaction is calculated from:

$$t_{1/2} = \frac{2,303}{k} \lg 2$$

Laboratory work 2

Determination of hydrogen iodide with hydrogen peroxide by the rate of constant of oxidation reaction

Work aim: to determine of activation energy of reaction:



Equipment and reagents: 200 ml of conical flask, burette 25 ml, 0,4% NaJ, 1 mole/l H_2SO_4 , 0,025 mole/l $\text{Na}_2\text{S}_2\text{O}_3$, 0,5% starch solution.

Work procedure: The test reaction is carried out in a thermostat at a temperature 10°C higher than the room temperature. First, calculate the speed constant at T_2 and calculate the activation energy.

$$\lg \frac{k_2}{k_1} = \frac{E_a(T_2 - T_1)}{2,303RT_1T_2}$$
$$E_a = \frac{2,303 \lg \frac{k_2}{k_1} RT_1T_2}{(T_2 - T_1)}$$

k_1 – reaction rate constant on T_1

k_2 – reaction rate constant on T_2

SECTION III. SURFACE PHENOMENA. THE CONCEPTS - SORPTION, ADSORPTION, ABSORPTION AND CHEMISORPTION. ADSORPTION ON A SOLID SURFACE. FREUNDLICH AND LANGMUIR EQUATIONS. ADSORPTION ON THE SURFACE OF A LIQUID.

ADSORPTION EQUATIONS.

The phenomena that are observed in dispersed systems at the phase boundaries are called surface phenomena. These include surface energy, adsorption, wetting, flotation, spreading, adhesion, cohesion, etc. All surfaces of the section are divided into two classes depending on the state of aggregation of the boundary phases:

1. Moving surface between liquid and gas (l – g) and two immiscible liquids (g – g);
2. Non-moving surface between solid and gas (s – g), solid and liquid (s – l),

solid and solid (s – s).

The cause of the surface phenomena is the special state of the molecules directly adjacent to the interfaces. These layers differ sharply in many physicochemical characteristics (specific energy, density, specific electrical conductivity, viscosity, etc.) from the properties of the phases in the bulk. In solutions, the composition of the surface layer, as a rule, does not coincide with the composition of the volume. Features of the surface layers due to the presence of surface energy. The greater the specific surface areas of the system, the more strongly surface phenomena are observed.

The study of surface phenomena is necessary for the development of many areas of science and practice. Surface phenomena are of great importance for pharmacy. Most dosage forms are dispersed systems with a large specific surface: powders, tablets, suspensions, emulsions, ointments, etc. In the production of these dosage forms, the development of rational technology, stabilization, storage, prolongation of action requires research in the field of physical chemistry of surface phenomena.

Chapter 8. Surface energy. Surface tension

Solids and liquids have interfaces with adjacent phases. The states of the molecules on the surface layer and in the volume are not the same. The surface of a solid and a liquid has an excess of Gibbs energy. This is due to incomplete compensation of the intermolecular attractive forces of the surface layer molecules, due to the fact that their weak interaction.

Surface energy is by nature a potential energy and according to the second law, thermodynamics tends to a minimum. One of the phenomena that leads to a decrease in surface energy is adsorption.

Chapter 9. Sorption processes

The process of absorption of gases or solutes by a solid material or liquid is called sorption. Sorbent: a usually solid substance that adsorbs another substance and sorbate: an adsorbed substance.

There are 4 main types of sorption: absorption, adsorption, chemisorption and capillary condensation.

Absorption. It is a process by which a substance incorporated in one state is transferred into another substance of a different state (e.g., gases being absorbed by a liquid or liquids being absorbed by a solid). During absorption, the gas molecules penetrate into the mass of the sorbent and a solid or liquid solution is formed. Gas absorption occurs due to diffusion. The diffusion rate in solids is small and absorption in them proceeds very slowly and after a considerable time equilibrium is established. An increase in temperature accelerates absorption. An example of absorption can be: absorption of hydrogen by palladium, absorption of CO₂ and NH₃ by water.

Adsorption. Adsorption is the deposition of molecular species onto the surface. It differs from absorption which is a physical or chemical phenomenon in which atoms, molecules or ions enter some bulk phase. Adsorbent: a usually solid substance that adsorbs another substance and adsorbate: an adsorbed substance. Activated charcoal is carbon that has been treated with oxygen. The treatment results in a highly porous charcoal. These tiny holes give the charcoal a surface area of 300-2,000 m²/g, allowing liquids or gases to pass through the charcoal and interact with the exposed carbon. The carbon adsorbs a wide range of impurities and contaminants, including chlorine, odors, and pigments. Other substances, like sodium, fluoride, and nitrates, are not as attracted to the carbon and are not filtered out. Because adsorption works by chemically binding the impurities to the carbon, the active sites in the charcoal eventually become filled. Activated charcoal filters become less effective with use and have to be recharged or replaced. Adsorption is a purely surface phenomenon in which the molecules or ions of the adsorbate interact with the surface of the adsorbent due to van der Waals forces, hydrogen bonds, electrostatic forces. The adsorbed gas on the surface of the solid adsorbent can form one layer and or several layers. When adsorption occurs in a single layer, it is called monomolecular adsorption, when several layers are polymolecular

adsorption. The degree of adsorption depends on the nature of the adsorbent and adsorbate, temperature, gas pressure, concentration, and the specific surface of the adsorbent.

Polar adsorbents had better adsorb polar adsorbates, non-polar adsorbents non-polar adsorbates. Activated charcoal adsorbs benzene well; silica gel better adsorbs water, amines, and alcohols.

Increasing the temperature reduces the adsorption of gases. This is explained from the molecular-kinetic point of view with an increase in the thermal motion of the adsorbate molecules.

Adsorption is characterized by a graph of the dependence of the amount of absorbed substance on the gas pressure or on the concentration of the solution at $T = \text{const}$ (Fig.9.1.) .

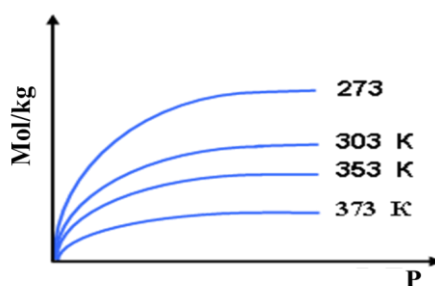


Fig.9.1. The graph of the dependence of adsorption on temperature

Increasing the pressure or concentration of the adsorbate leads to an increase in adsorption. In this case, the adsorption increases to a certain value, and then becomes constant. This value of adsorption is called the ultimate adsorption of G_{∞} .

Adsorption is a reversible process. During adsorption along with absorption, the adsorbate leaves the adsorbent surface. The release of adsorbate from the surface is called desorption. First, the rate of adsorption will be more. Over time, the rate of adsorption and desorption level off, and the system will establish adsorption-desorption equilibrium. Adsorption is accompanied with the release of heat, desorption with the absorption of heat.

Chemisorption. In chemisorption (an abbreviation of ‘chemical adsorption’), the molecules (or atoms) stick to the surface by forming a chemical

(usually covalent) bond, and tend to find sites that maximize their coordination number with the substrate. Chemisorption is a kind of adsorption which involves a chemical reaction between the surface and the adsorbate. New chemical bonds are generated at the adsorbent surface. An important example of chemisorption is in heterogeneous catalysis which involves molecules reacting with each other via the formation of chemisorbed intermediates. After the chemisorbed species combine (by forming bonds with each other) the product desorbs from the surface.

Sometimes chemisorption involves not only molecules that are on the surface of the adsorbent, but also molecules that are in the volume of the adsorbent. In this case, the resulting chemical compound forms a new phase. For example: the absorption of CO_2 by CaO leads to the formation of CaCO_3 . Physical adsorption involves the forces of molecular interaction which embrace permanent dipole, induced dipole, and quadrupole attraction. For this reason it is often termed van der Waals adsorption. Chemisorption, on the other hand, involves the rearrangement of the electrons of the interacting gas and solid, with consequential formation and rupture of chemical bonds. Physical adsorption is characterized by enthalpy changes that are small, typically in the range -10 to -40 kJ mol^{-1} (heats of adsorption of 10 - 40 kJ mol^{-1}), whereas heats of chemisorption are rarely less than 80 kJ mol^{-1} and often exceed 400 kJ mol^{-1} .

Capillary condensation: Capillary condensation is the "process by which multilayer adsorption from the vapor into a porous medium proceeds to the point at which pore spaces become filled with condensed liquid from the vapor. The unique aspect of capillary condensation is that vapor condensation occurs below the saturation vapor pressure, P_{sat} , of the pure liquid. This result is due to an increased number of van der Waals interactions between vapor phase molecules inside the confined space of a capillary. Once condensation has occurred, a meniscus immediately forms at the liquid-vapor interface which allows for equilibrium below the saturation vapor pressure. The process runs at high speed and ends within a few minutes.

Chapter 10. Adsorption on solid surface

At the end of the XVIII century, the Swedish chemist and pharmacist Carl Wilhelm Scheele (1742-1786) and the Italian prof. F. Fontana (1730-1805) independently discovered the phenomenon of adsorption. Fontana discovered that svezheprokalenny charcoal absorbs various gases, in volumes far exceeding its own volume. C.W. Scheele found that this process is reversible. When conditions change, the absorbed gas can be released.

All natural and artificial materials can be solid adsorbents, as they have a greater outer and inner surface. Adsorption of gases or solutes from solutions occurs on these surfaces. Examples of solid porous adsorbents are activated carbon, silica gel, aluminum gel, etc. Any solid surface has an excess supply of Gibbs surface energy. The greater the specific surface, the more Gibbs energy.

Adsorption due to the forces acting on the surface of the adsorbent. The force fields of the particles of the adsorbent located on the surface are partially compensated. Therefore, forces that can attract molecules of substances in contact with the surface of the adsorbent act on the surface of the adsorbent. Depending on the intensity of the force field, adsorption layers are formed on the surface of the adsorbent with a thickness of one molecule (monomolecular adsorption) or several molecules (multimolecular adsorption). The amount of adsorbed gas can be determined by increasing the mass of the adsorbent, as well as by reducing the pressure of the adsorbate. Gas adsorption on a solid is measured by the amount of gas adsorbed by a unit of surface or solid mass. (mol/sm², or mol/g)

$$A = \frac{x}{S} \quad \text{or} \quad A = \frac{x}{m}$$

A – specific adsorption;

x – amount of adsorbate;

S – surface of adsorbent;

m – mass of adsorbent.

Adsorption depends on the pressure (concentration) of the adsorbate. With

increasing pressure (concentration), adsorption increases to a certain limiting value A_∞ . The adsorption isotherm consists of three sections (Fig.10.1.):

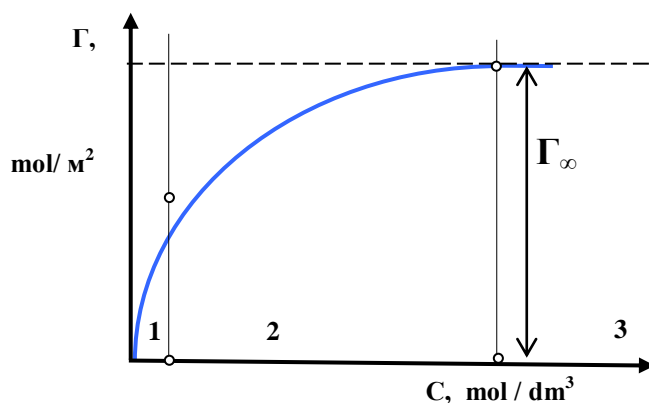


Fig.10.1. Isotherm of adsorption

The adsorption of gases on solid adsorbents is an exothermic process, i.e. accompanied by the release of heat. The reverse process - desorption is an endothermic process, i.e. accompanied by the absorption of heat. Therefore, with increasing temperature, the adsorption of gases by solid adsorbents decreases.

As can be seen from the graph for gases, solutions of non-electrolytes and weak electrolytes, the adsorption isotherm has the form of a parabola. The average plot curve for medium pressures and concentrations is expressed by Freundlich's

empirical equation: $\frac{x}{m} = KP^{1/n}$ or $\frac{x}{m} = KC^{1/n}$

P and C – balanced pressure and concentration of adsorbate;

K and $1/n$ - const.

The value of K depends on the nature of the adsorbent and adsorbate, as well as on temperature. $1/n$ adsorption index, its values lie in the range of 0.1 - 1 and depends on the nature of the adsorbent and adsorbate. With increasing temperature, K decreases and $1/n$ increases.

To find the values of the Freundlich equation, its logarithm:
 $\lg x/m = \lg K + 1/n \lg C$

This equation represents a line and it allows you to define graphically the constants of the equation K and $1/n$ (Fig.10.2.):

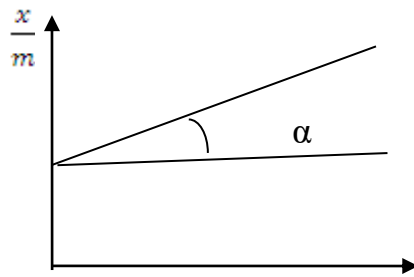


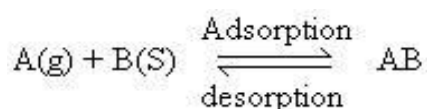
Fig.10.2.Graphical determination of Freundlich equation constant

The Freundlich equation is applicable only for medium pressures and concentrations. For low and high pressures and concentrations it is not applicable. For low and high pressures and concentrations in 1915, I. Langmuir proposed the monomolecular theory of adsorption.

In 1916, Irving Langmuir proposed another Adsorption Isotherm which explained the variation of Adsorption with pressure. Based on his theory, he derived Langmuir Equation which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure.

Assumptions of Langmuir Isotherm. Langmuir proposed his theory by making following assumptions:

1. Fixed number of vacant or adsorption sites are available on the surface of solid.
2. All the vacant sites are of equal size and shape on the surface of adsorbent.
3. Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is released during this process.
4. Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.



Where A (g) is unadsorbed gaseous molecule, B(s) is unoccupied metal surface and AB is Adsorbed gaseous molecule.

5. Adsorption is monolayer or unilayer.

Limitation of Langmuir theory:

(a) Langmuir's theory of unimolecular adsorption is valid only at low pressures and high temperatures.

(b) When the pressure is increased or temperature is lowered, additional layers are formed. This has led to the modern concept of multilayer adsorption.

Chapter 11. Adsorption at the liquid gas interface

The adsorption on the interface of the f-g is determined by the change in the surface tension of the liquid. The surface tension of various liquids depends on the nature of the liquid, its temperature, pressure and concentration of solutes. Dissolved substances can increase, decrease and practically not affect the surface tension of liquids. When a substance is dissolved in a liquid, the following cases are observed:

1. The solute reduces the surface tension of the solvent. Such substances are called surface-active (surfactant). With respect to water, surfactants are many organic compounds, for example, alcohols and aliphatic acids, esters, proteins, etc.

2. The solute increases the surface tension of the solvent. Such substances are called surface-inactive. In relation to water, inorganic acids, bases, salts and organic compounds such as glycerin, α -amino acids, etc. are surface-inactive substances.

3. The solute practically does not change the surface tension of the solvent. Surface-nonactive with respect to water substances are mono-, di - and polysaccharides.

Surfactants accumulate on the surface of the liquid. The concentration of surfactant on the surface will be greater than the concentration in volume. This is called positive adsorption. Surface-inactive substances dissolve in the volume of liquid. The concentration of these substances in the volume will be greater than on the surface. This is called negative adsorption. When dissolving surfactants inactive substances, the concentration of NVD will be the same on the surface and in volume. Surface activity mainly depends on the chemical structure of substances: the nature of the polar and the structure of the non-polar part. When

organic fatty acids are dissolved in water, the surface tension of the water is much lower. G. Duclos and P. Traube found that the stronger the polar asymmetry of the molecule, the greater the surface activity of the compound and formulated the following rule (Fig.11.1.):

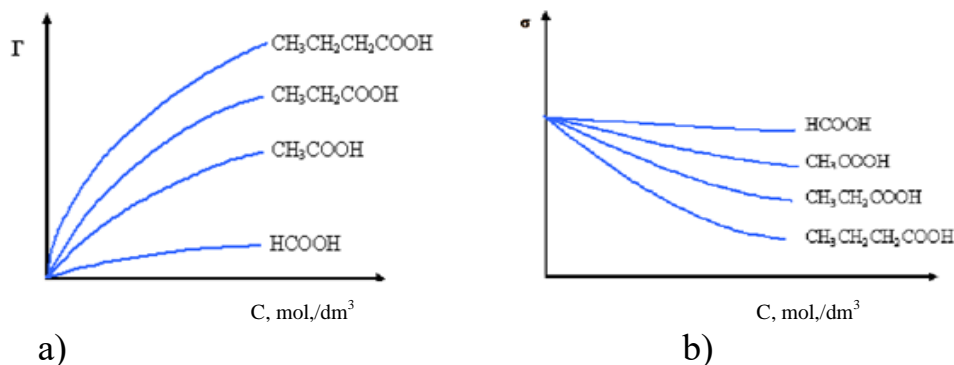


Fig.11.1. Isotherm of surface tension (a) and adsorption (b) homologous raw of fatty acids

The Duclos-Traube rule is used for diluted solutions only. The surface tension equally decreases in saturated solutions, independent of which compound.

Chapter 12. Polymolecular adsorption

Langmuir's theory explains that adsorption forces act at a distance of the size of a single molecule and a monomolecular adsorption layer is formed. But studies have shown that sometimes adsorption forces act at a great distance, and a polymolecular adsorption layer is formed.

Adsorption theory of the volume filling of micropores TVFM theory has been proposed by Dubinin and Radushkevich, but this approach has originated from the potential theory of adsorption introduced by Eucken and Polanyi. However, Dubinin in contrast to Polanyi who defined the differential molar work of adsorption A as the adsorption potential introduced the adsorption potential as the negative work performed by the sorption system which is $A = G$, giving thus opportunity to open gate to thermodynamics. According to their concept, the adsorbed layer has a multilayer character, therefore it is not two-dimensional as follows from the Langmuir theory, but it possesses a definite volume and applies to the van der Waals equation. The assumptions underlying the so-called potential theory of adsorption commonly named the Polanyi theory originates from the

earlier work by de Saussure. According to this assumption the adsorbed layer is considered as the 'thick', multilayer film of decreasing density and increasing distance from the solid surface. The basic concept of the Polanyi theory includes the adsorption potential and the characteristic adsorption curve. This characteristic curve presents a simple relationship between the adsorption potential and the distance from the solid surface.

This relationship was named as the characteristic adsorption equation. The aforementioned distance may be expressed in terms of volume units of the adsorbed phase. Polanyi assumed that the adsorption potential is independent of temperature over a wide range of the latter. It means that the characteristic curve of adsorption is temperature independent, too. Such a statement follows from the fact, that the van der Waals forces are also independent of temperature. However, for polar adsorbates this does not always hold true. Having calculated the curve characteristic for a given temperature it is possible to determine adsorption isotherms at other temperatures. The Polanyi potential theory does not give a definite equation of adsorption isotherm which, to some extent, replaces the characteristic adsorption equation. The Polanyi theory that assumes the description of a three-dimensional layer adsorbed by the van der Waals equation, implies not only that the adsorbate concentration increase at a suitably low temperature, but also its condensation into a liquid which takes place on the adsorbent flat surface.

In 1935–1940, The BET theory was developed by Hungarian chemist Stephen Brunauer and American chemical engineer Paul H. Emmett and Hungarian born theoretical physicist Edward Teller of polymolecular adsorption (Fig.12.1.). According to this theory:

- 1) energy-equal active centers exist on the surface of the adsorbent;
- 2) adsorbed molecules do not interact with each other;
- 3) each adsorption layer is the active center for the next layer after it.

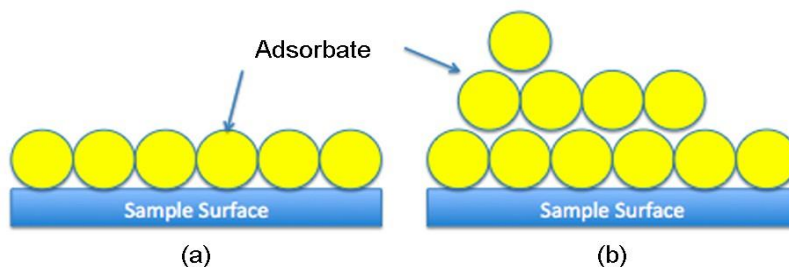


Fig.12.1. Schematic of the adsorption of gas molecules onto the surface of a sample showing (a) the monolayer adsorption model assumed by the Langmuir theory and (b) the multilayer adsorption model assumed by the BET theory.

The Langmuir theory is based on the following assumptions:

All surface sites have the same adsorption energy for the adsorbate, which is usually argon, krypton or nitrogen gas. The surface site is defined as the area on the sample where one molecule can adsorb onto. Adsorption of the solvent at one site occurs independently of adsorption at neighboring sites. Activity of adsorbate is directly proportional to its concentration. Adsorbates form a monolayer. Each active site can be occupied only by one particle.

The Langmuir theory has a few flaws that are addressed by the BET theory. The BET theory extends the Langmuir theory to multilayer adsorption with three additional assumptions:

Gas molecules will physically adsorb on a solid in layers infinitely.

The different adsorption layers do not interact.

The theory can be applied to each layer.

SECTION III. MONO- AND POLYMOLECULAR ADSORPTION. THEORIES OF POLYANY AND BET. MOLECULAR AND ION EXCHANGE ADSORPTION. IONITES. CHROMATOGRAPHY METHODS AND THEIR APPLICATION IN THE ANALYSIS OF DRUG PREPARATIONS.

Chapter 13. Adsorption on solutions

The adsorption of solutes by solid adsorbents is a more complex process than the adsorption of gases by solids. It is complicated by several factors:

- 1) the presence of a solvent whose molecules can compete with adsorbate

molecules for a place in the surface;

- 2) the interaction between the molecules of the adsorbate and the solvent;
- 3) electrostatic interaction between the surface of the adsorbent and adsorbate ions.

The adsorption from solutions by solids was discovered in 1785 by a Russian chemist - pharmacist, T.E.Lovits. He established that non-electrolytes and weak electrolytes on the surface of the adsorbent are adsorbed from solutions in the form of molecules. This process is called molecular adsorption. As a result of adsorption, the concentration of the substance dissolved in the solution decreases. Adsorption is determined by the formula:

$$A = \frac{(C_o - C)V}{m}$$

где: C_o – initial concentration of adsorbate, mol/l ;

C – balanced concentration of adsorbate, mol/l;

V – volume of solution, l;

m – adsorbent mass;

A – adsorption, mole/kg.

Adsorption of strong electrolytes

Ions are adsorbed from solutions of strong electrolytes. Ions are adsorbed only on polar and practically not adsorbed on non-polar adsorbents. Ion adsorption occurs in most cases under the action of chemical forces. Ion adsorption proceeds by two main mechanisms:

- 1) equivalent or ion exchange;
- 2) selective adsorption of ions on crystals.

By both mechanisms, a double electric layer is formed at the interface of the solid and liquid phases.

Ion-exchange adsorption consists in the fact that the practically insoluble adsorbent dissociates cations or anions from the surface and simultaneously absorbs an equivalent amount of ions of another kind. These sorbents capable of

exchanging ions are called ion exchangers.

Selective adsorption of ions obeys the rule established by the American physicist-chemist K.Fajans: On the surface of the adsorbent, those ions that can complete the crystal lattice of this adsorbent are predominantly adsorbed. According to the rule of Fajans on a solid surface, the ion that has a greater chemical affinity for the substance of the solid phase will be absorbed.

In the oral quiz of the topic, you can use the Insert and Boomerang pedagogical technologies.

Questions Boomerang method:

Group 1

1. Surface phenomena and their cause of occurrence
2. Sorption. Its types.
3. What substances can be adsorbents?

Group 2

1. Adsorption and factors affecting the adsorption process
2. Adsorption on a hard surface. Freundlich equation.
3. How to find the constants of the Freundlich equation?

Group 3

1. Monomolecular and polymolecular adsorption.
2. The monomolecular theory of Langmuir adsorption.
3. Polymolecular adsorption theory of Polanyi and BET.

Group 4

1. Adsorption on a liquid surface. Gibbs equation.
2. Surface-active, surface-inactive and surface-nonactive substances.
3. Adsorption of strong electrolytes.

Laboratory work 3

Study of adsorption of acetic acid on activated charcoal

Objective:

1. To study the adsorption on solid adsorbents on solutions and calculate the

value of adsorption.

2) Find the constant of the Freundlich equation for this system

Plan and organization of the structure of the lesson.

