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Chemistry of dispersed systems

Laboratory manual

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Предназначено для организации лабораторного практикума и самостоятельной работы студентов, изучающих курс общей химии на английском языке. Пособие призвано помочь в формировании целостного представления о структуре и свойствах дисперсных систем широко представленных в живой природе.

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CHAPTER 1

ADSORPTION

United we stand

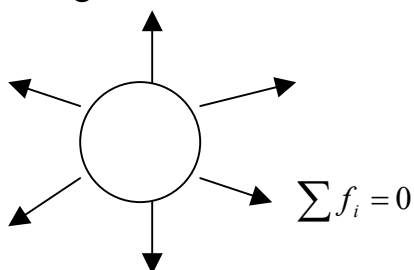
After reading this chapter, you should be able to:

- Explain the origin of Free surface energy accumulated in the interface monolayer;
- Define adsorption and its types;
- Discuss structure and special properties of surfagents; give mathematical description for their adsorption at liquid-gas interface;
- Describe molecular adsorption on solid sorbents; discuss the Langmuir, the BET and the Freundlich isotherms;
- Describe selective and ion exchange adsorption of electrolytes from aqueous solutions on solid sorbents.

1.1. Surface phenomena and surface tension

Surface phenomena are those processes, which run spontaneously at the interface surfaces. They are: adhesion, cohesion, adsorption, absorption and some others. Such phenomena play an essential role in metabolic processes in vivo.

Surface phenomena are promoted by **Free surface energy** (G_s), accumulated in a thin monomolecular layer at the boundary of two different phases. Accumulation of free energy is a result of non-balanced intermolecular forces affecting a molecule at a surface:



1.1

Fig. 1 A molecule in the interior of a liquid phase.

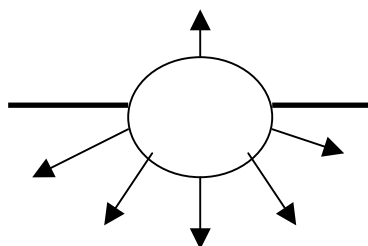


Fig. 2 A molecule at a liquid surface.

Free energy of an interface surface area unit is known as a surface tension (σ , N/m).

$$\sigma = \frac{G_s}{S}, \frac{kJ}{mol} = \frac{N}{m} \quad 1.2$$

Surface tension is an important characteristic of liquids, solutions and biological fluids. For example, surface tension of blood is 45.5×10^{-3} N/m. The factors affecting surface tension of liquids are:

- temperature;
- polarity of medium.

According to the Second Law of chemical thermodynamics free surface energy tends to zero. One way to diminish it is adsorption.

Adsorption is the attachment of particles of adsorbates to the surface of adsorbents. The process of adsorption involves separation of substances from one phase accompanied by its accumulation at the surface of another. Molecules and atoms can attach to surfaces in two different ways:

- In **physical adsorption** there is a van der Waals interaction between adsorbents and adsorbates. Such an interaction is weak and adsorption is reversible;
- In **chemisorption**'s the molecules (or atoms) stick to the surface by forming a chemical (usually covalent) bond. Chemisorption is an irreversible process.

Adsorption may occur at the different interface surfaces:
gas / liquid; gas / solid, liquid / solid and others.

1.2. Surfactants' adsorption at gas/ liquid interface surfaces

Surfactants or surface- active agents are dual-nature molecules consisting of polar hydrophilic head group and non-polar hydrocarbon tail (radical):



Fig. 3. Scheme of surfactant's molecule.

They are amines, carboxylic acids and their salts, sulfonic acids and their salts, alcohols and some others. Many biology active substances are surfactants:

- Phospholipids;
- Bile salts;
- Amino acids and proteins.

Surfactants' adsorption at gas / liquid interface surfaces obeys the rule: «Like dissolves like». Their polar hydrophilic head groups tend to be in water while non-polar hydrocarbon tails try to be in air:



Fig. 4. Surface monolayer at low surfactant's concentration.

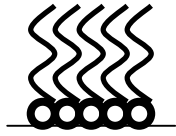


Fig. 5. Surface monolayer at high surfactant's concentration.

Surfactants' adsorption reduces surface tension of water because they decrease polarity of a medium. Adsorption and surface tension isotherms are represented in figures 6 and 7.

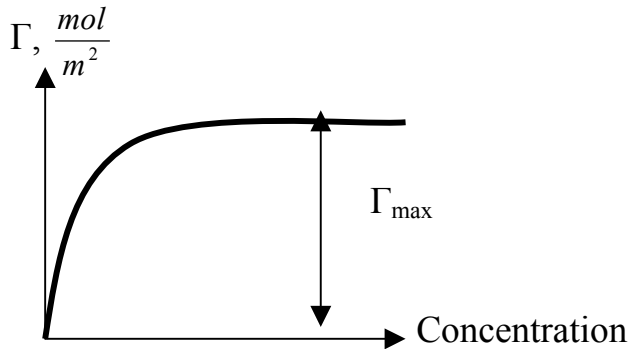


Fig. 6. Isotherm of surfactants' adsorption.

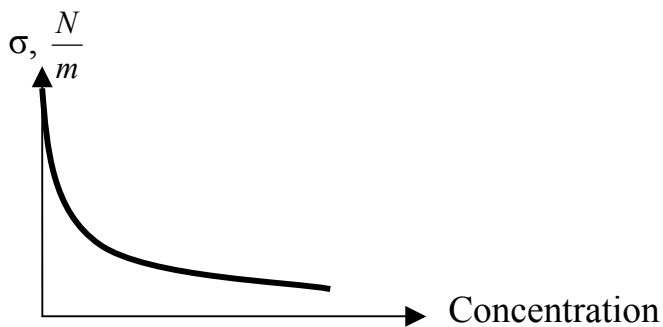


Fig. 7. Isotherm of surface tension.

Traube's Rule (1884–1888): the surface tension of the organic compounds belonging to the homological series of $R(CH_2)_nX$ shows certain regularity. For each additional CH_2 group the concentration required to give a certain surface tension was reduced by factor 2.6.

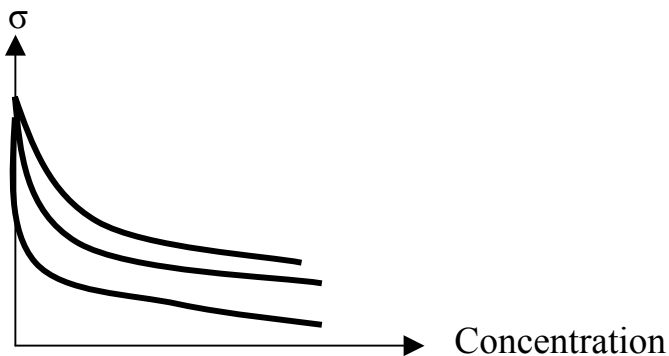


Fig. 8. The family of isotherm of surface tension.

The relationship between adsorbed amount (Γ) and surfactants' concentration in water solution is expressed by the Gibbs equation (1878):

$$\Gamma = - \frac{d\sigma}{dC} \times \frac{C(\text{sur})}{RT}, \quad 1.3$$

The influence of surfactants upon surface tension of solutions is expressed by the Shishkovsky equation:

$$\sigma = \sigma_0 - \alpha \times \ln(1 + b \times C_{\text{sur}}), \quad 1.4$$

where **a** and **b** — parameters of the equation.

The adsorbed amount may be calculated by the Gibbs-Shishkovsky equation:

$$\Gamma = \frac{a}{RT} \times \frac{bC_M}{1 + bC_M}, \quad 1.5$$

It is possible to compute a length of a surfactant' molecule (l) and an area occupied by it at interface surface (s) if maximal adsorbed amount Γ_{max} is determined:

$$l = \frac{\Gamma_{\text{max}} \times M}{\rho}, \quad 1.6$$

$$S = \frac{1}{\Gamma_{\text{max}} \times N_A}, \quad 1.7$$

where ρ — density of a surfactant;

M — it's molar mass;

N_A — Avogadro number.

1.3. Adsorption at solid sorbents

Solid sorbents are natural or artificial substances with highly developed surface area. They are characterized by their specific surface area (a_s).

$$a_s = \frac{A_s}{m}, \quad 1.8$$

where A_s — is the surface area of the solid sorbent;

m — mass of a sorbent.

Porous and powdered substances have a higher adsorption capacity than non-porous. Surface polarity corresponds to affinity with polar substances such as water or alcohols. Polar adsorbents are thus called «hydrophilic» and aluminosilicates such as zeolites, porous alumina, silica gel or silica-alumina are examples of adsorbents of this type. On the other hand, nonpolar adsorbents are generally «hydrophobic». Carbonaceous adsorbents, polymer adsorbents and silicalite are typical nonpolar adsorbents. These adsorbents have more affinity with oil or hydrocarbons than water.

Three main types of adsorption may be distinguished:

- Molecular adsorption from gaseous and liquid phases;
- Selective adsorption of electrolytes from aqueous solutions;
- Ion exchange adsorption.

Molecular adsorption is the adsorption of nonelectrolytes or weak electrolytes from gaseous and liquid phases. The physical and mathematical explanation for this type of adsorption was started by **Langmuir** in 1916. His theory assumes that:

1. Solid surface is not uniform; its unevenness and roughness act as the active or adsorption sites of the surface;
2. Each adsorption site adsorbs only one adsorbate molecule; all adsorption sites are equivalent:



Fig. 9. Molecular adsorption.

3. When all adsorption sites are occupied by adsorbate's molecules the monolayer is formed. This surface state corresponds to the maximum fractional coverage of a surface θ . The fractional coverage of a surface is defined as:

$$\theta = \frac{\text{number} \cdot \text{of} \cdot \text{occupied} \cdot \text{adsorption} \cdot \text{sites}}{\text{Total} \cdot \text{number} \cdot \text{of} \cdot \text{possible} \cdot \text{sites}}, \quad 1.9$$

At any temperature the coverage is a function of the applied adsorbate pressure or adsorbate concentration in a liquid phase. The variation of θ with p or c at a given T is called the **Langmuir adsorption isotherm**:

$$\theta = \frac{K_p}{1 + K_p} \quad 1.10$$

where K_p is an equilibrium constant, which is equal to k_a/k_d : In this equations, k_a and k_d are the rate constants for adsorption and desorption; p and c are the pressure of the adsorbate and its concentration respectively.

An assumption of the Langmuir isotherm is the independence and equivalence of the adsorption sites. Deviations from the isotherm can often be traced to the failure of these assumptions. Various attempts have been made to take these deviations into account. The **Freundlich isotherm** attempts to incorporate the role of substrate-substrate interaction on the surface

$$\mathfrak{a} = k \times p^{1/n} \quad 1.11$$

$$\mathfrak{a} = k \times c^{1/n}, \quad 1.12$$

where \mathfrak{a} — is a mass of an adsorbate adsorbed by one gram of an adsorbent;

k — is the Freundlich constant, n is a parameter of the equation.

In fig. 10 the Freundlich and Langmuir isotherms for one adsorption process are represented.

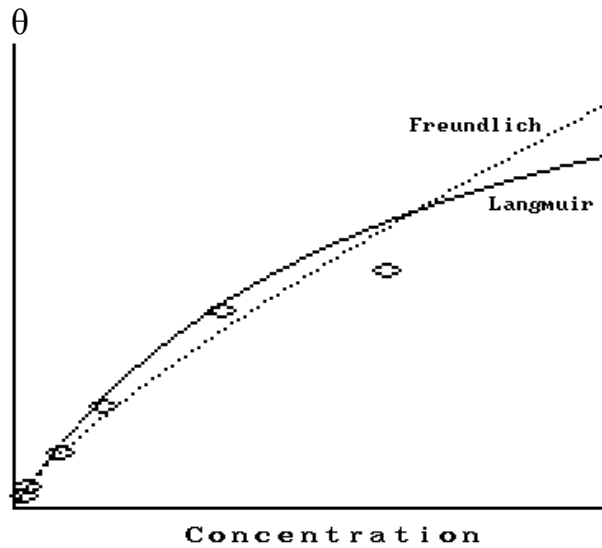


Fig. 10. The Freundlich and Langmuir isotherms.

The Langmuir isotherm gives us a wonderfully simple picture of adsorption at low coverage and is applicable in some situations. At high adsorbate pressures and thus high coverage, this simple isotherm fails to predict experimental results and thus cannot provide a correct explanation of adsorption in these conditions. What is missing in the Langmuir treatment is the possibility of the initial overlayer of adsorbate acting as a substrate surface itself, allowing for more adsorption beyond saturated (monolayer) coverage. This possibility has been treated by Brunauer, Emmett, and Teller (1938) and the result is named **the BET isotherm**. This isotherm is useful in cases where multilayer adsorption must be considered. The form of this isotherm is:

$$\frac{n}{n_{\text{mono}}} = \frac{cZ}{(1-Z) \times [1-Z(1-c)]} = \theta, \quad 1.13$$

where $\frac{n}{n_{\text{mono}}}$ — is the ratio of the moles adsorbed to the mole;

s — adsorbed in a single monolayer;

$z = p/p_0$, where p_0 is the vapor pressure of the pure condensed adsorbate.