- a quiz of a given material - 40 minutes
- performance of the lab work- 30 - 40 minutes
- calculation and execution of a report on the work done - 20-30 minutes
- clean of the workplace - 10-20 minutes.

Equipment and reagents: 8 conical flat-bottomed flasks, burette on 25 ml, acetic acid solutions at four concentrations, activated charcoal, NaOH solution with a known concentration, filter paper for 4 glass funnels.

Theoretical explanation: When absorbing dissolved substances by solid adsorbents, the specific adsorption, that is, the amount of adsorbed substance (adsorbate), is determined by the change in its concentration in solution. The value of specific adsorption for solid adsorbents and the equilibrium concentration in

solution are related by the Freundlich empirical equation: $\frac{x}{m} = KC^{\frac{1}{n}}$

x - amount of adsorbed compound, mol;

m – adsorbent mass, kg;

K and $1/n$ are constants.

The constant K depends on the nature of the adsorbent and the adsorbate and varies widely. With increasing temperature, the value of K decreases. Its physical meaning is that it shows the amount of adsorption at an equilibrium concentration equal to unity. The value of $1/n$ lies in the range of 0.1–1 and depends on the temperature and nature of the adsorbate. Both constants are defined graphically. For this equation to do logarithm:

$$\lg \frac{x}{m} = \lg K + \frac{1}{n} \lg C$$

Having determined experimentally several values of $\frac{x}{m}$, create a graph in coordinates $\lg \frac{x}{m} - \lg C$. The straight line cut off on the ordinate axis gives the

values of $\lg K$, and the slope of the straight line gives the value $1/n$.

Performance of the lab work:

1) Take four dry conical flat-bottomed flasks with a capacity of 100 ml. They are placed using pipettes of 50 ml of acetic acid solutions of different concentrations.

2) In each flask with a solution of acetic acid add 1 g of activated charcoal. Solutions with charcoal periodically stirred for 1 hour.

3) During this time, determine the concentration of the initial solutions. To do this, 10 ml of the solution are taken from each solution using a pipette into a titration flask and titrated with 0.1 normal KOH solution in the presence of phenolphthalein. In parallel, carry out three titrations. Of the three definitions, find the average result (alkali volume).

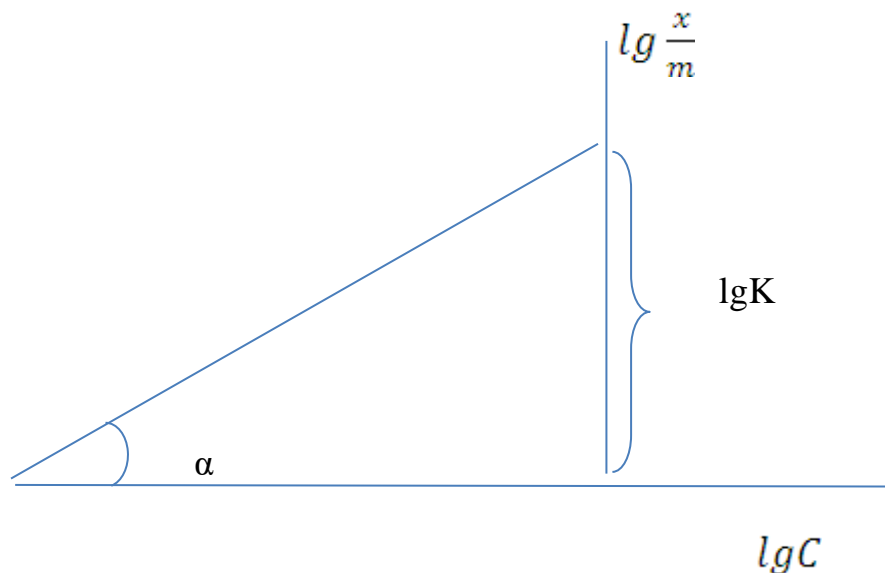
4) After a specified time, the contents of the flasks are filtered through filters in clean conical flasks with a capacity of 100 ml. The first portions of the filtrates are discarded, since the concentration of acetic acid in them can be lowered due to adsorption by filter paper. Equilibrium concentrations of acetic acid in the filtrates are also determined, as well as the initial ones, by titrating with an alkali solution. From the results of three titrations find the average volume of alkali for each solution. The initial (C_0) and equilibrium (C) concentrations of acetic acid are calculated by the formula:

$$C_a = -\frac{C_b V_b}{V_a}$$

From the differences between the initial and equilibrium concentrations, the specific adsorption value is found for each concentration.

$$\frac{x}{m} = (C_0 - C) \cdot 50$$

According to the measurement results build a dependency graph $\lg \frac{x}{m}$ or $\lg C$



Results fill into the table.

№	C_o	C	$\frac{x}{m} = (C_o - C) \cdot 50$	lgC	$lg\frac{x}{m}$	K=? n=?
1						
2						
3						

From the graph, lgK is found, the antilog of this value is equal to the constant K. The tangent of the angle α is $1/n$, it is equal to the ratio of the length of the opposite leg to the length of the adjacent leg.

Laboratory work 4

Study of the effect of adsorbent specific surface on adsorption

Objective: To study the effect of the specific surface of the adsorbent on the adsorption value

Equipment and reagents: Polydisperse powder of silica gel, methylene blue solution, tubes.

Performance of the lab work:

1. Preparation for performance of the lab work.
2. The tube is filled up to 1/6 of the silica gel powder.
3. Methylene blue solution pour into the tube.
4. The tube is strongly mixed and left for 15-20 minutes.
5. Observe the intensity of the color by height.

According to the results of the lab work, draw conclusions and answer the following questions:

What will be the color of the sediment in different layers?

How is the sediment column distributed by particle size?

How is the specific surface of the particle depending on the size?

In conclusion, explain in adsorption from solution the effect of the specific surface of the adsorbent on the value of adsorption.

Laboratory work 5

Measurement of the surface activity of an aqueous solution of isoamyl alcohol.

Objective: To study the effect of the concentration of a surfactant on the surface tension of a liquid.

Equipment and reagents: Stalagmometer, 4 flasks, glasses, measuring cylinder, 0.2 M aqueous solution of isoamyl alcohol, purified water.

Theoretical explanation: The surface tension of liquids is measured by the stalagmometric method. The name of the stalagmometer is taken from the Greek word “stalagma” drop. The method is based on measuring the mass drop, which flows from the capillary tube of the stalagmometer (Fig.13.1.).

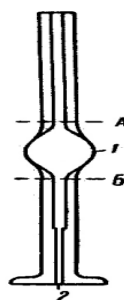


Fig.13.1. Stalagmometer

The mass of the drop is proportional to the size of the radius and the surface tension of the liquid. A drop of liquid flowing from the capillary according to the second law of thermodynamics tends to take the form of a ball, which leads to a decrease in the Gibbs free energy. In practice, it is convenient not to measure the mass of a drop, but the number of drops of a certain volume of liquid. The number of drops

is determined during the flow of a certain volume of liquid from the capillary stalagmometer. The number of water droplets with a surface tension σ_0 is denoted by n_0 , the number of droplets of the test liquid with an unknown surface tension σ_x is denoted by n_x . Calculate σ_x by the formula:

$$\sigma_x = \frac{n_0 \cdot d_x}{n_x \cdot d_0} \cdot \sigma_0$$

where: d_0, d_x – density of water and solution;

n_0, n_x - the number of drops water and solution.

To perform the work, the stalagmometer is immersed in a glass, first with water, then with liquids. Fluid with the help of a pear is pulled into a stalagmometer higher than the upper mark of the wide part. Then let the fluid flow. The reading of the drops will begin when the liquid level equals the upper mark. The reading of the drops is repeated 4-5 times and the average number of drops is determined. Calculate the surface tension of the solutions according to the above formula. The surface tension of water is $\sigma_0 = 0.7275 \text{ N/m}$. From the obtained results, a graph of the surface tension isotherm $\sigma = f(C)$ is plotted. On the x-axis put the value of C , on the y-axis values of σ . Fig.7. Using the isotherm, adsorption on the surface of the liquid is calculated using the Gibbs equation. For this purpose, the isotherms are tangent to the isotherm from several points. From these points, parallel lines are drawn to the abscissa to the intersection with the ordinate axis (Fig.13.2.).

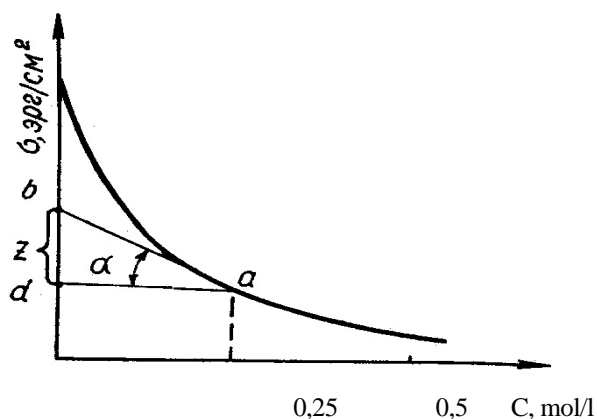


Fig.13.2. Surface tension isotherm (a), determination of constants Langmuir equations (b).

It turns out the triangle AED. The tangent of the acute angle of this triangle is in recent years. Colloidal systems include clouds, earth, paper, paints, bread, equal to the surface activity of the solution: $tg\alpha = \frac{AB}{BD}$ $tg\alpha = -\frac{d\sigma}{dC}$

SECTION V. DISPERSE SYSTEMS. NATURE AND CLASSIFICATION. PREPARATION AND PURIFICATION OF COLLOIDAL SOLUTIONS. MOLECULAR, OPTICAL AND RHEOLOGICAL PROPERTIES

Humanity has long been familiar with dispersed systems. But these systems began to be studied from the scientific side meat, dairy products and almost all medicinal substances, even the human body.

Colloid chemistry as a science originated in 1861, when the English scientist Thomas Graham observed that when dissolved, some substances diffuse rapidly, pass through the membranes of plants and animals, and easily crystallize. And some substances diffuse poorly, do not crystallize, fall into an amorphous precipitate. The first substances Gray called crystalloids, the second colloids, from the Greek word "colla" glue and "oidos" like.

According to the professor of the Kiev University I.G.Borschov there is a similarity between these two types of substances. Later, the Russian scientist P.P.Veymarn confirmed his views. In their opinion, the same substance, depending on the conditions, can be in the colloidal and crystalline states. One and that substance can take place both in a crystalline and in a colloidal state.

The colloidal state is a highly dispersed (finely divided) state of substances in which particles consist of aggregates of individual molecules.

Dispersion from the Latin word "disperses" means fragmentation, absent-mindedness. All the dispersed systems are characterized by two main features: high fragmentation (dispersion) and heterogeneity.

Dispersed systems are called systems consisting of many small particles distributed in a liquid or gaseous medium.

Disperse systems include soils, rocks, powders, scavengers, catalysts, etc. Dispersed systems consist of two or more phases: a dispersed phase and a

dispersed medium. The dispersed phase is a fragmented phase. It consists of particles of insoluble finely divided substance distributed throughout the entire volume of the dispersed medium.

Colloid chemistry studies the physicochemical properties and behavior of dispersed systems. According to Rebinde, it would be more correct to call colloid chemistry "The physical chemistry of dispersed systems and surface phenomena."

According to the degree of dispersion, colloidal systems occupy an intermediate position between coarse-dispersed systems and true solutions, from the Greek word "colla" / colla / - glue, "oidos" - like that is colloid is glue-like.

Chapter 14. Disperse systems. Their classification.

Dispersed systems consist of two or more phases: the dispersed phase and the dispersion medium, and can be in any state of aggregation. Therefore, colloidal systems can be gaseous, liquid and solid. Systems with a liquid dispersion medium are called liozols (Greek. Lyos-liquid). Depending on the nature of the dispersion medium, the liozols are called hydrosols or organosols. Dispersion medium of hydrosols is water, organosols - organic liquid, alcohols, ether, benzene, etc. In relation to the environment, all colloids were divided into two groups: lyophobic (Greek. Lyo-dissolving, phobos-fear) and lyophilic (Greek. Lyo- dissolving, philos-friend), or hydrophobic and hydrophilic, if the dispersion medium is water. Lyophobic colloids do not show affinity for the dispersion medium and are practically insoluble in it. They are stable due to a stabilizer, which causes an electric charge on the surface of colloidal particles.

Lyophilic colloids (starch, gum arabic, gelatin, rubber, etc.) have a high affinity for the dispersion medium, they are stable, well adsorb it on their surface. The differences in the properties of lyophobic and lyophilic colloidal systems were explained by different interactions of the colloid with the dispersion medium.

Colloid chemistry also studies more coarsely dispersed systems, called microheterogeneous, whose particle size is from 100 μm to several microns, so they are clearly visible under a microscope; These include emulsions, foams,

suspensions, powders, aerosols, which have a great practical application in pharmacy.

Classification of disperse system

Disperse system	Coarse disperse systems suspension, emulsion, powders	Colloid systems	True solutions
Diameter of particle	Up to 100 μm	100- 1 μm	Less than 1 μm
	Up to 10^{-5} sm	10^{-5} - 10^{-7} sm	Less than 10^{-7} sm

Chapter 15. Obtaining and properties of sols

Colloidal systems are intermediate between coarse and true solutions, so they can be obtained by two opposite methods: dispersion and condensation.

Dispersing methods are technically carried out by mechanical, electrical or ultrasonic crushing of substances up to sizes of colloidal particles. All dispersion methods are accompanied by an increase in the surface-phase separation. With mechanical dispersion in the laboratory, a small amount of solid can be crushed by prolonged grinding in an agate mortar in the presence of suitable stabilizers. In industrial conditions, special grinding machines called colloid mills are used (Fig.15.1.).

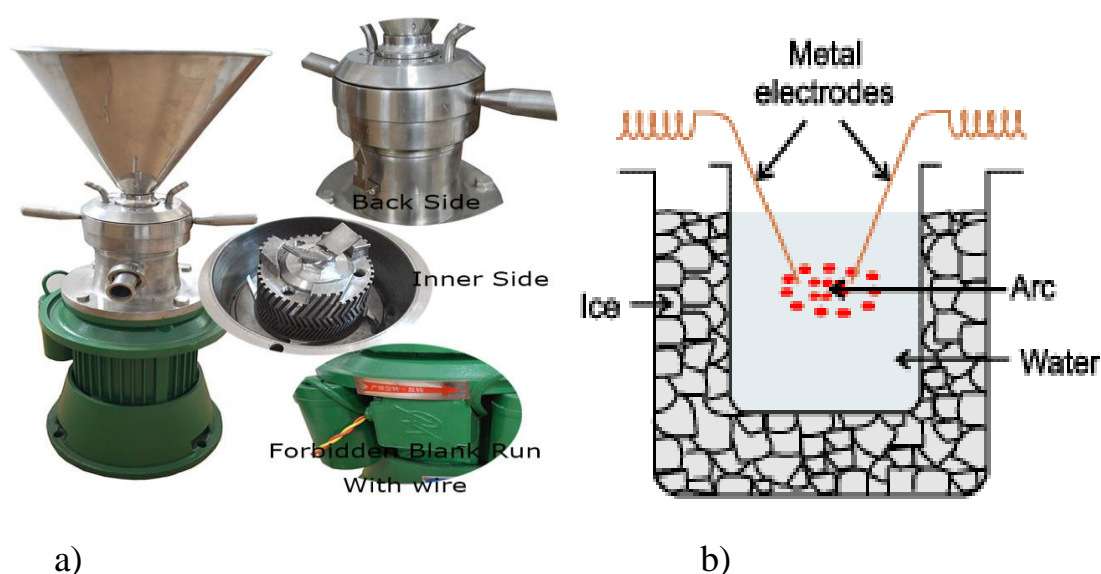


Fig.15.1. Colloidal grinder (a) and Electrical dispersion (b)

Electrical dispersion is used primarily in the preparation of sols of various metals. Colloidal solutions of silver, gold, platinum and other metals, which do not chemically interact with water, are obtained by this method.

Condensation methods are based on the transition of molecular or ionic solutions to colloidal ones. This method is divided into physical and chemical.

Physical condensation:

1) The method of replacing the solvent, when the solvent in which the substance dissolves, forming a true solution, is replaced by a dispersion medium in which this substance is insoluble. For example, if a true alcohol solution of sulfur is poured into water, a colloidal solution of sulfur in water is formed, since sulfur is insoluble in it;

2) Evaporation of substances of the constituents and the phase and the environment. This is reproduced on the device Shal'nikov-Roginsky. Sodium benzene was obtained from this method.

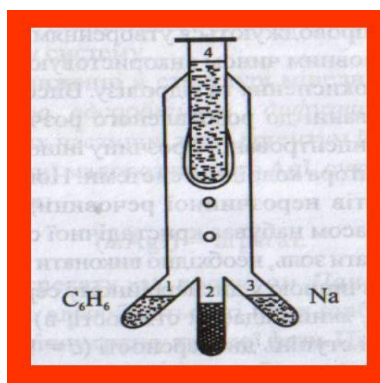


Fig.15.2. Instrument Shalnikov-Roginiski

Chemical condensation: Production of sparingly soluble substances during various chemical reactions (hydrolysis, reduction, oxidation, double exchange, etc.)

In both methods, a third stabilizer component is needed to obtain a stable colloidal system, which creates a protective adsorption layer around the colloidal particles or by reducing the surface tension at the interface. Electrolytes, polyelectrolytes and surfactants are commonly used as stabilizers. In chemical methods for colloidal systems, the reaction products act as a stabilizer.

Colloidal solutions can be obtained by peptization. Peptization is the process

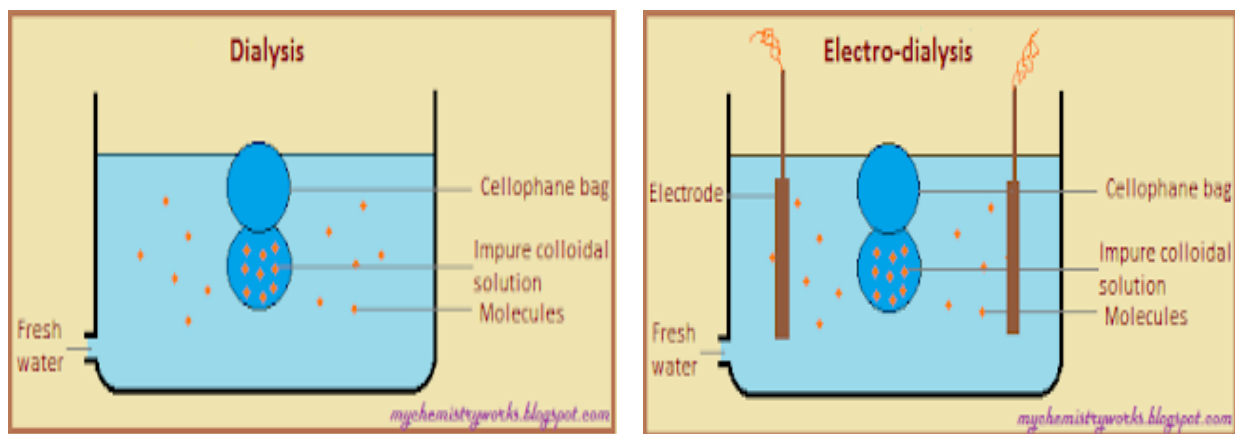
of forming stable colloids by using an electrolyte to break up a precipitate and disperse it into the colloid. So while coagulation uses charges to disrupt the colloid and form an aggregate, peptization uses charges to form a colloid from a precipitate.

In order to perform peptization we need an electrolyte, which is called a peptizing agent. The precipitate particles adsorb onto the ions of the peptizing agent, and then electrostatic repulsion (repulsion between two compound with like charges) causes the precipitate particles combined with the electrolyte ions to mix with the colloidal solution, thereby forming a stable colloid. So where do we see peptization in everyday life? Well, the clay that you use to do things like make pottery is produced through peptization. Clay can be mixed with water through peptization. It is possible to peptize sediments only when it has an amorphous, rather than crystalline, coagulation structure. During peptization, there is no change in the degree of dispersion of the sediment particles, which was formed during the coagulation (condensation) of the particles, but only their separation. Therefore, the method of peptization in the initial stages is dispersion, i.e. peptization method is intermediate between condensation and dispersion.

Chapter 16. Purification of sols.

For colloidal solutions with the highest stability and. To study their properties, it is necessary to remove from the sols of various impurities, and first of all, excess electrolytes, which, as a rule, are formed during the preparation of colloidal solutions.

Dialysis is widely used for cleaning solutions. The release of colloidal solutions from impurities that can penetrate plant, animal and artificial membranes is called dialysis, and the instruments used for dialysis are called dialyzers. The accelerated dialysis process using direct electric current is called electro dialysis, which is carried out in electro dialyzers (Fig.16.1.).



a)

b)

Fig.16.1.Simple dialyzer (a) and Electro-dialyzers (b)

One of the important methods for the purification of colloidal solutions is ultrafiltration, which is reduced to the separation of the dispersed phase from the dispersion medium. To do this, the colloidal solution is filtered through a membrane that does not allow colloidal particles or macromolecules. During ultrafiltration, the dispersed phase remains on the filter.

Chapter 17. Molecular - kinetic properties of colloidal solutions

Colloidal solutions have molecular-kinetic properties, as molecular solutions, between these solutions are not qualitative, but there are only quantitative differences, depending mainly on the shape and size of colloidal particles. These include Brownian motion, diffusion, sedimentation and osmotic pressure.

Under the influence of thermal and Brownian motion, the process of equalization of the concentrations of particles throughout the solution volume occurs. The process of diffusion proceeds not only in molecular, but also in colloid-dispersed solutions.

Colloidal particles also cause some osmotic pressure. Due to large particle sizes and low concentrations, their osmotic pressure is negligible. In addition, part of the measured osmotic pressure in colloidal solutions, mainly hydrophobic, due to the admixture of electrolytes.

Particles of substances that are suspended in a gaseous or liquid medium are

affected by two oppositely directed forces. These are gravity forces that tend to concentrate particles in the lower layers, and diffusion forces moving the dispersed phase of aerosols, colloidal solutions from higher concentrations to lower ones. The process of sedimentation of colloidal particles in a solution is called sedimentation. The ability of a dispersed system to maintain a uniform distribution of particles throughout the volume is called sedimentation, or kinetic stability. High-molecular systems (gases, true solutions) have a high kinetic stability and, conversely, coarsely dispersed kinetically unstable, because particles practically cannot perform thermal motion. Colloidal systems occupy an intermediate filling between them.

Chapter 18. Optical properties of colloidal solutions

Colloidal solutions have optical properties, which determine the nature of the solutions, determine their concentration, size of colloidal particles, etc. In a dark room, when looking sideways at the passage of a beam of light through a glass with a colloidal solution, Faraday and Tyndall discovered a luminous cone resulting from the scattering of light by colloidal particles. This is called the Faraday-Tyndall effect (Fig.18.1.).

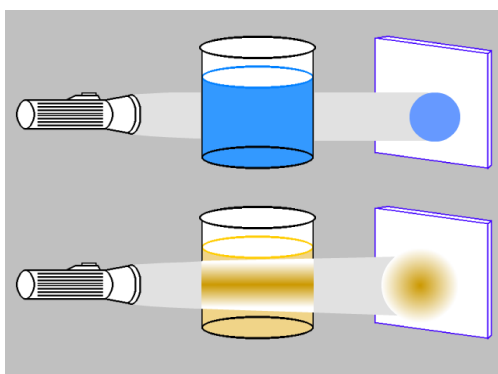


Fig.18.1.Faraday -Tyndall effect

According to the Faraday-Tyndall effect, it is easy to distinguish colloidal solutions from solutions of low-molecular substances.

Chapter 19. Electro-kinetical properties of disperse systems

The formation of colloidal systems, as a rule, occurs in media which containing electrolyte. When colloidal particles interact with electrolytes, usually

one of the ions is adsorbed on the surface of the particles in accordance with the rules of selective adsorption, Peskov-Fayans. As a result of selective adsorption, the dispersed phase acquires a certain electrical charge, and the dispersion medium acquires the opposite charge. Therefore, when an external electric field is applied, the phase and medium move to oppositely charged electrodes.

The movement of colloidal particles in an electric field is called electrophoresis. In 1808, the phenomena of electrophoresis and electroosmosis were discovered by prof of Moscow University Ferdinand Friedrich von Reuss (also Reuß). Electrophoresis and electroosmosis are of great importance for understanding the electrical properties of colloidal systems. The charge of colloidal particles is determined by electrophoresis due to the formation of a double electric layer (Fig.19.1.). From the modern point of view, for example, when you make a silver iodide crystal in a solution of potassium iodide, silver iodide crystals will adsorb iodine ions in accordance with the rules of selective adsorption. Ions adsorbed directly on the solid phase (which is the core of a colloidal particle) are called potential-determining, and the potential arising at the interface between the phases is called thermodynamic and is denoted by the letter.

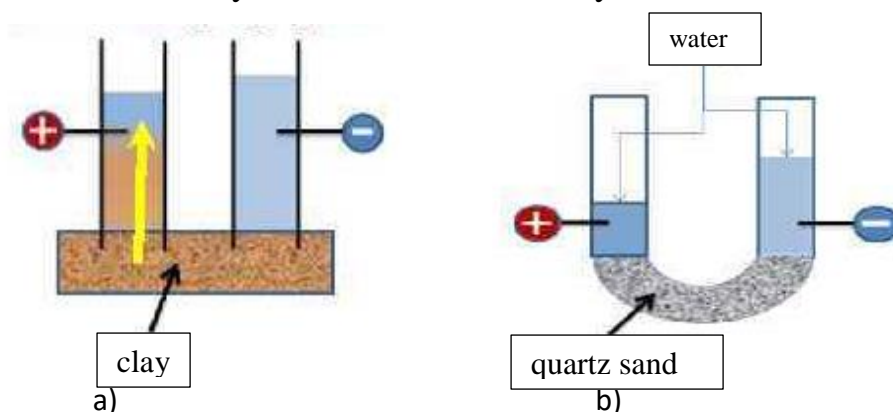


Fig.19.1. Electrophoresis (a) and electroosmosis (b)

Ions of the opposite sign (potassium cations), i.e. counterions form the outer lining of the double layer. According to the Stern theory, the first or even several first layers of counter-ions are oriented under the influence of both the electric field and the adsorption forces, forming an adsorption layer of counter-ions. The adsorption layer of counter-ions is firmly bound to the surface of the particles,

while the other part of counter-ions, under the influence of thermal motion, acquires the diffuse structure of the diffuse layer.

Structurally constructed unit of the nucleus and the electric double layer is called a micelle, it consists of:

- 1) the core of a crystalline structure or amorphous structure;
- 2) electric double layer, divided into adsorption and diffuse layers.

The nucleus, together with the adsorption layer of ions, is called a colloidal particle or granule. Unlike electrically neutral micelles, a colloid particle has a charge (Fig.19.2.).

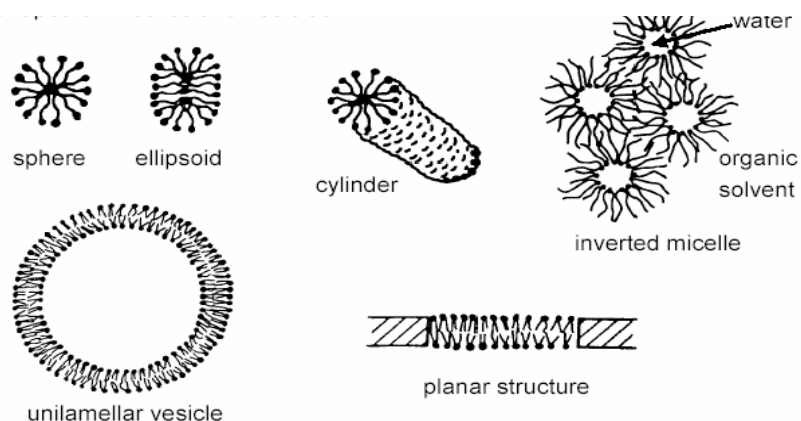
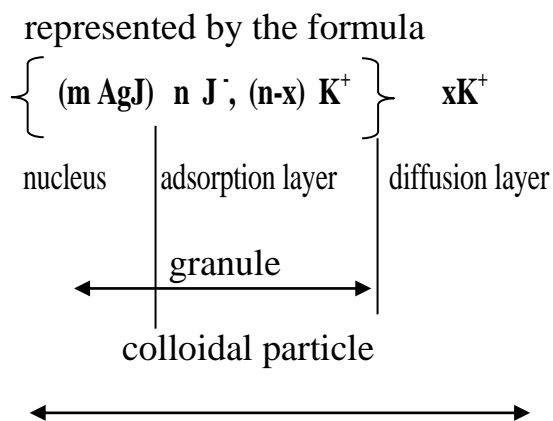


Fig.19.2.Shapes of micelles

A micelle sol of silver iodide stabilized with potassium iodide can be



Laboratory work 6

Obtaining sols

Objective: 1. Learn to get hydrosols. 2. Write the micelle structure

Plan and organization of the structure of the lesson

- a quiz of a given material - 40 minutes
- the performance of the experiment - 30 - 40 minutes
- clean of the workplace - 10-20 minutes.

Equipments and reagents: 4 conical flat-bottomed flasks with a capacity of 50 ml, test tubes, an alcoholic solution of resin, a solution of ferric chloride, silver nitrate, an alkaline solution of tannin, an ammonia solution, 0.1 n hydrochloric acid solution, purified water, an electric stove or a gas burner.

Experiment 1. Obtaining resin hydrosol. Performance of the lab work: 1) Approximately 10 ml of alcohol solution of resin is poured in the flask; 2) The mixture is vigorously mixed. 3) Heat to remove excess alcohol until boiling. Based on the experience done, conclude: Describe the properties of the sol, write the structure of the micelle, the method of obtaining the sol, look at the sol in the passing and reflected light.

Experiment 2. Obtaining hydrosol of $\text{Fe}(\text{OH})_3$. Performance of the lab work: 1) Pour about 10 ml of purified water into a flask.

2) Heat until boiling

3) Add of 5 drops of a 2% solution of iron (III) chloride into boiling water

4) Continue heating until red-brown color appears. On the basis of the experience done, conclude: Describe the method for obtaining sols, determine the electrolyte which is a stabilizer, write the reaction of the preparation and the structure of the micelle.

Experiment 3. Obtaining of Silver hydrosol. Performance of the lab work:

1) Pour about 10 ml of purified water into a flask.

2) Heat until boiling. Add 4-5 drops of a 0.1% silver nitrate solution

3) The mixture is heated until boiling.

4) In a boiling liquid drop by drop at intervals of 1 min, add 1% alkaline solution of tannin until a stable yellow color appears. Based on the experience done, conclude: Describe the method for obtaining sols, write the reaction of the preparation and the structure of the micelle, can potassium argentite $KAgO$ is a stabilizer, is it possible to purify this sol from impurities and truly soluble low-molecular substances?

Experiment 4. Getting hydrosols of the Prussian blue. Performance of the lab work: 1) Pour about 1 ml of a 0.05 N solution of iron (III) chloride into a flask. 2) Add 1 ml of a saturated solution of $K_4[Fe(CN)_6]$ 3) The precipitate obtained from Prussian blue is filtered and wash on the filter with purified water to remove excess of $K_4[Fe(CN)_6]$ 4) To the precipitate remaining on the filter add 2-3 ml of oxalic acid solution 5) The filtrate is collect in a tube

On the basis of the experience done, conclude: What is the color of the obtained sol, by which method it was obtained.

Laboratory work 7. Peptization

Aim of the lab work is peptization precipitate iron hydroxide (III).

- 1) Pour about 5 ml of a 0.5 M solution of iron (III) chloride into a test tube.
- 2) Add a solution of ammonia dropwise until complete precipitation of iron hydroxide.
- 3) The precipitate is washed with purified water by the method of decanting to remove excess ammonia.

4) Approximately 10 ml of purified water is added to the washed precipitate and stirred until a suspension is obtained.

5) The resulting suspension is equally poured into three tubes.

6) In the first tube add 10 drops of a solution of 0.1 n hydrochloric acid solution

7) In the second tube add 10 drops of a solution of a saturated solution of ferric chloride (III)

Tube№	Measure of precipitation $\text{Fe}(\text{OH})_3$	Added electrolyte	Observation	Peptization type	Formula of micelle of obtaining sol
1	half	FeCl_3 , saturated 10 drops			
2	approximately	HCl, 0,1 N solution 10 drops			
3	3-4 ml	-		Control	

8) The third tube is left for control.

9) The contents of each of the three tubes are thoroughly mixed and compared after 10 minutes.

On the basis of the experience done, conclude: By what signs can one judge a precipitation peptization?

What substances are peptizator?

Write the structure of the micelles of the obtained colloidal solutions.

Laboratory work 8

Determination of the sign of the charge of a colloidal particle

Objective: 1. To explain the structure of the electric double layer and the mechanism of formation. 2. Learn to determine the sign of the charge of colloidal particles. 3. Write the micelle structure Plan and organization of the structure of employment.

- a quiz of a given material - 40 minutes
- the execution of the experiment - 30 - 40 minutes
- calculation and execution of a report on the work done - 20 minutes
- clean of the workplace - 10-20 minutes.

Instruments and reagents: Test tubes, filter paper, U-shaped tube, DC source, solution of iron (III) chloride, $K_4[Fe(CN)_6]$

Experiment 1. Determination of the sign of the charge of colloidal particles of Prussian blue sol by capillary analysis.

Performance of the lab work:

1) For preparation of Prussian blue solution to get from solutions of 3 parts of 0.005 N $K_4[Fe(CN)_6]$ with one part of 0.005 N solution of $FeCl_3$ in one tube. 2) 3 parts of of $FeCl_3$ with one part of $K_4[Fe(CN)_6]$ add in another tube. 3) A droplet is applied to the filter paper with an eye dropper from the solution of the first tube. 4) Nearby at a distance of approximately 2-fold diameters a drop of solution from another tube. Comparing the nature of the formed spots determine the sign of the charge of colloidal particles in the resulting solutions. At the same time, keep in mind that the surface of the filter paper is negatively charged when wetted with water and aqueous solutions. Consider whether the sign of the charge of a colloidal particle depends on the excess of one or another salt? Experiment 2. Determination of the sign of the charge of colloidal particles of Prussian blue sol by electrophoresis Performance of the lab work: 1) In a tube a colloidal solution of Prussian Blue is prepared by mixing 3 parts of a 0.005 N solution of $K_4Fe(CN)_6$ with one part of a 0.005 N solution of $FeCl_3$. 2) The resulting colloidal solution is poured into a U-shaped tube. 3) Cover each hole with stoppers in which electrodes are embedded. 4) Through the solution pass a constant electric current of at least 40 volts. 5) After 15 minutes, observe the movement of particles of a colloidal solution. 6) By displacement of the level, the sol is judged on the direction of movement of the particles of the colloidal solution to one of the advantages. Based on the observation of the particles, the sign of the charge of colloidal particles is

determined. What method was used to obtain the Prussian Blue sol? Write the reaction equation, the formula of the resulting sols and name the constituent parts of the micelles. Issues for control on work 4, 5

1. Give the definition of concepts - colloidal solution, lyosol, hydrosol, organosol. What are the sizes of colloidal particles?
2. Count the methods for obtaining lyosoles and give them a brief description.
3. What are the basic conditions that must be met to obtain lyosol?
4. How to get sodium chloride hydrosol?

5. Is it possible to obtain a stable sol by a double exchange reaction if the reagents are taken in equivalent quantities?

6. What is the essence of obtaining sols by peptization?

7. Explain the need for a stabilizer in the preparation of colloidal solutions.

8. What disperse systems can be obtained by mixing: a) 0.005n solutions of FeCl₃ and

K₄Fe (CN)₆?

- b) 0.1n solutions of FeCl₃ and K₄Fe (CN)₆?

9. What is the difference between sols and:

- a) Suspension

- b) True solution.

10. How to purify the colloidal solution?

- a) from impurities of truly soluble low molecular weight substances

- b) from impurities of coarse particles.

11. Is it possible to completely clean the sol from the excess of low molecular weight electrolyte?

12. The dialysis method and for what purpose is it used?

13. Diagram of simple dialysis.

14. What are the requirements for dialysis membranes?

15. How to speed up dialysis?

16. What is ultrafiltration, for what purpose is it used?

17. What is the device of the simplest ultrafilter?

18. What optical phenomena causes color sols?
19. Explain the occurrence of the Faraday-Tyndall cone?
20. What factors and how does the intensity of stray light depend on?
21. What phenomenon is called peptization?
22. What types of peptization are known?
23. How is dissolution peptization different from adsorption?
24. What is electrophoresis and electroosmosis?
25. What methods can detect the electric charge of colloidal particles and determine the sign of the charge?
26. What is zeta potential? How is it defined?

What is the relationship between the magnitude of the zeta potential and the stability of the colloidal system?

27. Draw a scheme of the structure of the sol micelle of the three-sulfurous arsenic crammed by the interaction of the solution As_2O_3 with an excess of H_2S .

What kind of bond present in the solution will be potential-determining?

28. Write the micelle formula barium sulfate sol obtained by reacting H_2SO_4 with an excess of BaCl_2 . Write the micelle formula and specify the components of the micelle.

29. AgJ sol is obtained by adding to 20 ml of 0.01 N KJ solution 28 ml of 0.005 N AgNO_3 solution. Write the sol micelle formula and determine the direction of movement of the colloidal particles during electrophoresis.

30. Explain the rule for selective adsorption of Peskov-Fajans.

SECTION VI. THE STRUCTURE OF COLLOIDAL PARTICLES. ELECTROKINETIC PROPERTIES. STABILITY AND COAGULATION OF COLLOIDAL SOLUTIONS. SCHULZE-HARDY RULE

Chapter 20. Stability and coagulation of sols

According to the general definition, **coagulation** is one of the various properties exhibited by colloidal solutions. A colloid is a heterogeneous mixture of one substance of very fine particles (dispersed phase) dispersed into another

substance (dispersion medium). Substances like metals, their sulfides etc. cannot be simply mixed with the dispersion medium to form a colloidal solution. Some special methods are used to make their colloidal solutions. Such kind of sols is known as lyophobic sols. These kinds of colloidal solutions always carry some charge on them. Charge present on the colloidal sols determines their stability. If by any chance we can remove the charge present on the sol, the particles get closer to each other and they accumulate to form aggregates and precipitate under the action of gravity. This process of accumulation and settling down of particles is further known as coagulation or precipitation.

Coagulation Techniques:

The process of coagulation can be carried out in the following ways:

1. By electrophoresis: In this method, the colloidal particles are forced to move towards the oppositely charged particles and then they are discharged and collected at the bottom.

2. By mixing two oppositely charged sols: In this type of coagulation equal amounts of oppositely charged particles are mixed, they cancel out their charges and then precipitate.

3. By boiling: Whenever we boil a sol, the molecules of the dispersion medium start colliding with each other and with the surface, this, in turn, disturbs the adsorption layer. This reduces the charge on the sol due to which the particles settle down.

4. By persistent dialysis: Under the persistent dialysis parts of electrolytes are removed completely and the sol loses its stability and ultimately coagulates. The ability of the dispersed phase to maintain its original degree of dispersion of particles and their uniform distribution in the dispersion medium is called stability. N.P. Peskov introduced the concept of kinetic (sedimentation) and aggregative stability of colloidal systems.

The kinetic or sedimentation stability of colloidal systems is explained by Brownian motion, which counteracts the sedimentation of particles under the

influence of gravity and diffusion. Aggregative stability characterizes the ability of colloidal particles to maintain the degree of dispersion. This is due to the presence of electric charge on the particles. This charge prevents sticking of colloidal particles and contributes to the formation of a solvation shell in solutions around the particles. At the loss of aggregative stability, the coarsening of particles occurs, ie sticking them together to form larger aggregates. Coagulation of sols can be caused by various factors: temperature change, irradiation with elementary particles, etc. However, the most important factor causing coagulation is the action of electrolytes.

In 1882, Schulze established that the coagulating force of an ion is greater, the higher its valence. In 1900, Hardy confirmed these results and summarized them as follows:

1. The effective ions of the electrolyte in bringing about coagulation are those which carry charge opposite to that of the colloidal particles. These ions are called coagulating ions.

2. Greater is the valency of the coagulating or the Flocculating ion, greater is its power to bring about the coagulation. When preparing for work it is necessary to study the following questions from the textbook and notes: 1. Kinetic and aggregative stability of colloidal solutions, factors of stability. 2. Coagulation: slow and fast, hidden and pronounced. Signs of coagulation. Factors causing coagulation. 3. Coagulation of sols with electrolytes. Coagulating ability. The rules of Schulze- Hardy. Coagulation threshold and its definition.

Task I. Determine which ions are coagulating, the effect of ion valence on coagulation and whether the data obtained correspond to the Schulze-Hardy rules

Task 2. Determine the coagulation threshold of $\text{Fe}(\text{OH})_3$ hydrosol

Task 3. Compare the coagulation of lyophilic and lyophobic colloidal solutions.

Laboratory work 9.

Study of coagulation of sols

Objective: 1. To explain the structure of the electric double layer and the mechanism of formation. 2. Learn to determine the sign of the charge of colloidal particles. 3. Write the micelle structure. 1) Instruments and reagents: Test tubes, $\text{Fe}(\text{OH})_3$ sol, solutions 0.1N Na_2SO_4 , 0.1N MgSO_4 , 0.1N $\text{Al}_2(\text{SO}_4)_3$, solutions of BaCl_2 , concentration 0.1; 0.01; 0.001; 0.0001; 0.00001 N, gelatin solution, $(\text{NH}_4)_2\text{SO}_4$ solution and dry salt.

Experiment 1. Effect of ion valence on coagulation Completing of the work: 2) Pour 2 ml of Sb_2S_3 sol into three tubes. 3) To each test tube, gently shaking it drop by drop, add various electrolytes to the pipette until the first signs of coagulation appear. 4) Consider the number of drops of solutions left for coagulation.

5) The results of the experiment are entered in the table and draw conclusions.

Table 4.

№	Electrolyte solution	The number of electrolyte droplets are going to coagulation
1	0,1N Na_2SO_4	
2	0,1N MgSO_4	
3	0,1N $\text{Al}_2(\text{SO}_4)_3$	

Experiment 2. Determination of coagulation of $\text{Fe}(\text{OH})_3$ hydrosol

electrolyte BaCl_2

Performance of the lab work:

- 1) Measure out the cylinder in 5 tubes of 2 ml of Sb_2S_3 sol.
- 2) Add 0.5 ml of BaCl_2 solution of various concentrations to each tube.
- 3) The contents of the tubes are mixed and the concentration of BaCl_2 is noticed within the limits between which coagulation occurs.
- 4) The results of the experiment are entered in the table:

Table 5.

Tubes №	Number of BaCl ₂ solution	Concentration of BaCl ₂ solution	Coagulation threshold
	0,5	0,00001 N	
	0,5	0,0001 N	
	0,5	0,001 N	
	0,5	0,01 N	
	0,5	0,1 N	

1) Calculate the coagulation threshold of Sb₂S₃ sol with BaCl₂ electrolyte

Experiment 3. Comparison of coagulations of lyophilic and lyophobic colloidal solutions

Performance of the lab work:

- 1) Pour 2 ml of the hydrophobic Sb₂S₃ sol into a test tube.
- 2) To the sol, stirring up, add dropwise a saturated solution of (NH₄)₂SO₄ before the onset of coagulation.
- 3) To another tube pour 2 ml of hydrophilic gelatin solution.
- 4) A saturated solution of (NH₄)₂SO₄ is added dropwise, if coagulation does not occur, add dry salt (NH₄)₂SO₄ before coagulation.
- 5) The results of the experiment are entered in the table:

Table 6.

№	Sols	The number of electrolyte droplets are going to coagulation
1	Sb ₂ S ₃	
2	Gelatin	

6) On the basis of the experience done, make a conclusion about the stability of lyophilic and lyophobic sols and the effect of electrolytes.

Chapter 21. Colloid protection

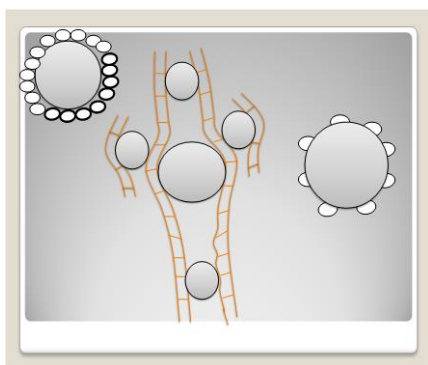
Hydrophobic sols are extremely sensitive to the action of electrolytes. When adding insignificant amounts of hydrophilic sol to a hydrophobic, significantly hydrophobic colloid, it is electrolyte resistant. Increasing the stability of the

hydrophobic will when adding a hydrophilic colloid to it is called the protection or protective action. The protective effect of lyophilic colloids is explained by their ability to adsorb on the surface of lyophobic colloid particles. For protection, a very small and strictly defined amount of lyophilic colloid, sufficient to cover the surface of lyophobic particles, is necessary. The colloid adsorbing on itself particles of lyophilic colloid, takes all its properties, the more pronounced, the better covered or protected hydrophobic surface.

The protective effect of lyophilic colloids depends on their individual properties and varies among different members of this class; also depends on the degree of dispersion of the colloid, the presence impurities, pH, charge mark of one or another colloid.

The protective effect lyophilic colloid

- Lyophilic sols are more stable than lyophobic sols.
- Lyophobic sols can be easily coagulated by the addition of small quantity of an electrolyte.
- When a lyophilic sol is added to any lyophobic sol, it becomes less



sensitive towards electrolytes. Thus, lyophilic colloids can prevent the coagulation of any lyophobic sol.

“The phenomenon of preventing the coagulation of a lyophobic sol due to the addition of some lyophilic colloid is called sol protection or protection of colloids.”

- The protecting power of different protective (lyophilic) colloids is different. The efficiency of any protective colloid is expressed in terms of gold number.

Gold number: Zsigmondy introduced a term called gold number to describe the protective power of different colloids. This is defined as, “weight of the dried protective agent in milligrams, which when added to 10 ml of a

standard gold sol (0.0053 to 0.0058%) is just sufficient to prevent a colour change from red to blue on the addition of 1 ml of 10 % sodium chloride solution, is equal to the gold number of that protective colloid”.

Thus, smaller is the gold number; higher is the protective action of the protective agent. Preservation of the original color of the sol with the addition of NaCl indicates a protective effect.

If instead of a gold sol, we take other sols, for example, silver, iron, and others, then in the same way silver and other protective numbers can be obtained.

Any of these numbers characterizes the protective action of the lyophilic colloid with respect to this sol.

By analogy with the gold number, it is possible to determine the protective effect of gelatin for the Sb_2S_3 sol, meaning by this term the amount of gelatin preventing coagulation of 10 ml of the prepared Sb_2S_3 sol by adding 1 ml of 10% NaCl solution.

Protection of colloidal particles is used in the manufacture of medicines. It is often necessary to introduce medicinal substances into the organism in a finely divided, colloidal state so that they are evenly distributed in it and, gradually dissolved, have the desired effect.

For this purpose, just suitable sols or suspensions of medicinal substances are suitable. The protective effect is of great importance in a number of physiological processes occurring in the human body and animals.

Laboratory work 10

The protective effect of high-molecular compounds.

Objective: To study the effect of the protective action of gelatin on the stability of the $\text{Fe}(\text{OH})_3$ sol.

Plan and organization of the structure of employment.

- a survey of a given material - 40 minutes
- the execution of the experiment - 30 - 40 minutes

- calculation and execution of a report on the work done - 20 minutes
- clean of the workplace - 10-20 minutes.

Instruments and reagents: Test tubes, $\text{Fe}(\text{OH})_3$ sol, 0.5% gelatin solution, 10% NaCl solution

Completing of the work:

- 1) In 6 tubes pour a 0.5% solution of gelatin in the volumes indicated in the table.
- 2) The volume of the solutions is adjusted to two milliliters.
- 3) To each tube add 2 mL of $\text{Fe}(\text{OH})_3$ sol to the measuring cylinder.
- 4) The contents of the tubes are mixed.
- 5) Add 1 ml of 10% NaCl solution to each tube and shake.
- 6) Observe the color change of the solutions.
- 7) Calculate the “antimony number” of gelatins.

Table 7.

№	Content of mixture	Units	1	2	3	4	5	6
1	Sb_2S_3 sol	ml	2,00	2,00	2,00	2,00	2,00	2,00
2	0,5% gelatin solution	ml	0,05	0,10	0,20	0,30	0,40	0,50
3	Water	ml	0,45	0,40	0,30	0,20	0,10	0,00
4	10 % NaCl solution	ml	1,00	1,00	1,00	1,00	1,00	1,00

If a color change is observed in the first three tubes, the protective effect should be expressed in numbers between 0.2 and 0.3 ml of gelatin solution. Based on the data, the protective effect of gelatin for the Sb_2S_3 sols is calculated. “Antimony number” of gelatins.