The n/n_{mono} ratio represents a generalized coverage' because its value can exceed unity. The constant c represents the relative strengths of adsorption and condensation of the pure adsorbate.

Different isotherms agree with experiment more or less well over restricted ranges of pressure, but they remain largely empirical. Empirical, however, does not mean useless for, if the parameters of a reasonably reliable isotherm are known, reasonably reliable results can be obtained for the extent of surface coverage under various conditions. This kind of information is essential for a discussion of physiological processes in vivo.

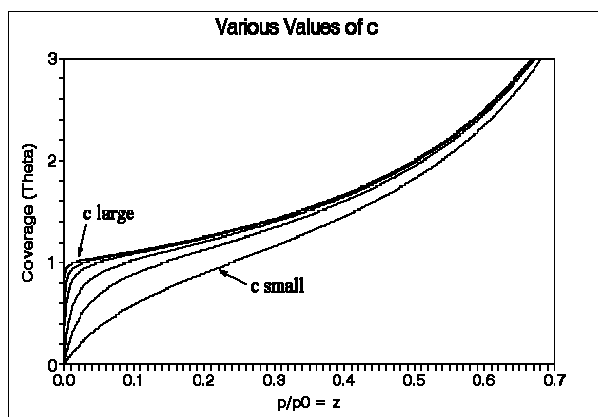


Fig. 11. BET isotherm

The selective adsorptions of electrolytes from aqueous solution obey the **Panet-Phayans Rules**:

Those ions are adsorbed at a solid surface from which this surface consists of (potential determining ions or PDI).

A charged surface adsorbs only oppositely charged ions (counter ions).

In the **ion exchange adsorption process** loosely held ions at fixed-charged sites on solids are exchanged with charged ions that are dissolved in solutions. Solid adsorbents able to take part in ion exchange are called ionites or ionic exchangers. They are widely used in medicine.

1.4. Laboratory Work

«SURFACE TENSION. ADSORPTION»

Experiment № 1.

Determination of a relationship between surface tension of solutions relationship between surface tension of solutions

Determine surface tension of 0.1 M aqueous solutions of the following alcohols: C₂H₅OH, C₃H₇OH, C₄H₉OH, C₅H₁₁OH using a stalogrametric method. Write the obtained data into the table 1.

Table 1

n	Alcohols and water	n	$\sigma \times 10^3, \text{N/n}$
1	H ₂ O		
2	C ₂ H ₅ OH		
3	C ₃ H ₇ OH		
4	C ₄ H ₉ OH		
5	C ₅ H ₁₁ OH		

A stalogrametric method is based on a comparison of a number of drops of water and a number of drops of a solution dropped from a capillary tube of a stalogrameter:

$$\sigma(X) = \sigma(H_2O) \times \frac{n(H_2O)}{n(X)}, \quad 1.14$$

where n — (H₂O) is a number of drops of water;

n — (X) is a number of drops of a solution.

Represent the obtained data in a graph form.

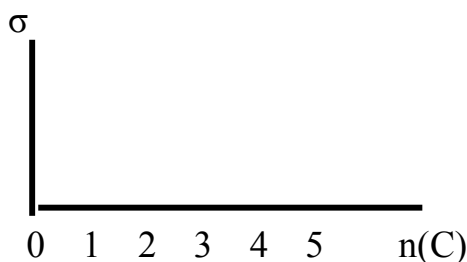


Fig. 12. Relationship between surface tension of solutions relationship between surface tension of solutions.

Make a conclusion

Experiment № 2

Determination of a relationship between surface tension of solutions and the surfactants' concentration

Determine surface tension of amyl alcohol aqueous solutions of the following molarity: 0.01, 0.025, 0.05, 0.1, and 0.2 M. Write the obtained data into the table 2.

Table 2

n	Molarity of C ₅ H ₁₁ OH	n	σ×10 ³ , N/n
1	0.01		
2	0.025		
3	0.05		
4	0.1		
5	0.2		

Represent the obtained data in a graph form.



Fig. 13. Relationship between surface tension of solutions and the surfactants' concentration

Make a conclusion.

1.5. Exercises for the self control

1. Specific surface area of the activated carbon is 1000 m² per gram. Compute a mass of carbon (II) oxide gas which may be absorbed at 0.10 m² of carbon surface if 1 g of a carbon adsorbs 0.440 L of CO.

2. Ammonia heat of adsorption at a dispersed copper is 29.3 kJ/mol. What ammonia volume will be absorbed by copper if 158.6 kJ of heat release?

3. The relationship between a surface tension of butyric acid solution and its concentration at 20°C is described by the Shishkovsky equation:

$$\sigma = \sigma_0 - 29.8 \times 10^{-3} \ln(1 + 19.64C),$$

Compute butyric acid adsorbed amount when $C_M = 0.01$ M.

4. The relationship between a surface tension of valeric acid solution and its concentration at 80°C is described by the Shishkovsky equation:

$$\sigma = 62.6 \times 10^{-3} - 17.7 \times 10^{-3} \ln(1 + 19.72C),$$

Compute valeric acid adsorbed amount when $C_M = 0.05$ M.

5. 0.0001 g of stearic acid form a monolayer at the water/ gas interface, which area is 470 sm^2 . Calculate an area occupied by one molecule of stearic acid if its density is 0.85 g/mL and Molar mass is 284 g/mol. Compute a length of its hydrophobic radical.

6. A natural pigment adsorption at the activated carbon may be described by the Freundlich equation:

$$x = 1.903 c^{0.7}$$

Calculate the mass of a carbon necessary to extract 90% of a pigment from 50 L of a solution which contains 0.04 g of a pigment per liter of a solution.

CHAPTER 2

CHEMISTRY OF DISPERSED SYSTEMS

The terms stable and stability are used in rather special and often different senses in colloid science: the relationship between these usages and the formal thermodynamic usage is outlined below.