Questions for control on Experiments 6 and 7.

1. What phenomenon is called coagulation?
2. What are the signs of coagulation?
3. What causes coagulation?
4. The mechanism of coagulation.
5. Coagulation threshold.
6. What is the Schulze-Hardy Rule?

7. The mechanism of the protective action of high-molecular compounds.
8. Factors that influencing on the protective effect of high-molecular compounds.
9. A measure of protective action.
10. Calculation of antimony number.

Tests

1. The founder of colloid chemistry:
 - a) Peskov
 - b) Lomonosov
 - c) Graham
 - d) Selmi
2. What is peptization?
 - a) The process of precipitation from a colloidal solution by adding electrolyte in an amount equal of the threshold concentration:
 - b) The process of transformation of loose sediments into colloidal solutions under the action of electrolytes on them, which can adsorb on the surface of colloidal particles;
 - c) The process of transformation of loose sediments into colloidal solutions under the action of high-molecular substances on them;
 - g) The process of precipitation from the colloidal solution with the addition of high-molecular compound.
3. What is the main reason for stability of colloidal sols?
 - a) Charge
 - b) Nature
 - c) Solvation shell
 - d) Brownian motion and diffusion
4. How is sodium benzene sol obtained?
 - a) Mechanical
 - b) using ultrasound

- c) physical condensation
 - d) chemical condensation
5. Which of the following systems is considered colloidal?
- a) Aqueous solution of sodium chloride
 - b) Aqueous solution of gelatin
 - c) clay
 - d) Milk
6. What is electroosmosis?
- a) Motion of colloidal solution molecules in an electric field;
 - b) Movement of a colloidal fluid through a porous solid under c) the action of an external electric field;
 - d) Movement of a colloidal solution in an electric field;
 - e) Motion of colloidal particles in an electric field.
7. Coagulation threshold:
- a) The highest concentration of electrolyte causing coagulation;
 - b) The highest concentration of surfactant causing coagulation;
 - c) The lowest concentration of electrolyte causing open coagulation and expressed in mmol/l;
 - d) The lowest concentration causing coagulation and expressed in gE / l;
8. Upon obtain of the silver chloride sol, potassium chloride was taken in excess. What ion is adsorbed on the surface of the nucleus?
- a) K^+
 - b) Cl^-
 - c) Ag^+
 - d) NO_3^-
9. With the addition of what protects the lyophobic sol from coagulation?
- a) Electrolyte solution
 - b) Another lyophobic sol
 - c) Lyophilic sol

g) Organic solvent

10. The sizes of colloidal particles?

- a) Less than 1 mmicron
- b) More than 100 MM
- c) 1-100 MMK;
- d) 0.1-1 mmk

11. What is lyozol?

- a) A dispersed system in which the dispersed medium is solid;
- b) A dispersed system in which the dispersed medium is a liquid;
- c) Dispersed system, with solid phase and gaseous medium;
- d) A dispersed system consisting of a solid medium and a liquid phase.

12. How are sol electrolytes purified?

- a) simple filtering
- b) decantation
- c) Sublimation
- d) Dialysis

13. What disperse systems include suspensions and emulsions?

- a) True solutions
- b) Mixtures
- c) Colloidal solutions
- d) Coarse dispersion systems

14. Rule of selective adsorption of Peskov-Fajans:

- a) The colloidal solution absorbs well the ions that enter its crystal lattice;
- b) The colloidal particle well adsorbs those ions that enter its crystal lattice;
- c) A colloidal particle adsorbs opposing ions;
- d) A colloidal particle adsorbs like charges.

15. What is called electrophoresis?

- a) The motion of uncharged particles in a constant electric field
- b) The motion of a colloidal solution in an electric field

- c) The motion of a colloidal particle in an electric field to the opposite charge
- d) Movement of a dispersed medium in an electric field;

SECTION VI. COARSE SYSTEMS. SUSPENSIONS, EMULSIONS, AEROSOLS AND POWDERS. SURFACTANTS. CLASSIFICATION. THE NUMBER OF HLB. THE IMPORTANCE OF SURFACTANTS IN THE NATIONAL ECONOMY AND PHARMACY

Chapter 22. Surface activity

The surface tension of various liquids varies considerably and depends on the nature of the liquid, its temperature, pressure, and concentration of solutes.

Solutes can increase, decrease, and/or no effect on the surface tension of liquids.

The ability of solutes to change the surface tension of the solvent is called surface activity.

A measure of surface activity is the derivative of surface tension by concentration with a minus sign

$G = -\frac{d\sigma}{dC}$. Unit of measurement J·M/mole or N·M²/mole, also in erg·sm/mole.

In 1876, Gibbs proposed an equation for the quantitative dependence of adsorption on surface tension:

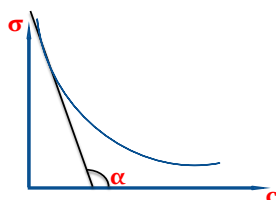
$$\Gamma = -\frac{C}{RT} \frac{d\sigma}{dC}$$

Γ – the amount of dissolved substance on the surface of the liquid;

σ – surface tension;

$\frac{d\sigma}{dC}$ - Rebinder called surface activity

It is determined by the dependency graph $\sigma = f(C)$



$$g = \left(- \frac{d\sigma}{dC} \right) = \operatorname{tg} \alpha$$

When a substance is dissolved in this liquid, the following cases are observed:

1. The dissolved substance lowers the surface tension of the solvent. Such substances are called surface-active agents (surfactant). In relation to water, surfactants are many organic compounds, such as alcohols and acids of the aliphatic series, esters, proteins, etc.

2. The dissolved substance increases the surface tension of the solvent. Such substances are called surface-inactivated agents (SIA). In relation to water, surfactants are inorganic acids, bases, salts, and organic compounds such as glycerol, α -amino acids, and others.

3. The dissolved substance practically does not change the surface tension of the solvent. Mono -, di -, and polysaccharides are surfactants that are inactive in relation to water.

Surfactants can accumulate on the surface of the liquid. This results in positive adsorption. G 0. Surfactants must have a lower surface tension than the solvent and a relatively low solubility. With good solubility, they would tend to go deep into the liquid. In other words, the interaction between surfactant molecules and solvent molecules is always less than the interaction between solvent molecules. Therefore, surfactants will be mainly pushed out of the solution volume to the surface, i.e. G 0. As a result of the accumulation of molecules of these substances on the surface of the solution that interact weakly with each other, the intermolecular interaction in the surface layer decreases and the surface tension falls.

With respect to water, many organic compounds are surface-active, namely fatty acids with a sufficiently large hydrocarbon radical, salts of fatty acids

(Soaps), sulfonic acids and their salts, alcohols, and amines.

Surface activity mainly depends on the chemical structure of substances: the nature of the polar part and the structure of the non-polar part. With increasing asymmetry of molecules (increasing the length of the hydrophobic chain), their surface activity increases. When organic fatty acids are dissolved in water, the surface tension of the water is much lower. G. Duclos and P. Traube found that the more pronounced the polar asymmetry of the molecule, the greater the surface activity of the compound and formulated the following rule: in the series of limiting fatty acids and alcohols, when the chain is extended by one CH_2 group, the surface activity of the homologue in an aqueous solution increases 3-3,5 times (Fig.22.1.).

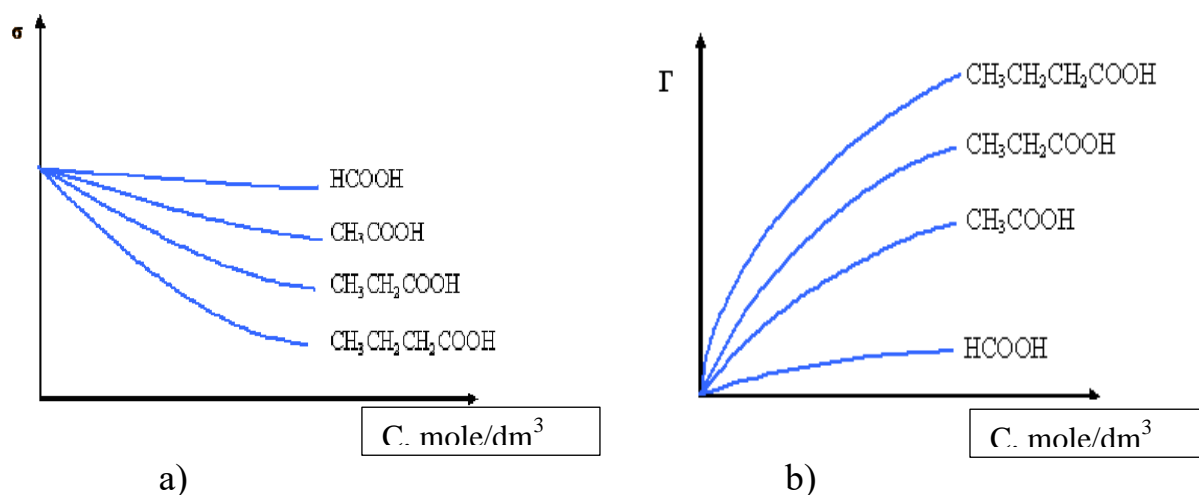


Fig.22.1. Isotherm of surface tension (a) adsorption (b) homologous line of fatty acids

The diphilicity of surfactant molecules is due to their tendency to gather at the phase interface, immersing the hydrophilic part in water and isolating the hydrophobic part from water.

This is most noticeable for such long-chain surfactants with the number of CH_2 groups in the hydrocarbon group 10-20. Surfactants are conventionally designated as: ●—

Chapter 23. Classification of surfactants

a) Low molecular mass surfactants

- Nonionic
- Ionic
- Amphoteric

b) Polymeric surfactants

- Synthetic
- Natural

c) Particles as surfactant

- Spherical or non-spherical
- Hydrophobic and

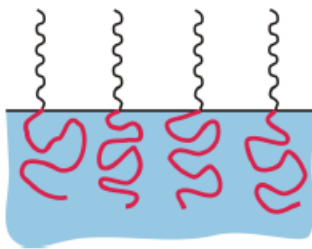
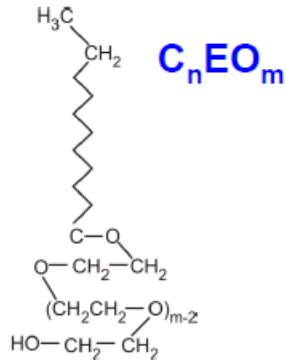
1. Classification of surfactants

- **Low molecular mass surfactants**
 - ✓ **Nonionic**
 - ✓ **Ionic**
 - ✓ **Amphoteric**
- **Polymeric surfactants**
 - ✓ **Synthetic**
 - ✓ **Natural**
- **Particles as surfactant species**
 - ✓ **Spherical vs. non-spherical**
 - ✓ **Hydrophilic vs. hydrophobic**

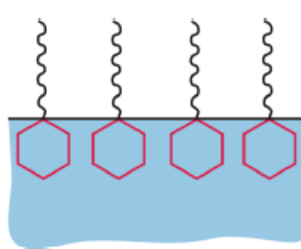
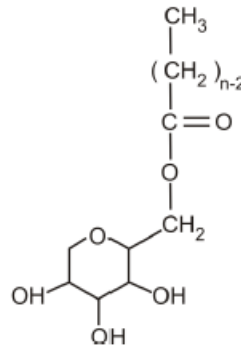
Low-molecular mass surfactants

1. Nonionic surfactants

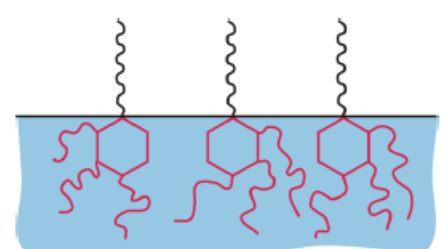
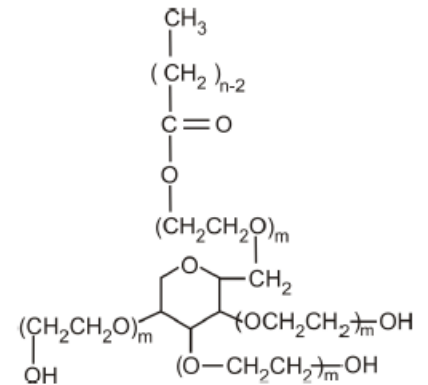
Alkylpolyoxyethylenes



Spans

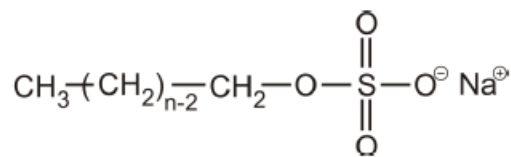


Tweens

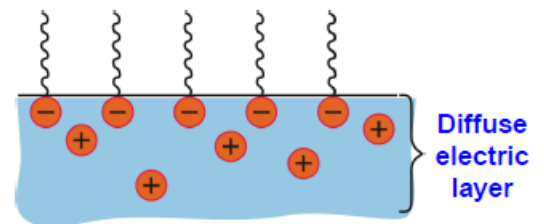


2. Ionic surfactants

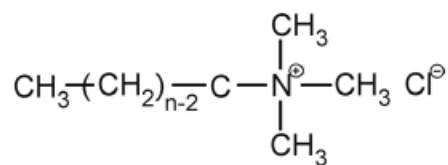
(a) Anionic



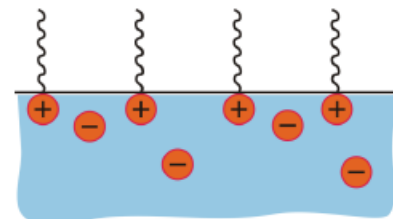
$n=12 \Rightarrow$ sodium dodecyl sulfate, SDS



(b) Cationic

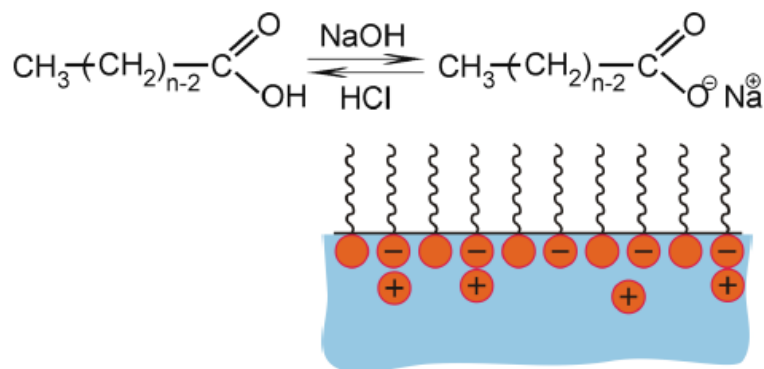


$n=12 \Rightarrow$ dodecyl trimethyl ammonium chloride, DTAC

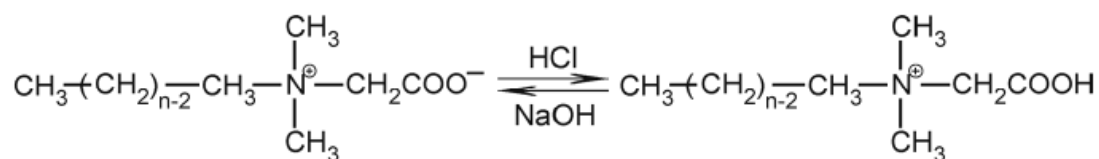


3. Amphoteric surfactants

(a) Natural soaps (alkylcarboxylates), Lipids



(b) Betaines



P. A. Rebinder divided all surfactants of diphilic structure into 2 groups:

- * True soluble surfactants;
- * Colloidal surfactants.

Surfactants of the first group are soluble organic compounds with a smaller radical. They form a molecular dispersion system and are rarely used as surfactants

Colloidal surfactants are substances that with the same solvent, depending on the conditions, form a true and colloidal solution. These include Soaps, detergents etc. For such systems is characterized by the following equilibrium:



As mentioned above, surfactant molecules are diphilic. They consist of polar and non-polar parts. In non-polar groups, there is no affinity for the polar solvent – water; in polar groups, it is high. There is a hydrophobic interaction between nonpolar groups. Due to this and the strong interaction of polar groups with water, surfactant molecules are associated and micelles are formed. The scheme of micelle formation in solutions of colloidal surfactants is shown in

Fig.22.2.

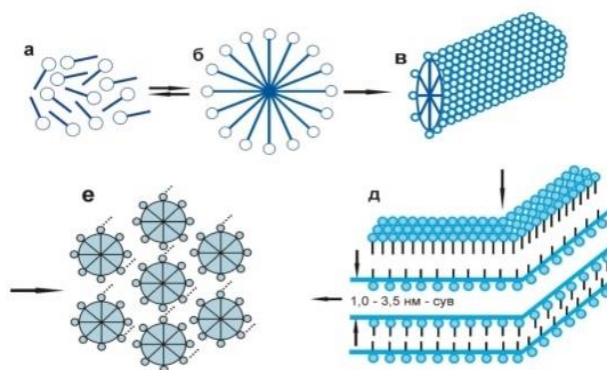


Fig.22.2.Scheme of micelle formation in solutions of colloidal surfactants.

The core of the formed micelles is made up of non-polar radicals, and the outer lining is made up of polar groups. The hydrophilic shell of micelles dramatically reduces the interfacial surface tension at the micelle-liquid (water) boundary. In this case, the micelles are formed spontaneously, and the lyophilicity of the micellar (colloidal) solution and its thermodynamic stability are met.

The minimum concentration of colloidal surfactant, starting from which micelles are formed in its solution, is called the critical micelle concentration (CMC).

The shape of the micelles formed depends on the concentration of the solution. At low concentrations, spherical micelles are formed. Increasing the concentration leads to a change in shape. At higher concentrations, first cylindrical and then lamellar micelles are formed.

In non-aqueous solutions, polar groups interact and reverse micelles are formed:



In the water – phospholipid system, spherical micelles – liposomes-are formed when shaken and stirred. Phospholipid molecules form a bilayer membrane in liposomes, in which polar groups face water and non-polar groups

face each other. Liposomes can be considered as a model of biological membranes. They are widely used for targeted delivery of drugs to certain organs or affected areas. For example, antitumor drugs for the treatment of tumors, insulin for the treatment of diabetes. Liposomes can be used to transport medicinal substances inside cells.

The value of the CMC depends on various factors: the nature of the colloidal surfactant, temperature, and the presence of impurities, especially electrolytes. It was found that with increasing length of the hydrocarbon radical and decreasing temperature, the CMC decreases. For non-ionogenic colloidal solutions of surfactants the presence of electrolytes leads to a decrease in CMC.

One of the most important properties of colloidal surfactant solutions is solubilization. Solubilization is the dissolution in surfactant solutions of those substances that are insoluble in this liquid. For example, as a result of solubilization, hydrocarbon liquids are dissolved in surfactant solutions. In particular, gasoline and kerosene, as well as fats that do not dissolve in water. The mechanism of solubilization consists in the dissolution of nonpolar substances in the hydrophobic core of the micelle. If solubilization occurs, the introduction of non-polar substances in micelles substances, which are called solubilization. If the solubilizate contains polar and non-polar groups, it is located in the micelle with the hydrocarbon end inward, and the polar group faces outward. Solubilization begins when the surfactant concentration reaches the CMC. When the surfactant concentration is higher than the CMC, the number of micelles increases, and solubilization is more intense. The solubilizing capacity of colloidal surfactants increases within this homological range as the number of hydrocarbon radicals increases. Ionogenic surfactants have a greater solubilizing ability compared to non-ionic surfactants. The phenomenon of solubilization is widely used in various sectors of the national economy: in the food industry, in the pharmaceutical industry for obtaining liquid medicinal substances. Solubilization and emulsification are the primary

processes of fat absorption. As a result of solubilization, fats are dissolved in water and then absorbed by the body.

Thus, the bulk properties of solutions of colloidal surfactants are due to the formation of micelles.

Determination of the critical concentration of micelle formation of CMC is based on the fact that at that concentration there is a sharp change in the properties of surfactant solutions. For example, the surface tension of surfactant solutions decreases with an increase in their concentration to CMC, then with a further increase in the concentration ceases to change significantly. This is due to the fact that when the concentration increases above the CMC, all the newly added surfactant passes into micelles. The concentration of the molecular-dissolved surfactant remains constant and equal to CMC. On the curve of the dependence of the surface tension on the logarithm of the concentration, a sharp fracture is detected, the abscissa of which corresponds to the critical concentration of micelle formation.

Laboratory work 11

Determination of critical micelle concentration

Objective: to Determine the critical concentration of micelle formation.

Devices and reagents: Rebinder device, flasks with a capacity of 200 ml-9 PCs, pipette with a capacity of 10 ml-1 PCs, a thermometer with divisions of 0.1-0.2 oC and a temperature interval of 15-40 oC, 0.1 M colloidal surfactant solution, 0.001 M alkali solution, purified water. As a colloidal surfactant solution, you can use sodium oleate, sodium stearate, sodium palmitate, sodium caprylate, etc.

Work procedure:

Prepare 10 solutions of 200 ml of different concentrations so that the expected critical micelle formation falls in the middle of the covered concentration interval. The initial 0.1 M surfactant solution is successively diluted 10 times with 0.001 M alkali solution. The aspirator is filled With water under the faucet, put the

glass to flowing water. In the vessel a, water is poured, closed with a rubber stopper with a capillary. In this case, the tip of the capillary should slightly enter the liquid. All three parts of the device are connected using rubber hoses. Vessel A is placed in a thermostat and waited for to the expected temperature. Record the height of the liquid h_1 in the pressure gauge. Open the bottom tap of the aspirator and present the liquid in it to slowly flow out of the aspirator into the glass.

In the aspirator and connected to it in the vessel, the air is rarefied. Atmospheric pressure pushes air bubbles through the capillary and the surface layer of the liquid in vessel A. When a bubble appears, the pressure gauge indicates the height h_2 , which corresponds to the pressure over the liquid in vessel A after creating a vacuum of air. The difference between h_2 and h_1 gives the pressure P , which is necessary for pushing air bubbles through the capillary opening into this liquid.

$$h_0 = h_2 - h_1$$

h_0 – height of liquid lift in the pressure gauge;

h_1 and h_2 – pressure gauge readings before and after thinning the air over the liquid.

After measuring h_0 , pour water from the vessel And wash it with alcohol or ether and dry it. Then, in turn, solutions of surfactants are poured into the vessel starting from the lowest concentration and the manometer readings are determined for them.

Calculate the height difference for solutions of all concentrations

$$h = h_2 - h_1$$

All measurements are carried out three times, taking the average value.

Calculate the surface tension for all solutions using the formula:

$$\sigma = \sigma_0 \frac{h}{h_0}$$

Here σ and σ_0 are the surface tension of water and surfactant solution, h_0 and h , and the height on the pressure gauge for water and surfactant solution.

After work, the vessel is thoroughly washed. The results are entered in the table:

	Surfactant concentration mole/l	H value				lgC _{surfactant}
		1	2	3	average	
	water					
1						
2						
3						
4						
5						

Using the results obtained, a graph of the dependence of the surface tension on the concentration of the logarithm $\sigma=f(C)$ is plotted. On the graph, find the point of sharp break corresponding to the CMC.

Self-test questions:

1. What is surfactant?
2. What colloidal surfactants are called cationic, anion-active? What is their difference? Given example.
3. What are semi-colloids?
4. Substance which when dissolved will form a micelle?
5. What structure do surfactant micelles have in dilute and concentrated solutions?
6. What is the difference between surfactant micelles and hydrophobic Sol micelles?
7. What is CMC?
8. What methods are used to determine the CMC?
9. What is the mechanism of solubilization?
10. Where is this phenomenon used?

Solubilization of surfactant solutions

To determine the solubilizing ability of surfactants, various methods are used: refractometric, photocolorimetric, turbidimetric, conductometric, etc. These

methods are based on the measurement of certain quantities whose changes during solubilization show the saturation state and calculate the amount of substance absorbed in this state.

Refractometric determination of solubilization

The method is based on the fact that the refractive index of the solution increases as the amount of colloid-dissolved hydrocarbon in it increases, reaching the highest and constant value when the solubilized solution is formed. The determination is usually carried out on a Refractometer of the Abbe and IR454 B2M type. the Principle of operation of such a device is based on phenomena occurring at the interface of media with different refractive indices across the light beam boundary, or rather on the phenomenon of total internal reflection. The optical scheme is shown in Fig.

The test medium is placed on the surface of the measuring prism 4 and pressed on top of the surface of the lighting prism 2. The light from the source passes through the illumination prism 2, falls on the medium under study, where it is refracted. The angle of refraction of light is determined by the physical characteristics of the medium. Light comes out through the measuring prism 4 in the form of an iridescent spectrum, is reflected from the mirror and enters the compensator 5. The compensator consists of several prisms made of special glass.