After reading this chapter, you should be able to:

- **Define dispersed systems and give their classifications;**
- **Describe preparation and purification of colloidal solutions (sols);**
- **Discuss the structure of hydrophobic sol's micelle; name its compartments;**
- **Describe temperature dependence of the reactions rate;**
- **Define coagulation of sols; give reasons for it;**
- **Describe Schulze-Hardy Rule and define critical coagulation concentration.**

2.1. Classification of the dispersed systems

Colloidal chemistry is a chemistry of dispersed systems. Dispersed system is a micro heterogeneous system in which fine particles of dispersed phase are distributed in a dispersion medium.

Depending on the degree of dispersity dispersed systems are:

- Coarse dispersed with particles size $10^{-5} - 10^{-7}$ m;
- Colloidal dispersed with particles size $10^{-7} - 10^{-9}$ m;

Depending on the intensity of interaction between dispersed phase and dispersing medium the dispersed systems are:

- Lyophilic (hydrophilic), which are stable due to their ability to solvate;
- Lyophobic (hydrophobic), which are not stable because their particles are not solvated.

Depending on the intensity of interaction between particles of dispersed phase dispersed systems are:

- Freely-dispersed (no interaction between particles);
- Binding-dispersed (there are intermolecular forces between particle).

Classification of dispersed systems according to the state of phases is given in the table 3.

Table 3.

TYPES OF COLLOIDAL DISPERSIONS

Dispersed phase	Dispersion medium	Name	Examples
Liquid	Gas	Liquid aerosol	Fog, liquid sprays
Solid	Gas	Solid aerosol	Smoke, dust
Gas	Liquid	Foam	Foam on soap solutions, fire-extinguisher foam
Liquid	Liquid	Emulsion	Milk, mayonnaise
Solid	Liquid	Sol, colloidal suspension; paste (high solid concentration)	Au sol, AgI sol; toothpaste
Gas	Solid	Solid foam	Expanded polystyrene
Liquid	Solid	Solid emulsion	Opal, pearl
Solid	Solid	Solid suspension	Pigmented plastics

2.2. Preparation and purification of colloidal systems

Basically, the formation of dispersed systems involves either degradation of bulk matter or aggregation (condensation) of small molecules or ions.

Dispersion of bulk material may be done:

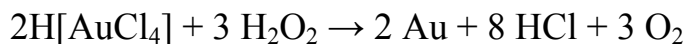
- By colloidal mills;
- By ultrasonic;
- By peptization method — preparing of sols by addition of electrolytes to freshly obtained precipitate.

A higher degree of dispersion is usually obtained when sol is prepared by aggregation (condensation) methods. Aggregation may be physical and chemical.

Physical aggregation involves:

- Cooling;
- Increase in pressure;
- Substitution of a solvent. For example, a coarse sulphur sol can be prepared by pouring a saturated solution of sulphur in alcohol in water just below boiling point. The alcohol vaporizes, leaving the water insoluble sulphur colloiddally dispersed.

Chemical aggregation is based on chemical reactions taking place in aqueous solutions which run with the formation of insoluble substances. For example, the colloidal gold solution is readily obtained by reducing auric chloride acid with hydrogen peroxide:



This sol is used in medicine for cancer healing.

Colloids always contain electrolytes or other substances from which they ought to be purified. There two main methods of their purification: **dialysis** and **ultrafiltration**.

Dialysis involves special membranes for separating particles of colloidal dimension. Dialysis is a phenomenon like osmosis except that in dialysis not only water molecules but also ordinary-sized ions and molecules can move through the membrane.

Colloidally-sized particles are blocked by dialyzing membrane.

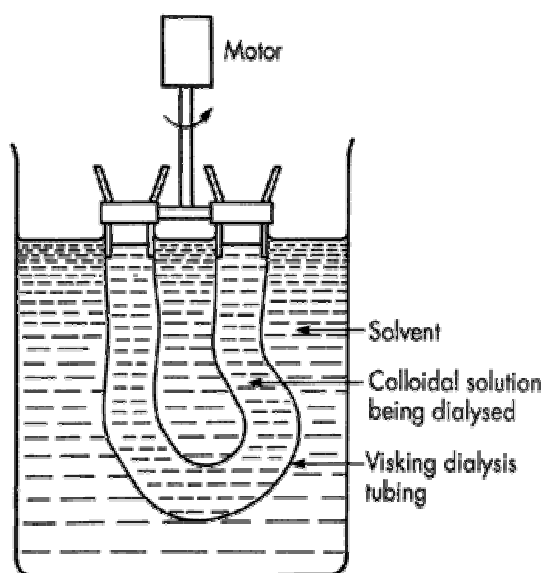


Fig. 14. A simple dialysis set-up.

Dialysis is particularly useful for removing small dissolved molecules from colloidal solutions or dispersions-e.g. extraneous electrolyte such as KNO_3 from AgI sol. The process is hastened by stirring so as to maintain a high concentration gradient of diffusible molecules across the membrane and by renewing the outer liquid from time to time. A further modification of dialysis is the technique of electro-dialysis, as illustrated in Figure 10. The applied potential between the metal screens supporting the membranes speeds up the migration of small ions to the membrane surface prior to their diffusion to the outer liquid.

Ultrafiltration is the application of pressure or suction to force the solvent and small particles across a membrane while the larger particles are retained. The membrane is normally supported between fine wire screens or deposited in a highly porous support such as a sintered glass disc. An important application of ultrafiltration is the so-called reverse osmosis method of water desalination.

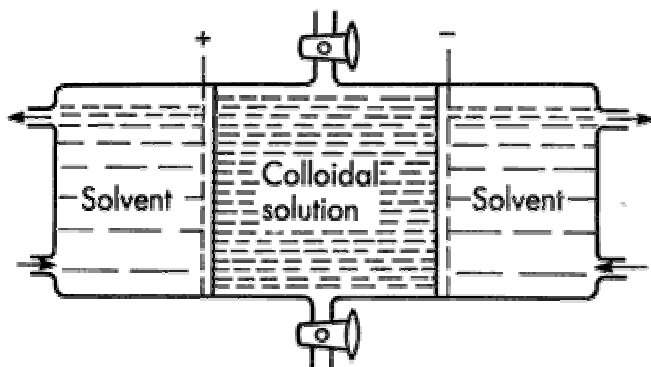


Fig. 15. Electrodialysis.

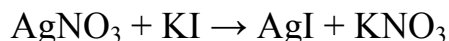
2.3. Structure of hydrophobic colloidal solutions (sols)

Sols consist of colloidal particles dispersed in water. They are not stable because dispersed particles are not solvated. Such systems may exist only in the presence of stabilizers: electrolytes, surfactants and polymers.