Measure the refractive index of the surfactant solution. Prepare several solutions with different volumes of benzene and determine the value of the refractive index for each.

On the curve of the refractive index dependence on the volume of added hydrocarbon introduced into a certain amount of surfactant solution, an inflection is observed, indicating that the state of elevation is approaching. Along with solubilization, partial emulsification of the hydrocarbon also occurs. Therefore, the inflection of the curve $n=f(V)$ can only approximate the amount of hydrocarbon solubilized with a surfactant solution at saturation. The true amount of colloid-dissolved hydrocarbon is calculated based on the known rule of additivity of

specific refraction, according to which the specific refraction of the i component mixture is determined by the expression:
$$P \frac{n^2-1}{n^2+2} \cdot \frac{1}{p} = \frac{n_i^2-1}{n_i^2+2} \cdot \frac{1}{p_i} P_i$$

where: P – amount of mixture or component, g; n – refractive index; p – density, g/dm³.

Laboratory work 12

Determination of the solubilizing ability of surfactants

Purpose: to Determine the solubilizing ability of sodium stearate.

Devices and reagents: Refractometer type Abbe and IR454 B2M pipette for 10 ml -1 PC, conical flasks with lapped cork volume of 50 cm³, microfurette, centrifuga0, 1 M of colloidal surfactant solution, benzene. As a colloidal surfactant solution, you can use sodium oleate, sodium stearate, sodium palmitate, sodium caprylate, etc.

Performance of work: in conical flasks with a lapped cork of 50 cm³, a pipette is applied with 10 cm³ of a surfactant solution of the same concentration. From the micro-curette, the hydrocarbon is introduced drop by drop in ascending order from flask to flask, so that the last flask contains a 1.5-2-fold excess of it over the expected solubility.

Tightly closing the flasks with plugs, thoroughly mix the contents of the flask with rotational movements and leave at room temperature for a day to achieve equilibrium solubilization. After complete separation of the emulsions and centrifugation, 1-2 drops over the sedimentary liquid are pipetted onto the prism of the Refractometer and the refractive index for each solution is measured with an accuracy of 1-2. 10⁻³.

The order of the Refractometer IP454 of B2M. Before starting work, check the adjustment of the Refractometer. Adjustment control can be carried out using distilled water or a control plate, preferably at a temperature of 20 ° C on a clean polished measuring prism with a glass rod or pipette, carefully, without touching the prism, apply two or three drops of liquid. Lower the lighting prism and press it with the clasp. Measurements of transparent liquids should be made

in passing light when it passes through an open window of the lighting prism, while the window of the measuring prism is closed by a mirror. Measurement of stained and cloudy samples should be carried out in reflected light. To do this, close the shutter and tilt the mirror to direct the light into the measuring prism, while the dark and light fields change places.

After installing the test sample on the measuring prism, point the eyepiece at the reference visibility of the crosshair. By turning the mirror, you can achieve the best illumination of the scale. By rotating the flywheel, enter the chiaroscuro boundary into the field of view of the eyepiece. Observing through the eyepiece, set the chiaroscuro boundary exactly at the intersection and calculate the refractive index scale. The index for the reference is the fixed vertical stroke of the prism 9. The price of dividing the scale is 5×10^{-4} . Whole, hundredth, and thousandth parts are counted on a scale, and decimal parts are evaluated by eye.

SECTION VIII. HIGH-MOLECULAR COMPOUNDS (HMC). STRUCTURE, CLASSIFICATION, STABILITY. SWELLING AND DISSOLUTION. LIMITED AND UNLIMITED SWELLING

High-molecular compounds include substances consisting of large molecules (macromolecules) with a molecular weight of at least 10,000. The molecular weight of natural high-molecular compounds reaches several million.

Due to their high molecular weight, HMC are non-volatile and cannot be distilled. They easily disintegrate under the influence of the smallest amounts of oxygen and other destructive agents. Most HMC tend to soften gradually when the temperature increases and do not have a specific melting point.

The properties of high-molecular substances depend not only on the size, but also on the shape of the molecules. HMC with isodiametric molecules (for example, hemoglobin, glycogen) are powdered substances. When dissolved, they almost do not swell. Solutions, even at relatively high concentrations, do not have a high viscosity and are subject to the Poiseuille viscosity law, Einstein's diffusion law, and

Van't-Goff's osmotic pressure law.

Chapter 24. Classification of HMC

HMC with highly asymmetric macromolecules (for example, gelatin, cellulose, rubber) swell very much when dissolved and form high-viscosity solutions, and these solutions do not obey the laws that solutions of low-molecular substances obey. Their molecules have a thread-like structure and have mechanical strength. Various fibers and films can be obtained from them. Some polymers have high elasticity. There are natural and synthetic high-molecular compounds.

There are natural and synthetic high-molecular compounds.

Natural HMC -proteins, starch, cellulose-not only form the animal and plant world, but also are part of food raw materials and food products. The most important branches of the pharmaceutical industry are based on the use of natural HMC.

Synthetic HMC are widely used in industry and in everyday life. They are used to produce large quantities of materials that do not exist in nature and with qualities that are not available to natural materials.

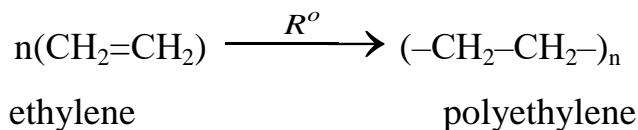
HMC and solutions have a number of properties that are typical for dispersed systems; in addition, they have their own specific properties, which, in particular, include swelling and gelatinization. This led to the formation of a section of colloid chemistry called "colloid chemistry of the HMC " Colloidal and specific properties of HMC solutions play a special role in pharmaceutical technology.

Most synthetic HMC are insoluble in water and are solids. A significant part of the natural, the HMC is able to dissolve in water.

Numerous polymer materials-polyethylene, fluoroplastics, polyamide, polystyrene, phenol-formaldehyde resins, etc. - are synthetic HMC.

HMC consist of macromolecules, which means "giant molecules"; their molecular weight is 10^4 - 10^6 (for example, the molecular weight of water is 18). Macromolecules are formed from a large number of repeating groupings of atoms called links. For polymers with a characteristic monomer units. Polymers are

formed from low-molecular-weight molecules. Molecules can react with each other or with molecules of other substances to form polymers. So, as a result of polymerization of ethylene, polyethylene is formed according to the following scheme:



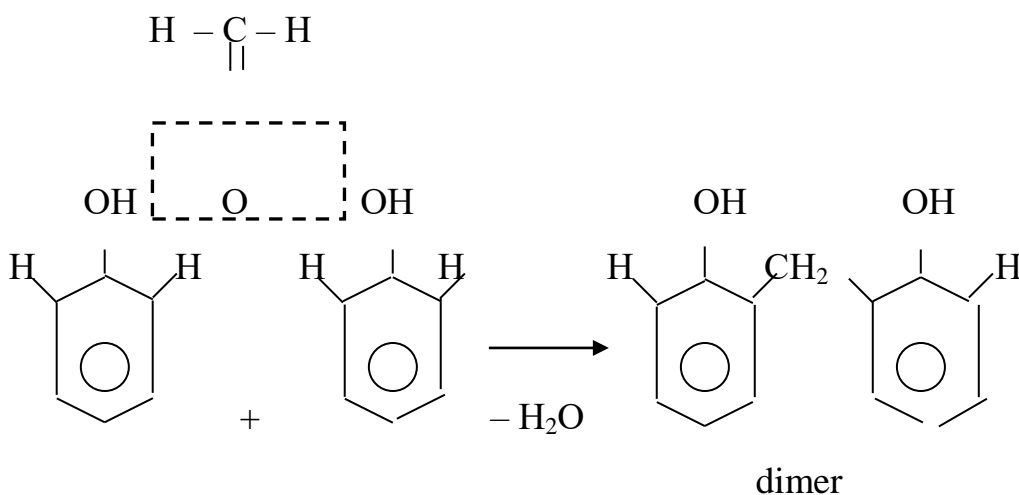
member $-\text{CH}_2-\text{CH}_2-$ are monomers.

The average number of structural units in a polymer molecule (n) is called the degree of polymerization. If the reaction involves molecules of the same monomer, then a homopolymerization reaction occurs, if different monomers-a copolymerization reaction.



When a phenol-formaldehyde resin is formed, a low – molecular compound-water-is formed in addition to the HMC molecule.

This is a polycondensation reaction



Natural or biopolymers include the most important HMC of plant and animal origin: proteins, nucleic acids, polysaccharides (starch, cellulose), natural rubber, etc. Proteins form the basis of all living organisms and are involved in almost all life processes.

Proteins are biopolymers consisting of amino acid residues.

The active substance of the known drug Cerebrolysin is a complex of biologically active neuropeptides derived from the pig's brain, whose molecular weight does not exceed 10,000 daltons. Cerebrolysin has an organ-specific multimodel effect on the brain, i.e. it provides metabolic regulation, neuroprotection, functional neuromodulation and neurotrophic activity.

It should be noted that colloidal chemistry owes its name to solutions of HMC that have an adhesive effect. "Colloid" means glue-like (from the Greek "Kolla" - glue). Thus, at the beginning of the origin of colloid chemistry, i.e. in the 60s of the XIX century, no one doubted that HMC solutions are objects of colloid chemistry. Later, in the 30s of the XX century, HMC solutions were excluded from the objects of colloid chemistry. The basis was the thermodynamic equilibrium of some HMC solutions. Indeed, HMC solutions have dispersion (a certain size of macromolecules) in the absence of heterogeneity, i.e. the phase boundary – one of the essential features of dispersed systems. In this regard, HMC solutions were considered as true, rather than colloidal.

In the last 30 years, a new scientific direction has been defined – colloidal chemistry of HMC (polymers) as an integral part of colloid chemistry.

HMC belong to both true and colloidal solutions. They have the properties of both true and colloidal solutions, as well as specific properties that are unique to them, namely:

as colloidal solutions-the ability to pass into Sol when replacing the solvent; gelation, similar to gelation; Brownian motion, diffusion, light scattering; formation of associates of molecules whose sizes are comparable to particles of highly dispersed particles (elements of heterogeneity), emulsions, suspensions and foams;

as true solutions-lyophilicity, spontaneous formation of solutions, homogeneity under certain conditions, thermodynamic stability;

specific – viscosity anisotropy depending on the structure and properties of the solvent, swelling and gelation.

Natural HMC -proteins, starch, cellulose-not only form the animal and plant world, but also are part of food raw materials and food products.

HMC and solutions have a number of properties that are characteristic of dispersed systems; in addition, they have their own specific properties, which, in particular, include swelling and gelatinization. This led to the formation of a section of colloid chemistry called "colloid chemistry of the HMC". Colloidal and specific properties of HMC solutions play a special role in pharmaceutical technology.

Most synthetic HMC are insoluble in water and are solids. A significant part of the natural, the HMC is able to dissolve in water.

Numerous polymer materials-polyethylene, fluoroplastics, polyamide, polystyrene, phenol-formaldehyde resins, etc. - are synthetic HMC.

The solutions of the HMC are typical of freeze-reversible systems. They form spontaneously and are thermodynamically stable. The dry residue of the HMC is able to spontaneously pass into the solution. These features are typical for true solutions.

At the same time, HMC solutions have some properties of colloidal solutions. The size of the macromolecules of the HMC corresponds to the size of the particles of highly dispersed systems: 1-100 nm, more often 40-80 nm. In a certain situation, HMC macromolecules can be considered as an independent phase. Recall that a phase is a part of the system that is homogeneous in its aggregate state, composition, and properties. A peculiar interface occurs between structures (macromolecules) and a structureless substance (solvent). In addition, macromolecules can interact and form associations. As the concentration of HMC increases or the temperature decreases, the size and lifetime of the associates increase, and their size corresponds to the size of the particles of highly dispersed systems.

Solutions depending on the nature of the solvent can be true or colloidal. Gelatin, for example, is a protein that includes polar groups that have a great affinity for water. Therefore, it is not surprising that in water, when heated, gelatin forms a true solution. But it is only necessary to replace the water with alcohol, as the true

gelatin solution turns into a colloidal one, and a sol is formed.

The reverse transition from colloidal solution to true solution is observed for natural and synthetic rubbers. They are soluble in benzene, gasoline, and other hydrocarbon solvents, but are insoluble in water and form colloidal solutions called latexes in the aqueous medium.

HMC macromolecules do not pass through membranes. For HMC solutions, as well as for true and colloidal solutions, osmosis, reverse osmosis and ultrafiltration are characteristic. HMC macromolecules in a liquid medium contribute to the formation of suspensions, emulsions, and foams. Macromolecules of HMC solutions, like particles of colloidal solutions, are capable of Brownian motion and diffusion, as well as light scattering.

Natural HMC-proteins, polysaccharides, natural rubber are characterized by a constant value of the molecular weight. Synthetic HMC are produced in polymerization and polycondensation processes (plastics, synthetic fibers). They are polydisperse systems, as they consist of a mixture of macromolecules that differ in length and mass. The molecular weight of such polymers is an average value- M . Quantitative changes in the molecular weight lead to a qualitative jump-the appearance of high plasticity and elasticity.

Synthetic HMC are used in technology and in everyday life due to the possibility of easy processing. They are used to produce a variety of plastics, in the form of organic glass, as ionites for water purification and isolation of individual substances from mixtures, for the manufacture of aircraft and car parts, etc. the Advantage of synthetic HMC is that they can be obtained with the desired properties-strength, elasticity, chemical resistance, dielectric constant. At the same time, the raw materials are selected and the technological process is regulated. In addition, products are obtained without loss by direct molding. For the synthesis of the HMC, oil and coal processing products, acetylene, and waste from a number of industries are used.

2. Classification of Polymers

Polymers are classified by different possible:

1. Classification by source;
2. Classification by structure;
3. Classification by synthesis;
4. Classification by molecular forces.

Natural (nucleic acids, polysaccharides, protein, natural rubber (polyisoprene));

Synthetic (polyethelene, teflon, polyvinilchloride, polystyrene).

Classification by structure:

Linear polymers. In these polymers, the monomers are joined together to form long straight chains of polymer molecules. Because of the close packing of polymer chains, linear polymers have high melting point, high densities and high tensile (pulling) strength.

Branched chain polymers. In these polymers, the monomer units not only combine to produce the linear chain (called the main chain) but also form branches along the main chain

Three-dimensional network polymers. In these polymers, the initially formed linear polymer chains are joined together to form a three-dimensional network structure. These polymers are also called cross-linked polymers The high-molecular compounds are compounds, which have 10.000 -10.000.000 Da molecular mass.

Biological role of polymers

1. Biopolymers, have a lot functions:
2. Catalytic effect– enzymes;
3. As regulators – hormones;
4. is the storage and transfer of genetic information.(DNA);
5. Storage energy (Starch, glycogen);
6. Protection - immunoglobulin;
7. Structural (collagen, keratins, fibril).

There are macromolecules everywhere, inside us and outside us. Some are natural: they include polysaccharides such as cellulose, polypeptides such as enzymes, and nucleic acids such as DNA. Others are synthetic: they include polymers such as nylon and polystyrene that are manufactured by stringing together and (in some cases) cross-linking smaller units known as monomers.

Life in all its forms, from its intrinsic nature to its technological interaction with its environment, is the chemistry of macromolecules.

Most of the reactions that have been examined so far have involved reactants and products of low molecular mass. Some of the most important organic compounds made by chemists, however, are giant molecules called polymers.

A polymer is a large molecule formed by the covalent bonding of repeating smaller molecules. Most polymerization reactions require a catalyst.

Monomers are molecules that combine to form the repeating unit of a polymer. Some polymers contain only one type of monomer. Others contain two or more types of monomers. The two most common ways for monomers to be joined are addition polymerization and condensation polymerization.

Synthesis of polymers

Addition polymerization occurs when unsaturated monomers react to form a polymer.

Addition polymerization occurs when unsaturated monomers react to form a polymer. It is a specific type of addition reaction. Ethene undergoes addition polymerization. The molecules bond one to another to form the long-chain polymer polyethylene.

Polyethylene is an important industrial product because it is chemically resistant and easy to clean. It is used to make refrigerator dishes, plastic milk bottles, laboratory wash bottles, and many other familiar items found in homes and laboratories. By shortening or lengthening the carbon chains, chemists can control

the physical properties of polyethylene.

Polyethylene containing relatively short chains ($x = 100$) has the consistency of paraffin wax. Polyethylene with long chains ($x = 1000$) is harder and more rigid.

Polymers of substituted ethenes can also be prepared. Many of these polymers have useful properties.

Condensation polymers are formed by the head-to-tail joining of monomer units. This is usually accompanied by the loss of a small molecule, such as water. The formation of polyesters is an example of condensation. Polyesters are high-formula-mass polymers consisting of many repeating units of dicarboxylic acids and dihydroxy alcohols joined by ester bonds.

The formation of a polyester is represented by a block diagram. Note that condensation polymerization always requires that there be two functional groups on each molecule.

Homopolymers and copolymers. Depending upon the nature of the relocating structural unit, polymers are divided into two categories:

- (1) Homopolymers
- (2) Co-polymers.

Polymers are classified in a number of ways:

- (a) Classification based upon source,
- (b) Classification based upon structure,
- (c) Classification based upon synthesis and
- (d) Classification based upon molecular forces.

I. Classification based upon source:

1. Natural (nucleic acids, polysaccharides, protein, natural rubber (polyisoprene));
2. Synthetic (polyethelene, teflon, polyvinylchloride, polystyrene).

II. On the basis of structures, polymers are divided into three types:

Linear polymers.

In these polymers, the monomers are joined together to form long straight chains of polymer molecules. Because of the close packing of polymer chains, linear polymers have high melting point, high densities and high tensile (pulling) strength.

Branched chain polymers.

In these polymers, the monomer units not only combine to produce the linear chain (called the main chain) but also form branches along the main chain

Three-dimensional network polymers.

In these polymers, the initially formed linear polymer chains are joined together to form a three-dimensional network structure. Only two cross-links per polymer chain are required to join together all the long chain polymer molecules to form a giant molecule. Because of the presence of cross-links, these polymers are also called cross-linked polymers. These polymers are hard, rigid and brittle.

There is great value of form of macromolecules (Fig. 24.1.).

III. By molecule form

1. Globular.
2. Fibril.

IV. By nature atoms, which are in molecule of polymer

1. Carbon contain polymers
2. Hetero polymers
3. Element organic
4. Inorganic

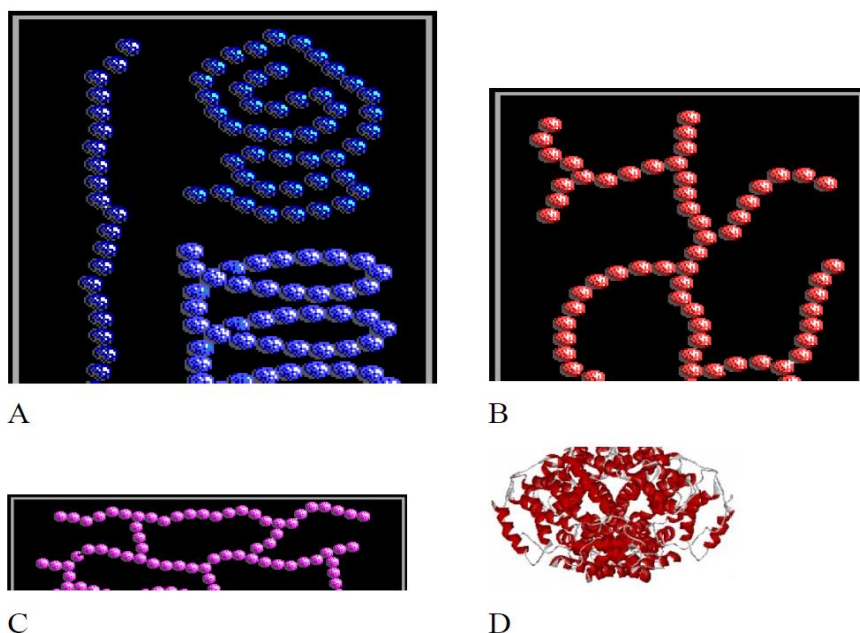
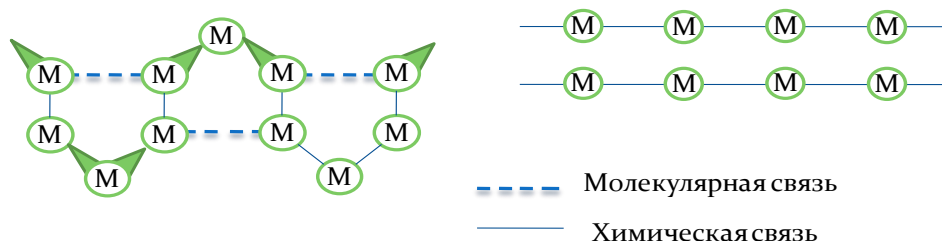


Fig. 24.1. Forms of macromolecules (a-liner, b-branched, c- spatial, d-globular)

Chemical structure and spatial shape of macromolecules

Properties of polymer materials are determined by chemical and molecular bonds. The chemical bonds between monomer units can be present in the form of $-M - M - M -$. These are strong bonds to energy. Molecular bonds occur between polymer chains or different parts of the same chain:



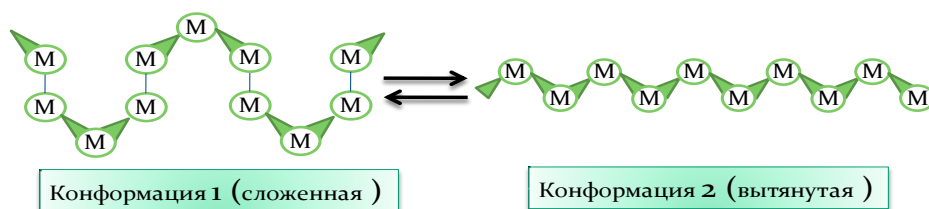
The energy of a single molecular bond . This value is small: 40 times less of the energy of the chemical bond. But there are many such bonds, and their influence on the properties of polymer substances is no less significant than the influence of chemical bonds. For example, when a polymer substance is heated, its evaporation is impossible. Indeed, at 400K (127°C), the average kinetic energy of the thermal movement of the link, equal to $3/2 RT$, is about 5 kJ/mol. Sending this energy to one Monomeric unit will not change the state of other Monomeric units.

For polymer molecules (macromolecules), an important characteristic is the

flexibility of the chain – the ability of macromolecules to change the spatial shape by moving from one conformation to another.

Conformation of macromolecules of the HMC – energy equivalent spatial forms that occur when turning Monomeric links of polymer chains without breaking the chemical bond.

For example, an HMC molecule can go from a complex to an elongated conformation:



Due to the thermal movement of the links, the most likely conformation of the HMC molecule is a tangle, or globule. For rice.2 the HMC globule is presented (Fig..24.2.).

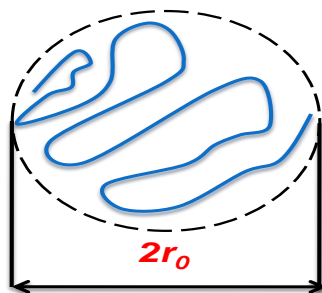


Fig..24.2. Globule of HMC. r_0 - sphere radius

Chapter 25. Dissolution and swelling

The interaction of the HMC with the solvent begins with the swelling process, which either stops at a certain stage, or ends with the dissolution of the polymer.

Swelling is a spontaneous process of absorption by the polymer accompanied by an increase in the volume and mass of the sample.

Upon contact of the polymer with the solvent, the mutual diffusion of the solvent molecules into the polymer and the polymer macromolecules into the solvent begins. However, the rate of diffusion in one direction and the other will

differ in the same proportion as the size and mobility of the diffused particles. Sharp changes in the mobility of solvent molecules and macromolecules cause swelling.

Quantitatively swelling is measured by the degree of swelling which has a volume and mass expression: $\alpha_m = \frac{m - m_o}{m_o}$ or $\alpha_v = \frac{v - v_o}{v_o}$

where: m_o - initial mass; v_o - initial volume of the polymer sample; m - mass; v - volume of the swollen sample.

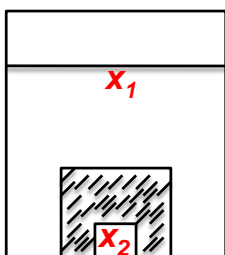


Fig.25.1. Increasing of volume and mass

During swelling process samples:
 X_1 — solvent; X_2 — swelling polymer
 sample:

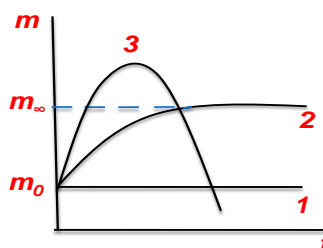


Fig.25.2. Swelling kinetics of HMC with different

of polymer chains 1 - ebonite in benzene;
 2 - rubber in gasoline and gelatin in cold water;
 3 - gelatin in hot water and natural rubber in benzene

Fig.25.1. and 25.2. schematically shows the swelling of the polymer. The degree of swelling depends on the stiffness of the polymer chains. In rigid polymers with a large number of cross-links (cross-links) between the chains, the degree of swelling is small. For example, ebonites-highly vulcanized rubbers-practically do not swell in benzene (curve 1). Rubbers do not swell in gasoline (curve 2). Gelatin in cold water is also characterized by limited swelling. Adding hot water to gelatin or benzene to natural rubber results in unlimited swelling of these polymers (curve 3).

With limited swelling (curve 2), α reaches the limit value, after which the swelling does not depend on time (as gelatin swells in cold water).

Unlimited swelling is characterized by a dependence (curve 3) that passes through the maximum, after which the α drops to zero as a result of gradual dissolution of the polymer (gelatin in hot water).

The limited or unlimited swelling is determined by the ratio of the bond energy in the polymer to the solvation energy and the entropy factor. In linear and branched polymers, macromolecules are bound by van der Waals forces, the energy of these bonds is small, so the solvation energy and entropy factor already exceed them at room temperature. Under these conditions, the swelling is unlimited. If there are chemical bonds between the polymer chains, then the solvation energy and the entropy factor are not enough to break them. Swelling is limited, and the polymer turns into jelly. Swelling cannot be considered a purely physical phenomenon in which solvent molecules mechanically penetrate the spaces between the polymer chains. At the core of the swelling process is the solvation of the macromolecular chains. The solvation mechanism of swelling is indicated by the release of the heat of swelling and contraction (a decrease in the total volume of the system). The reason for the contraction is the orientation of the solvent molecules in the solvate layers. Swelling, like solvation, is specific, since the polymer swells in a solvent corresponding to its nature.

Swelling plays an important role in the life of organisms. Thus, when the connective tissues of the kidney swell, excess water is released from the slag solutions, which then returns to the blood.

When choosing in the field of medical use of HMC, determining the degree of swelling is one of the important factors. For example, synthetic polymers that are used to make contact lenses must be limited to swell in the humid environment of the eye to give the material certain optical properties.

The degree of swelling of the polymer depends on its nature and the nature of the solvent. The polymer swells better in a solvent whose molecular interactions with macromolecules are large. Polar polymers swell in polar liquids (protein in water), and non – polar polymers swell in non-polar liquids (rubber in benzene).

Limited swelling is similar to limited solubility. As a result, jellies are formed.

In addition to the nature of the solvent on the swelling, the HMC is influenced by the presence of electrolytes, pH, temperature, pressure, degree of comminution, age of the substance.

The pressure of swelling. A significant increase in volume due to the penetration of the solvent leads to an osmotic pressure in it that is almost equal to the swelling pressure.

When polymers swell, their volume increases by 10-15 times and there is a swelling pressure that sometimes reaches hundreds of megapascals. This pressure is easily detected when an obstacle prevents an increase in the volume of the sample and can cause a rupture of containers filled with swollen materials.

Polymer solutions in well-dissolving liquids are aggregatively stable. You can break the stability of polymer solutions by worsening the solubility of the HMC-by introducing electrolytes or non-solvents.

Under the influence of electrolytes and non-solvents, the process of separating the HMC from the solution is called salting. The concentration of the electrolyte at which rapid deposition of the polymer occurs is called the HMC salting threshold.

Usually, the stronger salting effect is caused by anions that are located in the lyotropic series: $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{Br}^- > \text{I}^- > \text{CNS}^-$

The series for cations has the form: $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$

Salting out the HMC is of great practical importance. It is used for fractionation of proteins, polysaccharides and other substances.

In concentrated HMC solutions, associates can occur, which then become embryos of a new phase. Isolation of the newly formed phase in the form of tiny drops is called coacervation, and the resulting two-phase system is called coacervate. Coacervate is a thermodynamically nonequilibrium system similar in properties to emulsions. The process of coacervation is facilitated not only by a high concentration, but also by a low temperature, a change in the pH of the

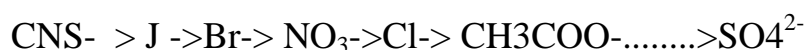
medium, and the introduction of low-molecular-weight electrolytes.

The practical importance of coacervation has increased with the development of microencapsulation technology.

Microcapsulation in the pharmaceutical industry is used to protect the medicinal substance from contact with the environment. Microcapsules are solid, liquid, or gaseous medicinal substances enclosed in a polymer envelope. Their shell is formed from adsorbed droplets of polymer coacervate, which merge into a solid film and are transferred to a solid state by special treatment.

Solutions of HMC as true solutions, and stable aggregate state is thermodynamically stable. As conditions change, due to the large dimensions of macromolecules HMC stability is violated. It arises at: centrifugation, dehydration, change pH (it is less pH=3 more pH=10), that is in sour and alkaline environments. Polymer solutions are stable over the pH range 4 to 9. To physical factors influencing stability of solutions of HMC are negative: temperature is higher than 500C; multiple freezing and thawing; buildup of pressure; ultrasound action; ultraviolet rays; radiation; introduction of electrolytes. The process of selecting the HMC from the solution by desolvation of macromolecules electrolytes called salting-out.

Salting-out reversible and require high concentrations (in contrast to the coagulation) salting-out effect depends on the electrolyte hydration abilities. In 1889 W. Hofmeister showed that salted-out mainly anions. By the force of the action he placed them in a row: Anions are arranged so:



- Ions standing in a row to the left of the chlorine ion reduce resistance, right - increase. The concentration of the electrolyte, at which a rapid precipitation of the polymer is called the threshold salting-out of HMC (Fig.25.3.).

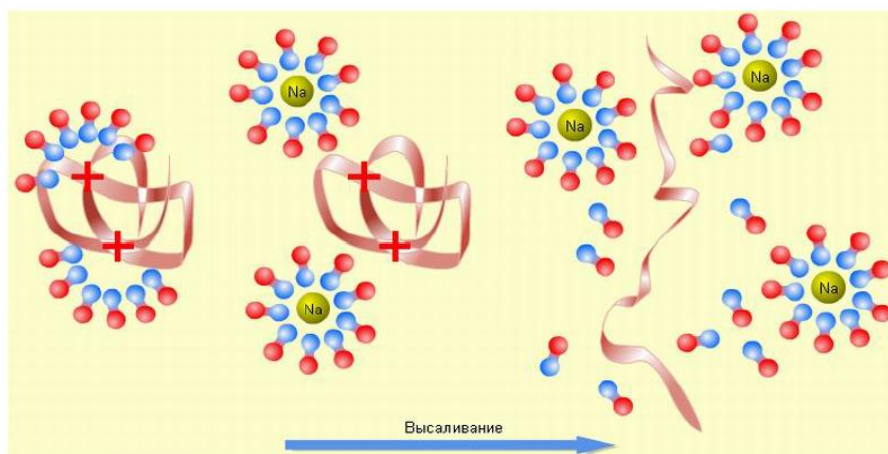


Fig.25.3.Salting-out b electrolytes

Laboratory work 13

Determination of the degree of swelling

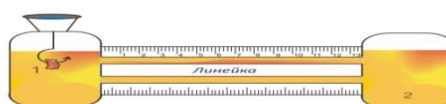
When preparing for the work, you need to study the following questions:

1. The concept of the HMC, obtaining and classification;
2. Structure, shape of macromolecules and types of connections between them;
3. Internal growth of the macromolecules;
4. The concept of molecular weight of the HMC;
5. Swelling and dissolution of the HMC;
6. Limited and unlimited swelling;
7. The degree of swelling and factors affecting on the degree of swelling.

Objective: to Determine the degree of swelling of rubber in benzene

Apparatus and reagents: nebulizer, benzene or toluene, plate rubber, analytical scale, roznowski, thin wire.

Operation: the Device shown in Fig.8, is two tanks connected by two graduated tubes. One of the tanks has a wide neck with a stopper for securing the sample.



Device for investigation of swelling kinetics.

Before starting work, note the temperature at which the experiment will be performed (room temperature). Weigh on the scales a rubber plate (m_0). The plate is strengthened with a thin wire on the hook of the device. The solvent is poured into the tank 1, then poured into the tank 2. Count the level on the graduated tube. The solvent should be taken so much that its level is not lower than the second small division, counting from top to bottom. Then the solvent is again poured into the first tank and closed with a stopper with the sample (make sure that the sample is completely immersed in the solvent). Notice the start time of swelling. Then, at certain intervals (at the beginning of the observation after 5 minutes, at the end – after 10 minutes), the solvent level is counted. Counts are made up to hundredths of a ml. These operations are performed for 3-4 hours until the swelling stops. At the end of swelling, the rubber plate is removed from the device, the wire with which it was suspended is removed, carefully dried with filter paper and immediately weighed (m). The remaining solvent is poured into a container intended for it, and the used rubber is placed in a flask for the processed samples. Experimental and calculated data are recorded in a table.

Table 1

Countdown time	Time elapsed from the beginning of the experiment, min	Solvent level in the graduated tube Solvent level in the graduated tube	Total amount of solvent absorbed		
			M_{π}	Γp	% from the mass of the original sample, %

The table shows the values to be calculated. When calculating the number of milliliters absorbed by the solvent sample into grams, the solvent density should be taken into account (for benzene $b=0.88$; for toluene $b=0.87$; for xylene $b=0.86$).

Knowing the mass of the polymer before swelling (m_0) and after swelling

(m), the degree of swelling is calculated:

$$\alpha = \frac{m - m_0}{m_0} \quad \text{or} \quad \alpha = \frac{m - m_0}{m_0} \cdot 100\%$$

Plot the dependence of the height of the liquid absorbed by the sample of rubber on the time of swelling.

Self-test questions:

1. What is the peculiarity of the process of dissolving the HMC?
2. What are the causes of swelling in the HMC?
3. What stages does the swelling process consist of?
4. What factors influence the swelling process?
5. Limited and unlimited swelling. Degree of swelling.
6. What is the degree of swelling?
7. How to carry out the measurement of the degree of swelling?

SECTION IX. THE VISCOSITY OF DISPERSE SYSTEMS. STAUDINGER EQUATION. THE OSMOTIC PRESSURE OF HMC SOLUTIONS. JELLIES AND GELS. THEIR IMPORTANCE IN PHARMACY.

Chapter 26. The viscosity of HMS solutions

A characteristic feature of HMC solutions is their high viscosity compared to pure solvent, even at low concentrations. This property is especially strong in polymers with long linear macromolecules. Solutions of polymers with the same molecular weight, but the spherical shape of the molecules have a lower viscosity. It follows that the viscosity of polymer solutions increases in proportion to the asymmetry of their molecules. With the same chemical structure of molecules, the viscosity of solutions increases with increasing molecular weight. The viscosity also depends on the polymer concentration.

Highly diluted HMC solutions obey the laws of Newton and Poiseuille. Increasing the temperature and dilution reduce deviations from the laws of Newton and Poiseuille. Medium-concentration solutions behave like abnormally non-Newtonian fluids.

The anomaly in the viscosity of HMC solutions can be explained by the fact that large macromolecules of polymers interact with each other, forming associates and easily destructible structures. Viscosity (internal friction) is a measure of the resistance of a medium to movement.

This value is characterized by a viscosity coefficient η

I. Newton for laminar (layer-by-layer) fluid flow established the dependence

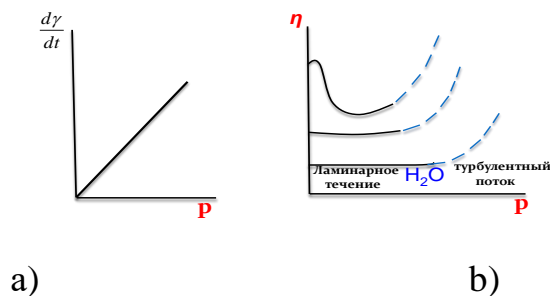
$$P = \eta \frac{d\gamma}{dt}$$

where: P – voltage, Pa; η – the coefficient of dynamic viscosity, Pa*s;

$\frac{d\gamma}{dt}$ – the rate of relative deformation, c⁻¹.

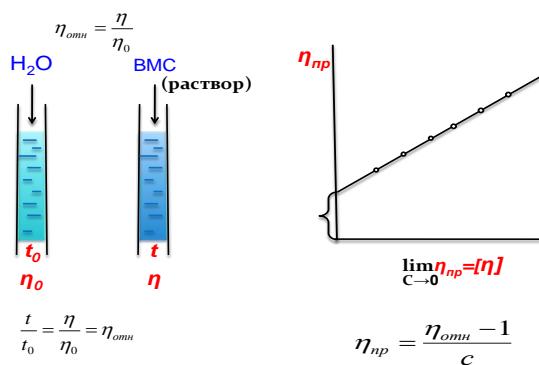
For polymer solutions, as stated above, they do not obey Newton's law. The dependence of the viscosity coefficient η on the voltage P is complex (Fig.6) and is described theoretically approximately, since the viscosity theory is developed only for dilute solutions.

If describe viscosity coefficient of the solvent via η_0 , but viscosity coefficient of the solvent HMC via $\eta_{solution}$, which relationship this values η_{p-p}/η_0 will equal to the expiration time ratio t/t_0 via capillary (Fig.7) and is called relative viscosity:



The dependence of the relative deformation rate for the laminar flow of Newtonian fluids (a) and the coefficient of dynamic viscosity of water and HMC solutions (s1, c2) on the applied motion

(b)



Relative $\eta_{rel.}$, reduced $\eta_{pr.}$ and intrinsic $[\eta]$ viscosity and the relationship between them
The specific viscosity determined by the formula is also used.

$$\eta_{y\delta.} = \frac{\eta_{p-p} - \eta_0}{\eta_0} = \eta_{omh.} - 1$$

And given viscosity: $\eta_{np.} = \frac{\eta_{y\delta.}}{C}$

where C is the concentration of the HMC in solution.

For small concentration ranges, there is a simple dependence $\eta_{np.} = a + bC$ where a, b – constant coefficients.

The graph of this dependence is a straight line from Fig. 7 that the segment cut off by a straight line on the ordinate axis,

$$a = \lim_{C \rightarrow 0} \eta_{np.} = [\eta]$$

The value of a is determined experimentally and is called the characteristic viscosity of the polymer. The intrinsic viscosity is related to the molar mass of the polymer by the Staudinger formula:

$$[\eta] = K \cdot M^\alpha$$

where K is the coefficient of proportionality determined experimentally;

α – a measure of the degree that varies within $\frac{1}{2} \leq \alpha \leq 1$.

The value α takes extreme values of $\frac{1}{2}$ for flexible (globules) and 1 for hard (sticks) polymers. The formula established by Staudinger empirically is used in

experimental measurements of the molecular weight of HMC. It follows from the Staudinger formula that the viscous flow of polymers is associated with the conformation of molecular chains and, therefore, with their rigidity. With an increase in the flow, the tangles (spheres) of the HMC molecules are stretched in the jets of liquid, and the flow resistance decreases. Molecules can stretch along these jets or across, changing the viscosity of the HMC solution.

By finding the intrinsic viscosity of the solution, the molar mass of the polymer can be calculated. To do this, log the Staudinger equation

$$\lg[\eta] = \lg K - \alpha \lg M$$

And calculate the molecular weight according to the formula:

$$\lg M = \frac{1}{\alpha} (\lg K - \lg[\eta])$$

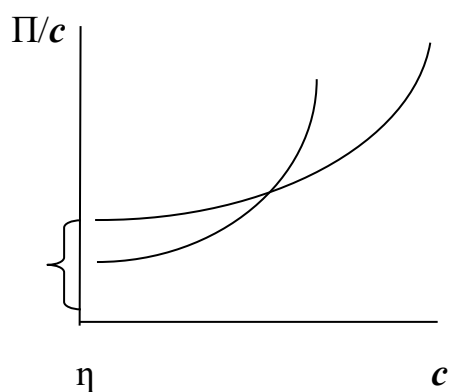
Osmotic pressure of solutions of the HMC

The osmotic pressure of HMC solutions can be measured with sufficient accuracy. By measuring osmotic pressure, you can determine the molecular weight of the HMC. This method is called osmometry.

As the concentration of HMCs increases, their osmotic pressure ceases to obey the Van't-Goff law and increases faster. The reason for this deviation is the flexibility of the HMC chains, due to which they behave like several short molecules. Haller proposed a more General equation for the osmotic pressure of HMC solutions: $\Pi = \frac{cRT}{M} + bc^2$

where b is a constant that characterizes deviations from the Van't-Goff law. It depends on the nature of the solvent and the solute, but does not depend on the molar mass of the solute. This equation can be represented as a straight line equation:

The constant b can be determined from the graph of the dependence of Π / c on C, as the tangent of the angle of inclination of the straight line to the abscissa axis.



The cut-off segment on the ordinate axis is equal to RT/M . Substituting this value into the Van't-Goff equation, we find the molecular mass of m .

"SWOT" game-analysis method

Comparison of specific and colloidal properties of solutions of the HMC

Distinctive features of HMC solutions	Properties of HMC solutions that characterized of colloidal systems

Students are given out handouts (forms) with a sign: "SWOT" game is an analysis method and they explain the conditions of the tasks. To complete the task, 5-7 minutes are given.

Properties of HMC solutions

The properties of polymers change significantly with the addition of low molecular weight compounds. For example, if a cellophane film consisting of cellulose is moistened with glycerol, small glycerol molecules penetrate the space between the cellulose molecules and form a kind of lubricant. In this case, intermolecular bonds are weakened and the film becomes more plastic.

Increasing the plasticity of the polymer with a small amount of HMC is called plasticization of the polymer.

I. Newton for the laminar (layer-by-layer) fluid flow established a relationship

$$P = \eta \frac{d\gamma}{dt}$$

where: P – voltage, Pa; η – the coefficient of dynamic viscosity, Pa*s;

$\frac{d\gamma}{dt}$ – relative deformation rate, s⁻¹.

For polymer solutions, it is shown that they do not obey Newton's law. The dependence of the viscosity coefficient η on the voltage P is complex (Fig.6) and is described theoretically approximately, since the viscosity theory is developed only for dilute solutions.

A characteristic feature of HMC solutions is their high viscosity compared to pure solvent, even at low concentrations.

Viscosity (η) is the internal friction between layers of a given substance moving relative to each other.

This property is especially strong in polymers with long linear macromolecules. Solutions of polymers with the same molecular weight, but the spherical shape of the molecules (globular HMCs) have a lower viscosity. It follows that the viscosity of polymer solutions increases in proportion to the asymmetry of their molecules. With the same chemical structure of the molecules, the viscosity naturally increases with increasing molecular weight. The viscosity of solutions depends on their nature, temperature, pressure, and the concentration of the solute.

Molecular weight is an important characteristic of any high-molecular compound, which determines all its main properties. Since in the process of obtaining an HMC, mixtures of polymers with different chain lengths are formed, and therefore with different molecular weights (mixtures of polymerhomologists), we have to talk only about their average molecular weight. This average value depends on which experimental method was used to find it. Usually the molecular weight of polymers is expressed in terms of so called average numbers (\bar{M}_n) and

average mass values (\bar{M}_w).

Average numbers molecular weight (\bar{M}_n) they are found using methods that allow us to determine the number of molecules in the studied solution of HMC. These include osmotic, cryoscopic and ebullioscopy methods. Average mass molecular weight (\bar{M}_w) is determined using those methods that allow you to set the average size of the molecule in the solution. Such methods include, for example, determining the molecular weight by the rate of diffusion, sedimentation in an ultracentrifuge, and light scattering.

For high molecular weight compounds with the same molecular weight

$\bar{M}_n = \bar{M}_w$, that is, polymers are monodispersed. With a high content of low-molecular fractions, the differences between \bar{M}_n и \bar{M}_w the ratio also increases dramatically \bar{M}_n / \bar{M}_w become large.

The average molecular weight found by the methods of osmometry, cryometry or ebulliometry does not allow one to judge the average mass of individual polymer fractions. Such information is provided by the mass-average molecular weight found by the method of viscometry, which is based on the Staudinger equation.

When measuring the molecular weight by the viscometric method, an average molecular weight, which is the average between \bar{M}_n и \bar{M}_w , close at the same time \bar{M}_w .

The viscometric method is the simplest and most practical method for determining the average molecular weight of an HMC. In this case, the viscosity of the test solution is determined using a capillary viscometer (Fig. 4) and the molecular weight is calculated using the Staudinger equations.

For dilute HMC solutions with long molecules, Staudinger found the following relationship between viscosity and the concentration of a substance in a solution:

$$\frac{\eta_{y\partial}}{C} = K \cdot M, \text{ where}$$

K - constant for a given polymer-homologous series in a given solvent;

$\eta_{y\partial}$ - specific viscosity of polymer solution with a specific concentration;

C – concentration of solvent; M – molecular weight of the polymer;

Relationship of $\eta_{y\partial}/C$ – called reduced viscosity, i.e. the ratio of specific viscosity to solution concentration does not depend on the concentration of the polymer solution and is proportional to its molecular weight.

At present, the Mark - Howing equation has been proposed to determine the molecular mass, taking into account the interaction of macromolecules even in dilute solutions and the change in constant (K) with the length of the molecule

$$[\eta] = K \cdot M^\alpha, \text{ where} \quad (I)$$

$[\eta]$ - characteristic viscosity of polymer solution;

α - a value characterizing the shape of macromolecules (degree of bending, torsion of HMC macromolecules in solution)

To use equation (I) to calculate the molecular weight, it is necessary to know the relative viscosity of the HMC solution

$$\eta_{OTH} = \frac{t_{p-p}}{t_{p-путель}} \quad (2);$$

$t_{solvent}$ - solvent flow time through the capillary of a viscometer;

$t_{solution}$ - solution flow time through the capillary of a viscometer.

The specific viscosity of the solution is calculated by the following formula:

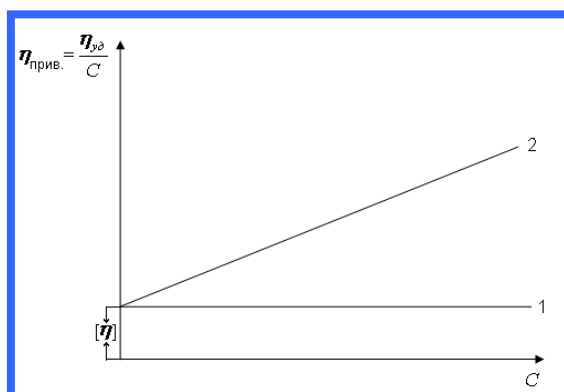
$$\eta_{y\partial} = \frac{t_{p-p} - t_{p-путель}}{t_{p-путель}} = \eta_{OTH} - 1, \quad (3)$$

The ratio of the specific viscosity of the concentration of the solution is called reduced viscosity and is determined by the equation:

$$\eta_{\text{прив.}} = \frac{\eta_{\text{уд}}}{C}$$

The reduced viscosity usually increases with increasing concentration of the high polymer, and this increase in the range of low concentrations occurs in a straight line (Fig. 9). The increase in η_{specific}/C is explained by the interaction of macromolecules with each other. The dependence is linear only in the region of low concentrations. The reduced viscosity is usually determined for several concentrations and the resulting curve is extrapolated to zero concentration. The segment cut off on the ordinate axis gives the value of the so-called characteristic viscosity $[\eta]$ and represents the viscosity with an infinitely large dilution of the

$$\text{solution: } [\eta] = \lim_{C \rightarrow 0} \left(\frac{\eta_{\text{уд}}}{C} \right)$$



The dependence of the reduced viscosity on the concentration polymer:
 1 - a solution with reduced viscosity, independent of C;
 2 - a solution whose reduced viscosity increases with C.

The intrinsic viscosity is found graphically and the molecular weight of the IUD is determined by its magnitude.

Having determined these values and making viscometric measurements, it is possible to calculate the molecular weight of any other homologous polymer homologue from equation (1) and evaluate the shape of macromolecules of a high molecular weight compound.

Experiments and theory show that the characteristic viscosity and slope of

the straight line depend not only on the molecular weight, but also on the nature of the solvent, on its thermodynamic affinity for the polymer.