Micelle is a solid dispersed particle surrounded by a double electric layer composed of electrolyte-stabilizer ions. It was proved by experiment that colloidal particles have definite electric charge. Thus, *electrophoresis* is an electrical transfer of dispersed particles while *electroosmosis* is an electrical transfer of dispersion medium through semipermeable membrane. The origin of this charge is attributed to the adsorption of ions at the surface of a particle. This adsorption obeys the Panet-Phayans Rules.

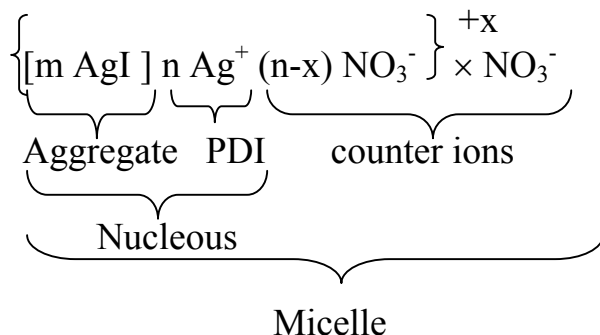
A structure of micelles is represented by congenital formulas.

EXAMPLE 1. Prepare silver (I) iodide sol according to the reaction:



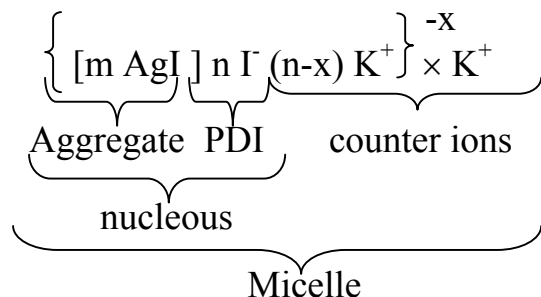
Write the formula of an obtained micelle if AgNO_3 is the excess. Give name to all the compartments of a micelle.

ANSWER: AgNO_3 is an electrolyte-stabilizer. Its ions are involved in the formation of a double electric layer around a dispersed particle. AgNO_3 is a strong electrolyte which completely ionizes into ions: $\text{AgNO}_3 \rightarrow \text{Ag}^+ + \text{NO}_3^-$.



EXAMPLE 2. Write the formula of silver (I) iodide micelle if KI is the excess. Give name to all the compartments of a micelle.

ANSWER: KI is an electrolyte-stabilizer. Its ions are involved in the formation of a double electric layer around a dispersed particle. KI is a strong electrolyte which completely ionizes into ions: $KI \rightarrow K^+ + I^-$.



2.4. Coagulation of sols

Colloidal stable means that the particles do not aggregate at a significant rate. Aggregation is the process or the result of the formation of aggregates. When a sol is colloidally unstable (i.e. the rate of aggregation is not negligible) the formation of aggregates is called coagulation. **Coagulation is the irreversible aggregation of dispersed particles into large particles followed by rapid precipitation.**

Sols coagulate when heated or under the mechanical disturbance but the chief reason for their coagulation is addition of electrolytes.

Schulze-Hardy Rule postulates that hydrophobic colloids are coagulated most efficiently by ions of opposite charge and high charge number.

B. Derjagin and L. Landau proved that:

$$\gamma_1 : \gamma_2 : \gamma_3 = \frac{1}{1^6} : \frac{1}{2^6} : \frac{1}{3^6} = 730 : 11 : 1, \quad 2.1$$

where γ — critical coagulation concentration (a minimal quantity of an electrolyte able to coagulate 1 L of a sol).

2.5. Laboratory Work

«COLLOIDAL SOLUTIONS»

Experiment № 1.

Preparing of $Fe(OH)_3$ sol by $FeCl_3$ hydrolysis

Pour 150 ml of distilled water into a flask and heat it up to the boiling point using an electric heater. Add 5 ml of concentrated $FeCl_3$ solution into boiling water. Use an analytical pipette to measure this volume. At the result dark-brown $Fe(OH)_3$ sol is prepared. Cool the prepared sol by tap water.

Write an equation of a chemical reaction $FeCl_3$ hydrolysis. Write the formula of a prepared sol micelle. Give name to all the compartments of a micelle.

Experiment № 2.

Coagulation of Fe(OH)₃ sol

In order to determine critical coagulation concentrations (c.c.c) of Fe(OH)₃ it is necessary to prepare electrolyte solutions with decreasing concentrations. For this purpose three sets of test tubes are taken each containing six test tubes. Each test tube is filled by water and electrolyte solution according to the table n2. After that 5 ml of Fe(OH)₃ sol must be added to each test tube. Time of exposition is 20 minutes. After that time examine solutions in the test tubes and mark presence or absence of coagulation in them by signs «+» or «-».

Critical coagulation concentration may be computed as follows:

$$\text{c.c.c} = C \times V \times 100 \text{ mmol / L,}$$

where C — concentration of electrolytes, mol/L;

V — volume of electrolyte, mL.

Table 4

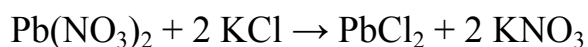
**Fe(OH)₃ COAGULATION UNDER THE INFLUENCE
OF ELECTROLYTES**

A set of test tubes	Coagulator		C.C.C Mol/L	Number of a test tube					
	Electrolyte	Ion		1	2	3	4	5	6
1	3.0 M KCl								
2	0.005 M K ₂ SO ₄								
3	0.0005 M K ₃ [Fe(CN) ₆]								
Volume, ml	Distilled water			0	1	2	3	4	4,5
	Electrolyte solution			5	4	3	2	1	0,5
	Fe(OH) ₃ sol			5	5	5	5	5	5

Make a conclusion.

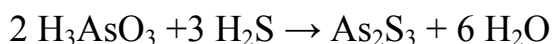
2.6. Exercises for the self-control

1. Prepare lead (II) chloride sol according to the reaction:



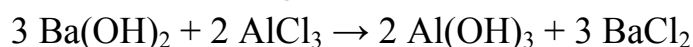
Write the formula of an obtained micelle if Pb(NO₃)₂ is the excess. Give name to all the compartments of a micelle.

2. Prepare As₂S₃ sol according to the reaction:



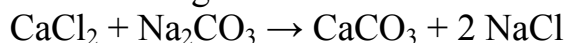
Write the formula of an obtained micelle if H₂S is the excess. Give name to all the compartments of a micelle.

3. Prepare Al(OH)₃ sol according to the reaction:



Write the formula of an obtained micelle if AlCl₃ is the excess. Towards what electrode this particle is drawn when a current is passed though the solution?