In very dilute solutions, isolated polymer macromolecules with flexible chains, because of their ability to bend, acquire a ball-like shape. During the rotation of glomerular molecules and their translational movement, friction of segments of macromolecules and solvent molecules occurs, which manifests itself in an increase in the viscosity of solutions in comparison with the viscosity of a pure solvent and is estimated by the value. The larger the size of the ball, the greater the friction force and.

The size of the coil depends on the nature of the solvent. The larger the polymer's solvent means, the more the coil swells in the solvent, the larger its size (with the same molecular weight), the larger.

K value and α for some polymers

Polymer	Solvent	T, °C	K	α
Polystyrene	Toluene	30	$5,4 \cdot 10^{-4}$	0,66
polymethyl methacrylate	benzene	25	$0,94 \cdot 10^{-4}$	0,76
polyvinyl alcohol	water	50	$5,9 \cdot 10^{-4}$	0,67

Laboratory work 14

Viscosimetric determination of the molecular weight of high-molecular compounds

When preparing for work, you should study the following questions from the textbook:

1. The viscosity of HMS solutions;
2. What is the essence of the laws of Newton and Poiseuille?
3. What liquids are classified as Newtonian or non-Newtonian?
4. Specific, reduced and characteristic viscosity;
5. Methods for determining viscosity;
6. Methods for determining the molecular weight of polymers

Objective: to Determine the molecular weight of a high-molecular substance using a viscometer using an Ostwald viscometer.

Devices and reagents:

Solutions of high-molecular compound-polyvinyl alcohol, polyvinylpyrrolidone, polystyrene or sodium salt of carboxymethylcellulose, Ostwald viscometer, thermostat, stopwatch.

The device of the viscometer of Ostwald

The viscosity of liquids is easily determined experimentally by the expiration time under the pressure of the volume of the liquid through the capillary of radius r and length ℓ . The relationship between these values is given by the poiseille formula:

$$\eta = \frac{\pi r^4 \rho \tau}{8 \rho \ell}$$

The expiration time is found using a viscometer, the simplest type of which is shown in Fig.11. The viscometer consists of two communicating glass tubes 1 and 2. The tube 1 has an extension 3, passing into the capillary 4. The test liquid flows under the influence of its own gravity into the tube 7. Above and below extension 3, there are marks 5 and 6 on tube 1. The volume of the expanded part of the tube is usually 3-4ml.

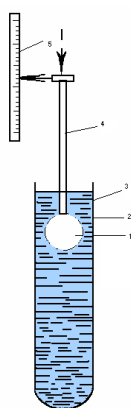
Viscosity changes dramatically with temperature, so it should be measured in a thermostat at a constant temperature. An increase in temperature leads to a decrease in viscosity.

Execution of work:

Before working, the viscometer must be washed with a chrome mixture and distilled water and dried in a drying Cabinet. The viscometer is fixed vertically in a thermostat in which the water is heated to a certain temperature. In the wide elbow 7 of the U-shaped tube, pour as many (and later as many) milliliters of solvent with a pipette, which then fills the narrow part 4 above the mark 5 and so that the capillary 4 and the extension 3 are completely immersed in the thermostating liquid. Maintain the viscometer in the thermostat for 10 minutes, then start measuring. With the help of a pear, the solvent is sucked into the extension 3 above the upper mark 5, the pear is removed and the time of the liquid expiration is

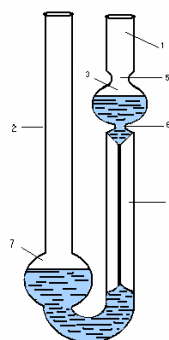
determined (t-solvent) according to the stopwatch from mark 5 to mark 6 (for this viscometer, the volume of the flowing liquid is constant, since it is equal to its the volume between the labels 5 and 6). Determination of the expiration time is carried out until at least three reproducible results are obtained and the average of the obtained values is taken.

Remove the viscometer from the thermostat, pour the solvent and fill the viscometer with an HMC solution. After 10 minutes of thermostating, the expiration time of this solution is determined (the expiration time of the solution is measured starting from the lowest concentration).



Scheme of a ball viscometer:

1-ball; 2-vessel; 3-suspension;
4-stem; 5-scale



Ostwald Capillary Viscometer

1 and 2 glass tubes,
3 and 7-tanks; 4-capillary; 5 and 6 tags
between meniscus

At the end, the device is thoroughly washed and the solvent expiration time is determined again. The results of observations are entered in the table.

Table

C, g/100 ml	expiration time t , in sek.				$\eta_{omh.}$	$\eta_{y\partial}$	$\frac{\eta_{y\partial}}{C}$	$[\eta]$
	1	2	3	aver.				

Having determined the expiration time for water and the test fluid, find the relative viscosity and specific viscosity for each solution. Build a graph of the dependence of η / C on C . This dependence should be straightforward. To find the intrinsic viscosity, the line is extrapolated to zero concentration. The segment cut off on the ordinate axis is the limit value of viscosity. To calculate the molecular mass, the found value, as well as K and taken from the table for the studied system, is substituted into the equation

$$[\eta] = K \cdot M^\alpha$$

and calculate the molecular weight of the HMC.

To calculate the molecular weight of the polymer, the above formula is logarithm:

$$\lg[\eta] = \lg K + \alpha \lg M$$

$$\lg M = \frac{1}{\alpha} (\lg[\eta] - \lg K)$$

Example: If resulting is found of the experiment, which $[\eta]=0,25$ for Polystyrene solution in benzene at 30 °C, was $K=0,94 \cdot 10^{-4}$, $\alpha = 0,76$,

$$\lg M = \frac{1}{0,76} \cdot (\lg 0,25 - 0,94 \cdot 10^{-4}) = \frac{1}{0,76} - (1,3979 - 1,973) + 4 = \frac{1}{0,76} (-0,6021 - 0,0269 + 4) = \frac{3,3720}{0,76} = 4,436$$

M=27290

Questions for self-testing:

1. Concepts about the molecular weight of polymers.
2. What is the basis for measuring viscosity using capillary viscometers?
3. Why do I need to pour the same measured solution into the Ostwald viscometer?

4. What is the relative, specific, reduced and intrinsic viscosity?
5. What is the difference between diluted IUD solutions from concentrated?
6. What is the composition and structure of proteins?
7. What factors influence the shape of a protein macromolecule in solution?
8. How does the specific and relative viscosity of protein solutions depend on pH?
9. How to calculate the molecular weight of the polymer as a result of viscometric measurements?

Laboratory work 15.

Study of the effect of electrolyte on the viscosity of an HMC solution

1. Instruments and reagents: viscometer, test tubes, 1% gelatin solution, solutions 1n K₂SO₄ and 1n KI.
2. Procedure of the work:
3. 1. 5 ml of 0.5% gelatin solution are poured into three test tubes.
4. 2. 5 ml of water are poured into the first tube, 5 ml of KI into the second tube, and 5 ml of K₂SO₄ into the third tube.
5. The contents of the flasks are stirred and left for 1 hour (assert)
6. Then measure the viscosity of each solution on an Ostwald viscometer at room temperature.
7. The data obtained are entered into the table and make a conclusion about the influence of anions.

Flask number	Solution	Temperature, °C	η_{relative}

Chapter 27. Coarse dispersions

Coarse dispersions are heterogeneous dispersed systems, in which the dispersed phase particles size in such systems is from 10^{-7} to 10^{-4} m. They are often called coarse-dispersions. Coarse dispersions are characterized by relatively fast sedimentation of the dispersed phase caused by gravity or other forces. Dispersed phase of coarse dispersions may be easily separated from the continuous phase by filtration. Coarse- dispersions are:

1. With a liquid dispersion medium (suspensions, emulsions, foams);
2. With a gaseous dispersion medium (aerosols, powders).

The properties of such systems are largely determined by surface phenomena - adsorption, wetting, and adhesion. However, they have their own characteristics due to the nature of the interface and dispersion.

Suspensions

Microheterogeneous systems with liquid disperse medium and solid disperse phase are called suspensions (from lat. suspensio the suspension). The particle size of the dispersed phase is in the range of 10^{-7} - 10^{-4} m. Like lyophobic sols, suspensions are obtained by dispersion and condensation methods. Depending on the concentration, suspensions are divided into: diluted and concentrated. Concentrated suspensions are referred to as pastes. Dilute suspensions are cloudy in both passing and diffused light. They differ sharply from lyophobic sols in their molecular-kinetic properties. Due to the large size of the dispersed phase, Brownian motion, diffusion, and osmotic pressure are practically absent in suspensions. The passage of light through the suspensions is not observed opalescence, but turbidity is manifested, since light rays are refracted and reflected by the suspension particles, rather than scattered. But at the boundary of these phases, a double electric layer may be formed.

Suspensions are kinetically unstable systems. Sedimentation stability is very small due to the large size. Particles of the dispersed phase settle under their own gravity. In pharmaceutical practice, increasing the sedimentation stability of the

suspension is carried out by selecting a medium close in density to the dispersed phase and adding substances that increase the viscosity of the system (syrups, glycerol). The settling velocity of the particles depends on the particle size, the density difference of the phase and environment, fluid viscosity and temperature.

The sedimentation rate:
$$V = \frac{2 r^2 (\rho - \rho_o) g}{9 \eta}$$

Aggregate instability is associated with a large supply of surface Gibbs energy. Stabilizers are used to increase the stability of suspensions. Surfactant is used as a stabilizer. In this case, surfactant molecules adsorbed on the surface of the dispersed phase particles form a thin structured film. This film has mechanical strength, increases wetting by the dispersion medium and prevents aggregation. This not only increases the aggregate stability, but also slows down sedimentation, as the viscosity of the medium increases. In pharmaceutical practice, gelatose, starch, MC, synthetic polysaccharides (aubazidan, xanthan), twins, spenes, egg powder, etc. are used as highly hydrophobic stabilizers (talc, streptocide, sulfodimethoxine) and hydrophobic suspensions (menthol, thymol, camphor).

Suspensions are widely used in the national economy and medicine. Many medicinal substances are used as a suspension. For example, Almagel (Bulgaria) is used for gastritis and ulcers, Amoxiclav (Slovenia) is used as a strong antibiotic, Smecta (France) and Navbahtit (Tashfarmi) is an antidiarrheal drug, and Insulin (Denmark) is used for diabetes.

Emulsions

An emulsion is a mixture of two immiscible liquid phases where one phase is dispersed into another. Basically, an emulsion is consisting of a continuous phase which is known as external phase, where the droplets are dispersed, and a dispersed phase which is defined as internal or discontinuous phase . Emulsions are found in different industries such as food, pharmaceutical, agricultural, cosmetics, and petroleum . An emulsion is not contained only water and oil; it may also contain some solid particles and even gas.

Inherently, an emulsion is an unstable system due to the unfavorable contact between oil and water phases. Although, some emulsions are stable as a result of the An emulsion is a mixture of two immiscible liquid phases where one phase is dispersed into another.

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Although, some emulsions are stable as a result of the small drop sizes and the existence of interfacial film, which surrounds the drops. To form an emulsion a mechanical force is required to disperse one phase into another. However, the emulsions formed without adding any surface active material would not be stable, and the emulsion phases will start to separate in different layers based on their density differences. Therefore, addition of surfactants are necessary to make a stable emulsion for a period of long time.

Types of emulsions

Essentially, there are three types of emulsions which are water-in-oil (W/O), oil-in-water (O/W), and complex emulsions such as water-in-oil-in-water (W/O/W). The complex emulsion also known as a multiple emulsion. The three types of emulsion are displayed in Fig.27.1.

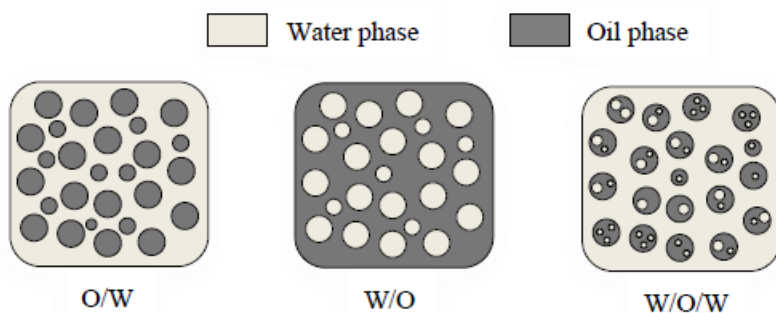


Fig.27.1.Types of emulsion

Typically, if the oil is dispersed phase, the emulsion is named O/W, but if the aqueous medium is the dispersed phase, the emulsion is named W/O . On the other hand, the multiple emulsions are complex systems. They can be considered as emulsions of emulsions.

Emulsion formation

The process of emulsion formation is called “emulsification”. Emulsification is a dynamic and non-spontaneous process, and energy is required to produce the droplets. The emulsification process usually requires a considerable amount of mechanical energy, to disperse one of the liquids in the form of small droplets in the continuous phase. There are several methods of emulsification including; simple shaking, mixing with rotor-stator systems, liquid injection through porous membranes, or high pressure homogenizers and ultrasound generators. To break up a droplet into smaller sizes, the form of the droplet must be changed and this deformation occurs during the shearing or stirring of the emulsion [17,18]. The process of droplet deformation and breakup is shown in Fig.27.1.

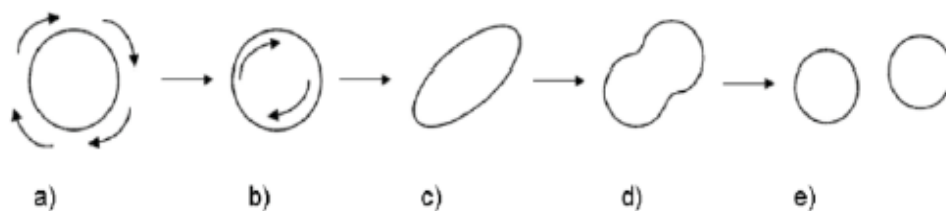


Fig.27.1.Droplet deformation during the emulsification process

The main problem in production of crude oil is the formation of an emulsion stabilized by heavy crude oil components such as asphaltenes, resins, and waxes. In the oil field the most common emulsion is the W/O type, and these emulsions are very stable due to the existence of natural surfactants such as asphaltenes, and resins [20]. For the formation of an emulsion three conditions are necessary:

- Immiscibility between phases of the emulsion
- Agitation to disperse one liquid in another

➤ Existence of surfactants

The emulsion characteristics are changeable from the beginning of the formation to their full resolution, and they depend on various factors such as temperature, agitation speed, time, and pressure. To form a stable emulsion, an emulsifying agent must be added to the system.

Depending on the concentration of the dispersed phase, emulsions are divided into:

- 1) diluted (less than 1%);
- 2) concentrated (1-74%);
- 3) highly concentrated (more than 74%).

The main properties of emulsions, first of all, the stability depends on the concentration of the dispersed phase. In diluted and concentrated emulsions, the drops have a spherical shape. In highly concentrated emulsions, the drops have the shape of polyhedra. The dispersion medium is arranged in the form of thin layers. At concentrations above 90%, emulsions acquire the properties of gels, lose fluidity, and are not sedimented. Therefore, they are called gelatinized.

Emulsions, like other dispersed systems, are obtained by condensation and dispersion methods, usually by mechanical dispersion. Emulsions are kinetically stable and an unstable system. When droplets of the dispersed phase collide, they merge, which is called coalescence. As a result of coalescence, the emulsions are stratified into two layers.

Emulsifiers are used to increase the stability of emulsions. As a result of their adsorption, a mechanically strong adsorption film is formed on the surface of the particle. As an emulsifier, salts of higher fatty acids, esters of higher fatty acids and polyatomic alcohols, long-chain amines are used. Also use finely ground insoluble powders of clay, gypsum, soot, oxides and sulfides of some metals. Emulsifiers by dispersion are divided into: 1) coarse emulsifiers (clay, soot, gypsum, graphite, coal, etc.); 2) colloid-dispersed emulsifiers (albumin, casein, gelatin, dextrin, etc.); 3) molecular-dispersed emulsifiers (Soaps). The mechanism of stabilizing action of

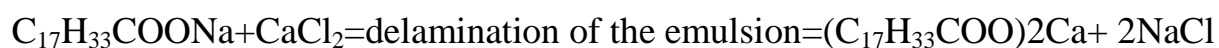
the stabilizer is explained by the Bancroft rule: hydrophilic emulsifiers stabilize emulsions of the first kind, hydrophobic emulsions of the second kind. The type of emulsion formed depends on the properties of the emulsifier. The dispersion medium is always the liquid that best dissolves the emulsifier. The emulsifier is selected based on its hydrophilic-lipophilic balance (GLB). Surfactants with a number of GLB 10-18 have highly hydrophilic properties (Soaps of alkaline metals, alkylsulfates, alkylsulfonates) and are used in the preparation of direct emulsions M/V. surfactants with a number of GLB 3-8 have hydrophobic properties (Soaps of alkaline earth and polyvalent metals). They are used to produce reverse-type emulsions in/M.

The stability of emulsions is judged by the time of delamination into two layers.

The type of emulsion can be determined:

- 1) measurement of electrical conductivity;
- 2) mixing with one of the liquids (polar or non-polar);
- 3) staining with water-soluble or oil-soluble dyes;
- 4) by wetting a hydrophobic or hydrophilic surface;
- 5) fluorescence;
- 6) by wetting the filter paper.

Under certain conditions, the phenomenon of phase reversal occurs in emulsions. The essence of this phenomenon is to change the nature of the emulsifier. For example, if a solution of calcium chloride is added to an m/V emulsion stabilized with sodium oleate during intensive mixing, a reverse b/M emulsion is formed. this is due to the reaction:



A new surfactant, calcium oleate, is formed, which is better soluble in a non-polar liquid.

Sometimes it is necessary to destroy the resulting emulsion. Destruction of emulsions is called demulsification. Demulsification is carried out by increasing or decreasing the temperature, exposure to an electric field, centrifugation, addition of

electrolyte, mineral acids, higher alcohols, esters, surfactants that are not emulsifiers.

Emulsions are widely used in various areas of the national economy: food industry (margarine, mayonnaise), perfume industry (creams, lotions), agriculture for pest control and weeds.

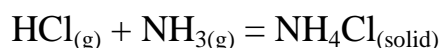
Emulsions are a form of medication. Emulsions of the first type for internal use, emulsions of the second type for external use. For example, benzyl Benzoate (Russia) is an antimicrobial agent.

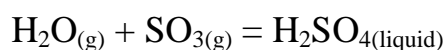
Emulsions are considered very important in everyday life. A huge number of products from food to cosmetics deal with emulsions such as mayonnaise, milk, butter, creams, shampoos and many other daily products. This review focused on the study of emulsion types, stability mechanisms and rheology. Based on the reviewed articles, it was found that emulsions stability is related to many factors such as phase ratios, surfactant concentrations, agitation, temperature, and other existed compounds in the system. It is also found that in a stabilized emulsion by a surfactant, the surfactant monomers surround the droplets like a thin film and prevents them from the mechanism of coalescence.

Aerosols

Aerosols (from Greek. aer-air and lat. solutio-solution) is called a dispersed system with a gaseous dispersion medium and a dispersed phase consisting of solid or liquid particles. According to the aggregate state of the dispersed phase, aerosols are classified into: 1) fogs (W/g)- the dispersed phase consists of liquid droplets; 2) smoke, dust (g/g) – the dispersed phase consists of solid particles; 3) smog (from the English. smoke – smoke, fog-fog) with a mixed dispersed phase. The highest dispersion in smoke particle size 10^{-9} - 10^{-5} m, the lowest dispersion in dust, particle size greater than 10^{-5} m, fog particle size 10^{-7} - 10^{-5} m.

Aerosols are obtained, as well as other disperse systems, by dispersion and condensation methods. Some aerosols are obtained by chemical reaction:





Aerosols have the ability to scatter light. They show a Faraday-Tyndall cone. The light scattering intensity of aerosols is higher than that of solutions due to the large difference in the refractive indices of the dispersed phase and the dispersion medium.

Molecular-kinetic properties of aerosols is governed by the same laws that solutions. However, due to the low viscosity of the density of the gas dispersion medium, the intensity of Brownian motion and the rate of diffusion of sedimentation is significantly higher than that of solutions. In addition, smoke and fog are easily carried by the wind.

Aerosols do not have a double electric layer on the surface of dispersed phase particles. But particles have electric charges that occur due to a collision with another particle or surface. Adsorption of ions formed during ionization is also possible. Often aerosol particles are charged in the opposite way. In large-volume aerosols, particle size separation results in a strong electric field. In the clouds, this leads to a thunderstorm. Aerosols are kinetically and aggregatively unstable systems, since there is no double electric layer at the phase interface. Therefore, the aerosols coagulated with greater speed.

Aerosols are widely used in the national economy and in medicine. AgJ and PbJ2 aerosols are used to artificially induce rain and to combat hail formation. In medicine, aerosols are used in inhalation therapy, to protect damaged skin, and for disinfection.

Sometimes the formation of aerosols is extremely undesirable and harmful to the health of living organisms. Hazardous aerosols are formed during the extraction and processing of various minerals. Coal aerosols cause lung disease-anthraxosis, silica gel-silicosis, asbestos-asbestos. Allergic diseases are caused by aerosols formed by plant pollen, dust formed during the processing of cotton, flax, hemp, etc. Microbiological or bacterial aerosols-suspensions of bacteria, molds and viruses are one of the ways of transmitting infectious diseases: pulmonary

tuberculosis, influenza, and acute respiratory diseases. Smog is especially dangerous for health. In 1952, smog formed in London, containing several tons of smoke and SO₂, led to the death of 4 thousand people. The fight against smoke and industrial dust is carried out by filtering gases through fabric filters, deposition of particles in installations such as cyclones, etc.

The word aerosol was introduced about 90 years ago as an excuse to the term hydrosol, a stable liquid suspension of the solid particle.

The atmospheric aerosols are actually atmospheric molecules and the ion chemical species in one cubic centimetre of air; also contain a substantial number of other suspended particles in liquid, solid, gas as well as fluid phases varying in size from a few nanometers to several microns depending on the climate condition. In clean air, the size of it is about 1 nanometer to 100 micrometres and in the polluted air, their size can be 10,000 microns or more including bacteria, dust and industrial waste.

There are several types of aerosols; smoke, haze and fog are some most common examples of them. Smoke is a cloud of particles produced by burning wood, coal, oil and other carbonaceous fuels . The haze is a system of particles, grown to large size by water vapour condensation on it and it reduces the visibility; and fog is a collection of the small liquid droplet containing water. These particles on colliding and combining together form large droplets and their radius become greater than 100 micrometres, they appear as drizzle or even as rain. Smoke and fog on combining together form a new type of aerosol, known as smog . In this way, the fog is an example of natural aerosols and haze, dust, particulate air pollutants and smoke are the examples of artificial aerosols. Thus the atmospheric aerosols are characterised by extensive variation in composition, size, physical characteristics, latitudinal and altitudinal distributions.

Powders

Powders are free-dispersed systems with a gaseous dispersion medium and a solid dispersed phase. The particle size of powders is from 10⁻⁸ to 10⁻⁴m.

Powders are obtained in two ways:

1) physical and mechanical. Solid materials are crushed by crushing, and liquid materials are sprayed;

2) physical and chemical. Using chemical methods-oxidation, reduction, combustion, electrolysis, etc. for Example, soot and silica gel powders are obtained by burning hydrocarbons to carbon and silicon tetrachloride, respectively.

The gaseous medium and high concentration of solid particles of the dispersed phase give the powders flow properties.

Depending on the particle size, powders are called:

$20 \cdot 10^{-3} - 10^{-5}$ m-sand; $2 \cdot 10^{-5} - 10^{-6}$ m-dust; less than $2 \cdot 10^{-6}$ m-powder.

Pharmaceutical powders of the most fine grinding have a size $(10-20) \cdot 10^{-6}$ m (xeroform, griseofulvin). Powders are characterized by the following properties: bulk density, stickiness, flowability(fluidity), electrical resistivity, combustibility, and explosiveness.

Bulk density is defined as the mass of a unit volume of powder that is freely poured into a container.

By clumping, we mean the tendency of powder particles to form aggregates. This property is due to the cohesive interaction of the powder particles with each other and the adhesive interaction in a multi-component system.

Flowability is the mobility of powder particles relative to each other and the ability to move under the influence of an external force. The flowability depends on the particle size, humidity, and degree of compaction.

The fluidity of the powder as well as the flowability depends on the nature of the contact between the powder particles. Fluidity is affected by the density , size, and shape of the particles, their surface condition, and humidity.

Hygroscopicity and wettability of powders is the ability of a powder to absorb moisture from the environment. Moisture absorption leads to changes in many properties of powders. The moisture content is expressed in terms of humidity and moisture content.

Humidity is the ratio of the mass of moisture in the material to the mass of the substance (dry matter together with moisture). Moisture content – the ratio of the mass of moisture to the mass of completely dry material.

The hygroscopicity of the powder can be increased or decreased by treatment with surfactants. For example, adding oleic acid to a hydrophilic powder contributes to a monolayer that makes the surface of the powder particles hydrophobic and turns the powder into a less hygroscopic substance.

A very important property of powders is the ability to granulate. When granulating, conglomerates (granules) of spherical or cylindrical shape are formed, more or less uniform in size. This process can go on spontaneously, as it leads to a decrease in the surface energy of Gibbs. Granulated products have less dispersibility, greater storage stability, and convenient packaging and dosage. Granulation can be caused by adding a certain amount of liquid to the powder. Wetting the surface of the particles, the liquid forms a layer of high viscosity on them, so that the particles stick together. In the pharmaceutical industry, firstly, granules are one of the dosage forms, and secondly, they are an intermediate product in the preparation of tablets.

By composition, pharmaceutical powders can be single-component or multi-component. For their production, chemical and pharmaceutical plants must be equipped with different grinding mechanisms. Crushed raw materials are separated by dispersion by sieve analysis or sedimentation analysis.

Laboratory work 16

Obtaining emulsion O/W and determination its type

Purpose of work: To obtain an O/W emulsion and to learn to determine the type of emulsion.

Devices and reagents: magnetic stirrer, burette, 3 glasses, dividing funnel, liquid paraffin, 0.1 M surfactant solution, purified water.

Completing of the work:

1-experience. Obtaining an emulsion of the first kind.

In three glasses, 10 ml of surfactant solutions of different concentrations from a 0.1 M solution are prepared as shown in table

Flask number	1	2	3
Volume surfactant solution, ml	2,5	5	10
Water volume, ml	7,5	5	0
Volume of Vaseline Oil	10	10	10

Then emulsions are prepared: the Glasses are put on a magnetic stirrer in turn.

A burette is placed over a glass and 10 ml of vaseline oil is poured into it. The agitator is connected to a DC outlet and the "Network" toggle switch is turned on. Start mixing the surfactant solution. From the burette for 5 minutes with constant stirring, add vaseline oil drop by drop to the glass. After adding the vaseline oil, the mixture continues to mix for another 10 minutes. From the resulting emulsion, 1 ml is poured into a test tube, the time is recorded and the separation time, i.e. the life time, is left to be determined. The same method is used to obtain emulsions in the other two glasses. Similarly, the time of separation of emulsions from 2 and 3 glasses is determined. The rest of the emulsions are used to determine the type of emulsions.

Experiment. Determination of the type of emulsions.

1) by the method of staining:

From the first glass, 1 ml of the emulsion is taken into a test tube. Add 1-2 drops of methylene blue, mix well. Place a drop of emulsion on a slide and look under a microscope. Conclusions are drawn in the form of a picture.

2) by the dilution method.

One drop of emulsion is dropped on the slide. Next, at a distance of 2 cm, apply 1 drop of water. The glass is tilted so that the water flows towards the emulsion. Observe the mixing of drops and make a conclusion.

3) Wetting the hydrophobic surface.

One drop of emulsion is dropped on the paraffin surface of the glass plate. Based on how it occurs, wetting is concluded about the type of emulsion.

Questions for independent training:

1. What systems are called emulsions?
2. How are emulsions classified?
3. What methods are used to obtain emulsions?
4. Emulsifiers. What substances are used as an emulsifier?
5. Bancroft's Rule.
6. Classification of emulsifiers.
7. How do I choose an emulsifier to produce emulsions of one type or another?

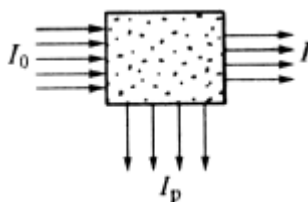
Number of GLB.

8. What methods determine the type of emulsion?
9. What is coalescence?
10. How can you break the stability of emulsions?
11. What is demulsification?
12. Give examples of practical use of emulsions.

Laboratory work 17

Determination of particle size by turbidimetric method

Justification of the topic: the Suspension of the smallest solid particles in a liquid, part of the light is scattered by solid particles and as a result becomes less intense (weakened). Nephelometric and turbidimetric analysis methods are based on this phenomenon. The nephelometric analysis method measures the intensity of the scattered light flux (I_p). The measurement is performed at an angle of 90° with respect to the incident light stream (Fig. V. 10).



The scheme of passage of the light flux through the suspension

The method of optical analysis is called turbidimetric, based on measuring the attenuation of the intensity of the light flux passing through the suspension due to absorption and scattering of the light flux by the suspension

If any ion can be isolated as a stable suspension of a sparingly soluble substance, then the turbidimetric method can be used to quantify it. The intensity of the light flux passing through the suspension is determined by the equation

$$\lg \frac{I_0}{I} = K' \frac{cld^3}{d^4 + \alpha\lambda^4}$$

where I_0 — intensity of the original light output;

I — intensity of the light flux passed through the suspension;

c — concentration of suspension;

l — thickness of the absorbing layer (cuvettes);

d — the average particle diameter;

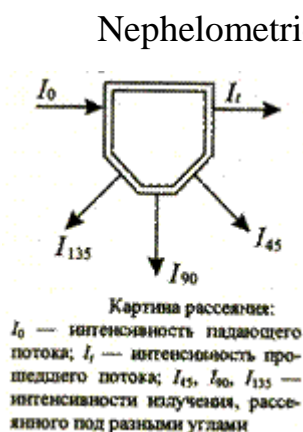
λ — wavelength of the light output;

K', α — constants.

$$\lg \frac{I_0}{I} = klc \quad \text{or} \quad A = klc.$$

The K coefficient is called the molar turbidity coefficient. It is equal to the optical density of 1 M of an insoluble substance suspension measured in a layer 1 cm thick. Turbidimetric analysis is less accurate than photolorimetric analysis. This is due to the fact that light scattering is caused not so much by the concentration of scattering particles in the suspension, as by the shape, size and nature of the surface of the solid phase particles. Therefore, turbidimetric analysis is used only for determining those ions for which there are no satisfactory colorimetric methods. This applies mainly to sulfate and chloride ions. Equation (1) shows that the optical density of the solution is proportional to the average diameter of the suspension particle. The widely used method for determining the dispersion of particles in a suspension is based on the existence of this kind of dependence.

When using turbidimetric analysis, it is necessary to take into account that the following factors influence the measurement results: the concentration of ions that form the precipitate; the order of mixing solutions; the speed of mixing solutions; the temperature of solutions; and the stability of the suspension.



Nephelometric and turbidimetric analysis uses the phenomenon of light scattering by solid particles in a suspended state in solution. The sample is illuminated by a stream of light with an intensity of I_0 , and then, as in molecular absorption spectroscopy, the intensity of the transmitted radiation is measured. Or the intensity of the radiation scattered at a certain angle is determined (for example, I_{90} at 90°). As the number of suspension particles increases, the I_t/I_0 ratio decreases, and the I_{90}/I_0 ratio increases, at least to moderate concentrations. For very dilute suspensions, measuring at an angle is much more sensitive than measuring when the source and receiver of the radiation are on the same line, since weak scattered light can be observed on a dark background. The method that uses the intensity of the transmitted light I_t is called turbidimetry, and the method with the measurement at an angle of 90° (or some other) - nephelometry. In turbidimetric measurements, a value called turbidity corresponds to the optical density and can be determined from a ratio similar to the basic law of light absorption:

$$S = \lg (I_0/I) = k b N,$$

where S – turbidity; k – coefficient of proportionality, called the coefficient of turbidity; b – rate length; N – the number of scattering particles per unit volume.

Any photometer or spectrophotometer can be used for turbidimetric measurements. If the solvent and the scattering particles are colorless, the maximum sensitivity is achieved by using radiation of a blue or near ultraviolet region. For colored systems, the optimal wavelength must be selected experimentally.

The calculated ratio used in nephelometry is as follows:

$$I = K_\alpha c I_0,$$

where K_α - empirical constant of the system (α - angle at which measurements are performed); c – concentration.

The use of methods based on the measurement of light scattering is quite limited, because the measured signal is strongly influenced by the particle size. Therefore, it is necessary to strictly observe the identity of the conditions for constructing the calibration schedule and analyzing the test solution.

The concentration of colloidal solutions can be determined on the nephelometer device. The principle of operation of the nephelometer is based on comparing the intensity of the scattered light in the ash under study with the intensity of the scattered light in the standard ash. In this case, the measurement is performed at a 90-degree angle relative to the incident light.

The nephelometer consists of two identical glass cylinders. In one of them, pour the standard Sol, in the second studied Sol. Both cylinders on the side are illuminated by a light source. The scattered light falls in sols into the eyepiece on the top of the device. The concentration of both sols should be the same. In this case, both semicircles of the eyepiece are equally illuminated. Then change the height of the cylinders to the same illumination of both semicircles. The volume of the Sol particle under study is calculated using the formula:

$$v_2 = v_1 \frac{h_1}{h_2}$$

v_1 - standard sol particle volume.

The turbidimetric method is based on measuring the decrease in the intensity of incident light. In turbidimetric measurements, the value called “turbidity ” coincides with the optical density and can be determined according to the basic law of light absorption:

$$S = \lg \frac{I_0}{I} = kbN$$

Where S –turbidity; b – rate length; N – the number of scattering particles per unit volume.

k – the molar coefficient of turbidity, it is equal to the optical density of 1M

suspension with a thickness of 1 cm. In nephelometry use the following ratio:

$$I = K_{\alpha} C I_0$$

The turbidimetric method is less accurate than the photolorimetric method. The reason for this is that light scattering depends not only on the concentration of particles, but also on the shape, size, and nature of the particle surface. When using the turbidimetric method, the following factors must be taken into account: the concentration of ions forming the precipitate, the mixing rate, the temperature, and the stability of the suspension.

Laboratory work 18

Study of rheological properties of ointments on a rotary viscometer

Purpose of the work: Measuring the viscosity of ointments on a rotary viscometer.

Devices and reagents: Rotary viscometer, 100 ml measuring cylinder, stopwatch, 200 ml glass, watch glass, glass stick, water-soluble polymers, purified water, glycerin.

Work procedure: weighed on an analytical balance and placed in a glass. Purified water is also poured there. Stir with a stick until the ointment is completely dissolved. First, the viscosity of the standard Newton-glycerol liquid is measured on a viscometer. To do this, glycerine is poured into the space between the two cylinders of the device. Remove the outer cylinder. Measure the depth of the liquid by graduated division of the device. Then collect the device, bring the indicator of the device to zero and put the minimum load. Releasing the lock of the pulley, twist the inner cylinder. Measure the time three times the turnover with the help of a stopwatch. If the cylinder with the load turns unevenly, the load rises. When working with glycerine, the stopwatch is switched on immediately, with the polymer solution after stationary rotation. After the measurement, the lock is fixed. For each load, the number of measurements must be at least three. The experiment will be repeated up to three times the exact measurement.

Liquid	Triple turnover of time, τ , sek					Loading q, Γ	Turnover time, N turnover/sek
	T	T	T	T	T		

Test

1. The founder of colloid chemistry:

- a) Peskov
- b) Lomonosov
- c) Graham
- d) Selmi

2. What is peptization?

a) The process of precipitation from a colloidal solution by adding electrolyte in an amount equal of the threshold concentration:

b) The process of transformation of loose sediments into colloidal solutions under the action of electrolytes on them, which can adsorb on the surface of colloidal particles;

c) The process of transformation of loose sediments into colloidal solutions under the action of high-molecular substances on them;

g) The process of precipitation from the colloidal solution with the addition of high-molecular compound.

3. What is the main reason for stability of colloidal sols?

- a) Charge
- b) Nature
- c) Solvation shell
- d) Brownian motion and diffusion

4. How is sodium benzene sol obtained?

- a) Mechanical
- b) using ultrasound

- c) physical condensation
 - d) chemical condensation
5. Which of the following systems is considered colloidal?
- a) Aqueous solution of sodium chloride
 - b) Aqueous solution of gelatin
 - c) clay
 - d) Milk
6. What is electroosmosis?
- a) Motion of colloidal solution molecules in an electric field;
 - b) Movement of a colloidal fluid through a porous solid under c) the action of an external electric field;
 - d) Movement of a colloidal solution in an electric field;
 - e) Motion of colloidal particles in an electric field.
7. Coagulation threshold:
- a) The highest concentration of electrolyte causing coagulation;
 - b) The highest concentration of surfactant causing coagulation;
 - c) The lowest concentration of electrolyte causing open coagulation and expressed in mmol/l;
 - d) The lowest concentration causing coagulation and expressed in gE / l;
8. Upon obtain of the silver chloride sol, potassium chloride was taken in excess. What ion is adsorbed on the surface of the nucleus?
- a) K^+
 - b) Cl^-
 - c) Ag^+
 - d) NO_3^-
9. With the addition of what protects the lyophobic sol from coagulation?
- a) Electrolyte solution
 - b) Another lyophobic sol
 - c) Lyophilic sol

g) Organic solvent

10. The sizes of colloidal particles?

- a) Less than 1 mmicron
- b) More than 100 MM
- c) 1-100 MMK;
- d) 0.1-1 mmk

11. What is lyozol?

- a) A dispersed system in which the dispersed medium is solid;
- b) A dispersed system in which the dispersed medium is a liquid;
- c) Dispersed system, with solid phase and gaseous medium;
- d) A dispersed system consisting of a solid medium and a liquid phase.

12. How are sol electrolytes purified?

- a) simple filtering
- b) decantation
- c) Sublimation
- d) Dialysis

13. What disperse systems include suspensions and emulsions?

- a) True solutions
- b) Mixtures
- c) Colloidal solutions
- d) Coarse dispersion systems

14. Rule of selective adsorption of Peskov-Fajans:

- a) The colloidal solution absorbs well the ions that enter its crystal lattice;
- b) The colloidal particle well adsorbs those ions that enter its crystal lattice;
- c) A colloidal particle adsorbs opposing ions;
- d) A colloidal particle adsorbs like charges.

15. What is called electrophoresis?

- a) The motion of uncharged particles in a constant electric field
- b) The motion of a colloidal solution in an electric field

- c) The motion of a colloidal particle in an electric field to the opposite charge
- d) Movement of a dispersed medium in an electric field;

Glossary

An aggregate is a constituent part of a micelle of a lyophobic sol, insoluble in a dispersion medium, a crystalline or amorphous microparticle.

Adhesion- adhesion of dissimilar bodies brought into contact (a kind of contact interaction).

Adsorbate- a substance adsorbed by an adsorbent.

An adsorbent is a condensed phase on the surface of which adsorption occurs.

An adsorptive is an adsorbable *substance* (a potentially possible adsorbate).

Adsorption- spontaneous concentration of a gaseous or solute on the interface:

-hydrolytic- a type of *exchange* adsorption, in which the adsorbing substance displaces hydrogen ions or a hydroxyl group from the surface of the adsorbent;

- exchange - a process in which a substance with increased adsorption properties displaces an equivalent amount of surface ions of the same sign into the solution from the surface of the adsorbent while maintaining the electroneutrality condition;

-specific- selective concentration of ions on the surface of a solid adsorbent;

-equivalent- concentration of neutral molecules on the surface of the adsorbent.

Antagonism- a decrease in the coagulating action of an electrolyte in the presence of another electrolyte.

Aerosols are systems with a gas dispersion medium and a solid or liquid mobile dispersed phase.

Proteins are biopolymers formed by polypeptides built from α -amino acid residues:

- *globular* - proteins, the shape of which is close to spherical, and the ratio of the length of the peptide chain to its width is less than 10;

- *fibrillar* - fibrous proteins in which the ratio of the length of the peptide chain to its width is greater than 10.

Brownian motion is the disordered motion of particles of the dispersed phase, which is caused by the collisions of these particles with molecules of the dispersion medium in continuous thermal motion.

Van der Waals forces are forces caused by the electrostatic attraction of negatively charged electrons of one atom by the positively charged nucleus of another atom.

Interaction in dispersed systems:

- *hydrophobic* - interaction in an aqueous medium of non-polar molecules or radicals of complex molecules, the result of which is the association of the named particles with the formation of a hydrophobic region capable of further interaction with other non-polar radicals;

- *electrostatic* - attraction between charged groups.

Salting out - precipitation of a dissolved component of a high-molecular compound under the action of high concentrations of electrolytes or non-electrolytes due to the destruction of the protective solvation shells of IUD molecules.

High-molecular compounds (HMCs) are natural and synthetic substances formed from chain macromolecules, the mass of which is tens and hundreds of thousands of units, and the sizes correspond to the sizes of sol particles.

Viscosity - the property of liquids and gases to resist the movement of individual parts relative to each other under load. Quantitatively, viscosity is represented as the frictional force that occurs between two laminar moving layers of liquid or gas.

Gels are structured dispersed systems with a liquid dispersion medium formed as a result of coagulation of sols.

Heterogeneous system- a system consisting of parts of different properties, separated by the surface of sectiona.

Hydrophilicity is the affinity of surfactant molecules (surfactants) for water due to polar groups.

An electric double layer (DEL) of a colloidal micelle is a formation that includes the surface of an aggregate and adjacent charged layers of adsorbed ions and a near-surface liquid (diffuse layer).

Denaturation is a partial or complete destruction of the spatial structure of a polymer molecule while maintaining the primary structure.

Desorption is the reverse process of adsorption (often performed by displacing the adsorbate with another substance, decreasing pressure or increasing temperature).

Zeta (ζ)-potential is the potential difference arising at the boundary between the mobile and stationary parts of the sol micelle.

Dialysis is the diffusion of low molecular weight substances (ions, less often small molecules) through the membrane.

Dispersion - fine grinding of solids or spraying of liquids, leading to the formation of dispersed systems (usually microheterogeneous and coarsely dispersed, including powders, suspensions, emulsions).

The dispersion- heterogeneous multiphase system, wherein one phase is a continuous dispersion medium and the other phases are dispersed therein in the form of chalks particles.

Dispersion is a measure of material fragmentation.

Diffusion is a spontaneous equalization of the concentration of a substance (ions, molecules, particles of the dispersed phase) in an initially inhomogeneous system under the action of a chemical potential gradient and thermal motion of molecules.

Smoke is a sedimentation-stable two-phase system of t / g (solid / gas) with particles of a dispersed phase of a colloidal degree of dispersion.

The protective effect of IUDs is the ability of surface-active high molecular weight compounds to form mechanically strong protective layers on the surface of dispersed particles.

Sols (colloidal systems) are dispersed systems in which the particles of the dispersed phase have a size in diameter equal to approximately 10^{-5} - 10^{-7} cm:

-hydrophilic- thermodynamic stable colloidal systems, consisting of two parts: a hydrophobic hydrocarbon radical and a hydrophilic polar group (such as OH⁻, -COOH, etc.);

-hydrophobic- thermodynamically unstable colloidal systems, in which the dispersed phase is formed by micelles from inorganic substances with an aggregate that is poorly soluble in a given dispersion medium.

The isoelectric point of a protein molecule is the pH value at which the protein is in the isoelectric state, characterized by the same number of sums of positive and negative charges.

Coagulants are electrolytes, the additives of which are capable of causing or accelerating the coagulation of sols.

Coagulation is a combination due to adhesion during mutual collisions of particles of a dispersed phase into aggregates that precipitate.

Coacervates are IUD solutions in which coacervation occurs.

Coacervation is the separation of a system into two phases, one of which is a solution of an IUD in a solvent, and the other is a solution of a solvent in an IUD.

The diffusion coefficient, the main characteristic of the diffusion process, is numerically equal, as follows from the analysis of the Fick equation, to the number of molecules of the diffusing substance provided that the concentration gradient, diffusion time, and the cross-sectional area are equal to unity.

Laminar motion is a motion that does not disrupt the continuity of fluid layers.

A *lyophilic disperse system* is a thermodynamically stable dispersion, the particles of which interact well with the dispersion medium and, as a rule, are formed spontaneously upon dissolution of organic matter.

A *lyophobic disperse system* is a thermodynamically unstable dispersion of, as a rule, inorganic substances that form particles that poorly interact with the dispersion medium.

Membranes are permeable dividing walls (films, plates, tubes or hollow filaments made of glass, metal, polymer) that selectively transmit ions and molecules.

Micelles –neutral particles of the dispersed phase of colloidalp Dimensions uniformly dispersed in the dispersion medium;the structure of the micelle is characterized by some formation (for example, an aggregate of an inorganic substance in the case of lyophobic disperse systems) surrounded by an electric double layer.

Micellar mass is the product of the micelle mass by the Avogadro number.

Molecular adsorption- adsorption of non-electrolytes from solutions.

Swelling is the spontaneous absorption of a liquid or its vapors by a solid, the structure of which is formed by IUD molecules:

-*neo bordering*-ends complete dissolution of the sample in a low molecular weight solvent;

-*limited*- ends with the formation of a swollen jelly that retains the shape of the original polymer sample.

Opalescence is the scattering of light (in the simplest case, due to diffraction).

Osmosis- transport of a solvent through a semipermeable membrane from a weakly concentrated true or colloidal solution to a more concentrated one; the process proceeds spontaneously and has a diffusional character.

Osmotic pressure is a parameter that characterizes the tendency of a solution to decrease in concentration when in contact with a pure solvent.

Peptide bond is a structural fragment (–CO – NH–) formed by the interaction of α -amino acids.

Pep CHIDA- connection with a peptide bond.

Surface-active substances (surfactants)-a substance that is well adsorbed on the interface between the phases, reducing the surface tension.

Surface tension- Gibbs surface energy of a unit surface, equal to the work expended to form a unit of surface.

Surface-inactive substances (SIS) are substances that are poorly adsorbed on the surface and increase the surface tension.

Polymers- see *High Molecular Weight Compounds*.

The rule

-*Traube-Duclos*:lengthening the chain in the series of fatty acid molecules by the –CH₂ radical increases their ability to adsorb by 3.2 times;

- *Peskova-Fayans-Paneta*: on the surface of the crystalline aggregate, ions are significantly adsorbed from the surrounding solution, which are capable of sharpening the crystal lattice or forming poorly soluble compounds in oppositely charged ions of the crystal surface, i.e. better adsorbed ions are the same or isomorphic with the ions on the surface of the crystal.

Dust is a sedimentation unstable two-phase system (solid / gas) with particles of a dispersed phase of a microheterogeneous degree of dispersion.

Free surface energy is a value equal to $\Delta G^S = \sigma \Delta s_{1,2}$.

Freely dispersed systems are systems in which the particles of the dispersed phase are not connected with each other and can freely move in the dispersion medium.

Connected-dispersed systems are systems, the particles of the dispersed phase of which are interconnected by molecular forces and form spatial networks or structures.

Synergism is an increase in the coagulating effect of one ion in the presence of other ions.

Syneresis is the spontaneous release of fluid from a coagulation thixotropic structure.

The degree of dispersion (D) is a value inversely proportional to the smallest size in the diameter α of a particle of the dispersed phase ($D = 1 / \alpha$).

Thixotropy is the ability of a dispersed system to form a gelatinous mass, which, under mechanical action or when heated, easily turns into a viscous liquid.

Fog is a sedimentation unstable two-phase system (liquid/ gas) with particles of a dispersed phase of a microheterogeneous degree of dispersion.

Specific surface- the ratio of the total interfacial area ($s_{1,2}$) to the volume (V_1) or mass (m_1) of the dispersed phase.

The equation

-*Langmuir*- characterizes monomolecular adsorption;

-*Nernst*- describes the electrochemical equilibrium at the surface-solution interface;

-*Fick* (equations) give quantitative relationships between the rate of diffusion and the concentration gradient;

-*Freundlich*- empirical, for the presentation of adsorption data.

A stable system is a system in which the main parameters that determine the dispersion and equilibrium distribution of the dispersed phase in the dispersion medium change at a negligible rate.

Chemisorption is chemical adsorption.

Chromatography is a method of separating complex mixtures of dissolved and suspended substances by sorption or extraction using a specially selected sorbent or extractant, followed by fractional extraction of concentrated components with a suitable solvent.

Electrodes Allz - transport of ions through the ion-exchange membrane interposed between two electrodes connected to an external power source.

Electrophoresis is the movement of dispersed phase particles in a dispersion medium under the action of an external electric field.

Emulsions are dispersed systems with a liquid dispersed phase and a liquid dispersion medium:

-*multiple*- the dispersion medium is partially dispersed in the droplets of the dispersed phase;

-*reverse*- a more polar liquid forms a dispersed phase;

-*straight lines*- the dispersion medium is a polar liquid (often water), the dispersed phase is formed by a non-polar liquid.

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