4. Prepare CaCO_3 sol according to the reaction:



(a) if CaCl_2 is the excess;

(b) if Na_2CO_3 is the excess.

What ions may coagulate a prepared sol: K^+ , Ca^{2+} , Cl^- , Al^{3+} , $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$? Write the ions according their ability to start a coagulation process.

5. Fine radioactive particles are contained in drinking water. It was decided to purify water by electrolytes addition. What electrolyte: AlCl_3 or Na_3PO_4 is preferable? It was determined that in electric field the particles migrate towards cathode.

CHAPTER 3

MACROMOLECULES AND THEIR SOLUTIONS

If you want to understand function, study structure.

-Francis H. Crick

After reading this chapter, you should be able to:

- Define macromolecules and their classification;
- Describe swelling and dissolving of polymers in different solvents and under different conditions;
- Describe structure and specific properties of polyelectrolytes at isoelectric point;
- Discuss methods of pI focusing.

A macromolecule is a chemical species distinguished by a high molar mass ($10^4 - 10^{10}$ g/mol). Their molecules length is approximately 10^6 . The chemistry of macromolecules, which are called polymers differs greatly from the chemistry of small, ordinary molecules. Studying the properties of these giant molecules requires special techniques.

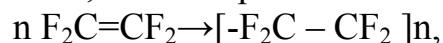
3.1. Polymers' classification

Polymers may be classified as:

- Natural (proteins, nucleic acids, polysaccharides, rubbers),
- Synthetic (polyethylene, polypropylene, Teflon).

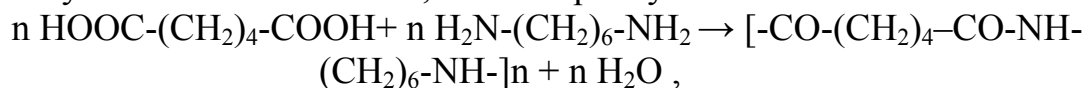
Synthetic polymers may be prepared by:

- Polymerization reactions, for example Teflon:



which is used to prepare cooking utensils, electrical insulation, and also blood vessels and heart's vents for transplantation.

- Polycondensation reactions, for example nylon:



which is used as sewing material in surgery.

According to the values of their molar masses polymers are:

➤ **Monodisperse** (polymeric systems whose molecules all have the same molar mass);

➤ **Polydisperse** (polymeric systems whose molecules do not have identical molar masses). The molar mass for such polymers may be defined in different ways. The two most common definitions are:

(a) Number-Average Molar Mass (M_n)

$$M_r \text{ (number average)} = \frac{\sum n_i M_{r,i}}{\sum n_i}, \quad 3.1$$

where n_i — is the number of molecules of relative molecular mass $M_{r,i}$;

(b) Weighted-Average Molar mass (M_w)

$$M_r \text{ (mass average)} = \frac{\sum n_i M_{r,i}^2}{\sum n_i M_{r,i}}, \quad 3.2$$

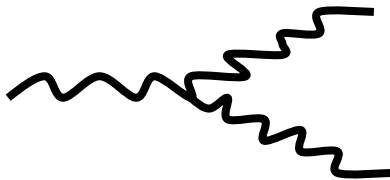
For any polydispersed system, M_r (weighed average) > M_r (number average), and only when the system is monodispersed will these averages coincide. The ratio M_r (mass average)/ M_r (number average) is a measure of the degree of polydispersity.

According to the structure of macromolecules four types of polymers may be distinguished:

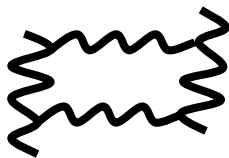
➤ Polymers with long threadlike straight molecules (e.g. rubbers);



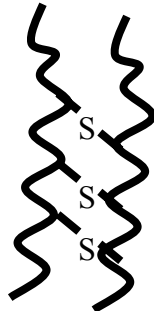
➤ Polymers with branched-chain molecules;



➤ Polymers with three-dimension molecules;



➤ Polymers with sewn cross linked molecules;



Volcanated rubber

The specific properties of polymers are:

- **Flexibility** (due to rotation about carbon-carbon and other bonds);
- **Strong intermolecular forces.**

3.2. Polymers' solutions

Polymers may form true and colloidal solutions. The first step in their dissolving process is swelling. **Swelling is a spontaneous irreversible diffusion of solvent molecules into a polymer phase. At the results of swelling polymers' volume and mass increases.** Swelling percent (α) is calculated as follows:

$$\alpha = \frac{m - m_0}{m_0} \times 100\%, \quad 3.3$$

where m_0 — initial mass of a polymer;
 m — mass of a polymer after swelling.

$$\alpha = \frac{V - V_0}{V_0} \times 100\%, \quad 3.4$$

where V_0 — initial volume of a polymer, mL;
 V — volume of a polymer after swelling.

Limited swelling results in gels formation, **unlimited** swelling results in formation of true solutions, which are stable lyophobic systems.

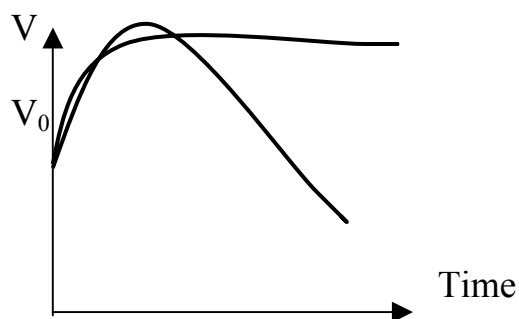


Fig.17. Kinetics curves of swelling

Polymers' solubility depends upon:

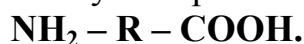
- Nature of polymers and solvents: «like dissolves like»;
- Structure of macromolecules;
- Temperature;
- Presence of electrolytes, which may affect polymers solubility in two different ways: (a) **salting-in effect** — the increase in solubility under the influence of electrolytes; (b) **salting-out effect** — the decrease in solubility under the influence of electrolytes;
- Acidity of solutions (for polyelectrolytes only).

3.3. Polyelectrolytes

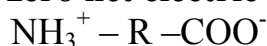
Polyelectrolytes are polymers which contain ionisable groups:

- Acidic (-COOH, -SO₃H);
- Basic (-NH₂).

Polyelectrolytes containing both acidic and basic ionisable groups are known as amphiprotic electrolytes. The bright example of such polyelectrolyte is protein. Its simplified formula may be represented as follows:



Proteins exhibit their specific properties being in the isoelectric state, which is characterized by the zero net electric charge on macromolecules:



Isoelectric point (pI) is the pH at which the net charge on a macromolecule is zero. pI is an important characteristic of each protein:

Table 5

Isoelectric points of some proteins

Protein	pI
Hemoglobin	6.7
Bovine serum albumin	4.9
Carboxypeptidase	6.0
Cytochrome c	10.7

Above 85% of proteins have pI in the range of 4.5 to 8.5.

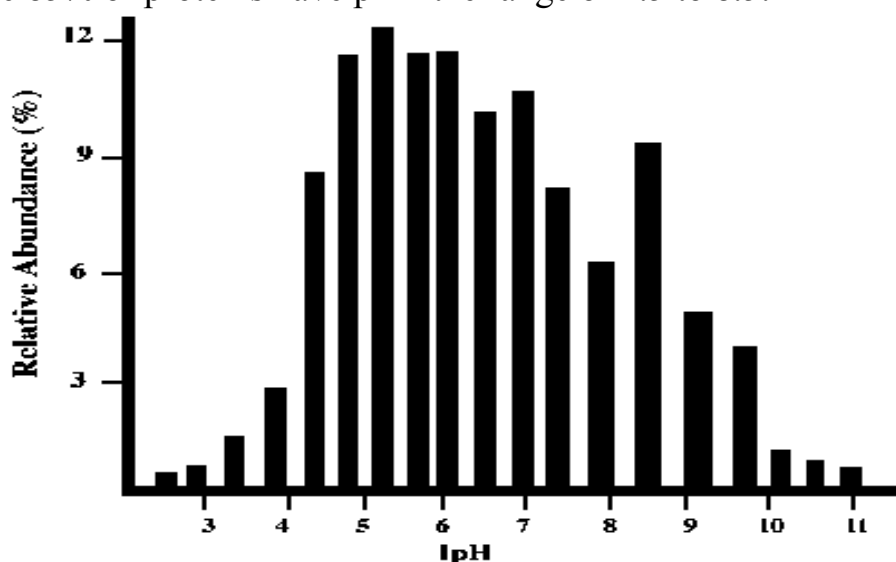


Fig. 18. Isoelectric pH distribution of various proteins.

About 85% of proteins have IpH in the range of 4.5 to 8.5.

The specific properties of proteins in isoelectric state are:

1. minimum swelling percent;
2. maximum percent of coagulation;
3. absence of electrophoresis mobility ($u=0$).

Electrophoresis is the migration of charged molecules in a solution in response to an electric field. Electrophoresis mobility depends upon the number of charges on macromolecules (z):

$$u = \frac{ze}{6\pi\eta r}, \quad 3.4$$

where e — electronic charge;

η — viscosity.

Electrophoresis is used to separate proteins and to focus their pI.

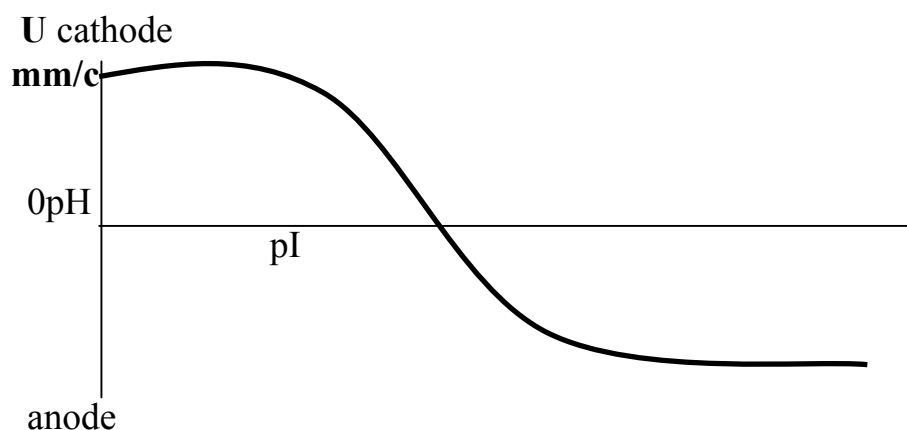


Fig.19. The curve of polyampholites' electrophoretic mobility

3.4. Laboratory Work **«POLYMERS' SOLUTIONS»**

Experiment № 1.

Determination of swelling percent of rubber in different solvents.

Weight 3 rings of a rubber and immerse them into flasks with (a) water, (b) benzene, (c) After 30 min. take the rings out of the solutions and weight them again. Write the obtained data into the table № 6. Compute swelling percent of a rubber according to the formula:

$$\alpha = \frac{m - m_0}{m_0} \times 100\%$$

where m_0 — initial mass of a rubber;

m — mass of a rubber after swelling.

Table 6

Solvent	Initial mass of a rubber m_0	Mass of a rubber after swelling m	$m - m_0$	Swelling percent of a rubber, α
Water				
Turpentine oil				
Benzene				
Hexene				

Experiment № 2

Studying of a relationship between gelatin swelling percent and pH of medium.

Add 0.5 mL of gelatin into the four test tubes and pour 10 mL of solvents according to the scheme:

The first test tube— 0.1M. HCl (pH = 1)

The second test tube — a buffer solution (pH = 4.7)

The third test tube— distilled water (pH = 7)

The fourth test tube— 0.1 M. NaOH (pH = 13).

Stir the solutions by a glass stick. After 30 minutes determine the gelatin volume and calculate its swelling percent according to the formula:

$$\alpha = \frac{V - V_0}{V_0} \times 100\%$$

where V_0 — initial volume of a gelatin, mL;

V — volume of a gelatin after swelling.

Table 7

Solvent	pH	V_0 , mL	V , mL	$V - V_0$	Swelling percent of a rubber, α , %
0.1M. HCl	1	1.0			
A buffer solution	4.7	1.0			
Distilled water	7	1.0			
0.1 M. NaOH	13	1.0			

Represent the obtained data in graph form (plot of α versus pH of solutions). Determine isoelectric point of gelatin. Make a conclusion.

Experiment № 3

Isoelectric point of a protein focusing

Take 5 centrifuge test tubes and pour 1 mL of acetate buffer solution ($\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$) with the pH values 3.8; 4.1; 4.7; 5.3; 6.2 into each test tube.

Add 0.5 mL of 1% protein solution and 1 mL of acetone (use a corresponding analytical pipette). Stir the prepared solutions and determine turbidity in each test tube using marks from 0 up to 5. Write the obtained data into the table N2. Highest turbidity corresponds to the maximal protein's coagulation and it's isoelectric point. In order to get more accurate results the protein's precipitate is separated from solutions using a centrifuge.

Pour a liquid above the precipitate into other test tubes and add 2 mL of the biuret reagent ($\text{CuSO}_4 + \text{NaOH}$) into each of them. After the precipitate dissolving in the reagent compare intensity of the violet color in each test tube using marks from 0 up to 5. Write the obtained data into the table 8.

Table 8

pH	3.8	4.1	4.7	5.3	6.2
Turbidity degree					
Intensity of a color					

A sample with the highest turbidity and lower intensity of a color corresponds to isoelectric point of a protein.

3.5. Exercises for self-control

1. In what solution the swelling percent of a rubber is higher, if it's mass after swelling in benzene was 22 g, while after swelling in toluene — 41.4g. The initial mass of a rubber is 10 g.

2. In what pH range is it better to separate proteins by electrophoresis if their pI are 4.8 and 7.9 correspondently. Prove your answer.

3. pI of gelatin is 4.7. It was dissolved in a solution with H^+ concentration 1000 times large than in pure water. What electric charge (positive or negative) will gain gelatin's molecules in this solution?

4. In what solvent — water, alcohol, benzene, and physiological solution — gelatin exhibits the highest swelling percent? Explain your answer.

5. pI of albumin is 4.8. Albumin was dissolved in a buffer solution with $[H^+] = 10^{-6} M$. Toward what electrode protein molecules migrate in the electric field?

6. At pH = 6 insulin doesn't migrate in the electric field. Toward what electrode it will migrate in the electric field when dissolved in 0.1 M hydrochloric acid?

7. A mixture of enzymes contains enzyme A (pI = 5) and enzyme B (pI = 9). In what pH range it is possible to separate proteins by electrophoresis?

GLOSSARY

Adsorbate. The substance adsorbed. The substance on which another substance is adsorbed.

Adsorption. The attachment of particles to a surface.

Adsorption. The relation between fractional coverage and partial pressure of a substrate.

Chemisorption. Adsorption by the formation of a chemical bond.

Colloid. A colloid is a heterogeneous mixture composed of tiny particles suspended in another material. The particles are larger than molecules but less than 1 μm in diameter. Particles this small do not settle out and pass right through filter paper. Milk is an example of a colloid. The particles can be solid, tiny droplets of liquid, or tiny bubbles of gas; the suspending medium can be a solid, liquid, or gas (although gas-gas colloids aren't possible).

Colloidal particles. Particles which have some characteristics of both species in solution and larger particles in suspension, which range in diameter from about 0.001 micrometer (μm) to about 1 μm , and which scatter white light as a light blue hue observed at right angles to the incident light.

Desorption. The detachment of an adsorbed substance.

Dialysis. The process by which low-molar mass solutes are removed from colloidal solution by means of diffusion across a semipermeable membrane.

Diffusion coefficient (D). A coefficient that indicates how quickly a substance will diffuse in a particular medium at a specific temperature and under the influence of a given concentration gradient.

Diffusion. Migration of particles down a concentration gradient.

Electrophoresis. A process in which a macromolecule with a net electric charge or a colloidal particle migrates in a solution under the influence of an electric field.

Electrophoretic mobility. Mobility of charged particles per unit electric field.

Emulsion. A colloid formed from tiny liquid droplets suspended in another, immiscible liquid. Milk is an example of an emulsion.

Foam. A colloid in which bubbles of gas are suspended in a solid or liquid. Aero gel (solid smoke) and Styrofoam are examples of solid foams; whipped cream is an example of liquid foam.

Fractional. The fraction of adsorption sites occupied.

Hydrophilic colloids Generally consist of macromolecules, such as proteins and synthetic polymers, which are characterized by strong interaction with water resulting in spontaneous formation of colloids when they are placed in water.

Hydrophobic colloids. Interact to a lesser extent with water and are stable because of their positive or negative electrical charges.

Isoelectric focusing. A technique in which a mixture of protein is resolved into its components by subjecting the mixture to an electric field in a supporting gel medium that has a supporting gel medium that has a previously established pH gradient.

Isoelectric point (pI). The pH at which the net charge on a macromolecule such as a protein does not move in an electric field.

Micells A spherical cluster formed by the aggregation of soap molecules in water.

Monolayer. A single layer of molecules on a surface.

Physisorption. Adsorption by Van-der-Waals interaction between the adsorbent and adsorbate.

Salting-in Effect. The increase in solubility of an electrolyte at a low ionic strength.

Salting-out Effect. The decrease in solubility of an electrolyte at high ionic strength.

Self-assembly. The spontaneous formation of complex structures of molecules or macromolecules held together by molecular integration.

Sol. A colloid with solid particles suspended in a liquid. Examples are protoplasm, starch in water, and gels.

Swelling. Swelling is a spontaneous irreversible diffusion of solvent molecules into a polymer phase. As a result of swelling polymers' volume and mass increases.

Tyndall effect. The characteristic light scattering phenomenon of colloids results from their being the same order of size as the wavelength of light. Light passing through a colloid is scattered by suspended particles. The light beam becomes clearly visible; this phenomenon is called the Tyndall effect. For example, car headlight beams can be seen in fog, but the beams are invisible in clear air.

Van der Waals forces. The weak attractive forces: dipole-dipole, dipole-induced dipole and dispersion forces.

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CONTENT

CHAPTER 1 ADSORPTION	3
1.1. Surface phenomena and surface tension	3
1.2. Surfactants' adsorption at gas/ liquid interface surfaces	4
1.3. Adsorption at solid sorbents.....	6
1.4. Laboratory Work «Surface tension. Adsorption».....	9
1.5. Exercises for the self-control	10
CHAPTER 2 CHEMISTRY OF DISPERSED SYSTEMS	11
2.1. Classification of the dispersed systems.....	11
2.2. Preparation and purification of colloidal systems.....	12
2.3. Structure of hydrophobic colloidal solutions (sols).....	14
2.4. Coagulation of sols.....	15
2.5. Laboratory Work «Colloidal Solutions».....	15
2.6. Exercises for the self-control	16
CHAPTER 3 MACROMOLECULES AND THEIR SOLUTIONS	17
3.1. Polymers' classification	17
3.2. Polymers' solutions.....	19
3.3. Polyelectrolytes	20
3.4. Laboratory Work «Polymers' solutions».....	21
3.5. Exercises for self-control	23
GLOSSARY	24
LITERATURE.....	26

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