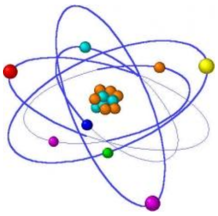
ZAPOROZHYE STATE MEDICAL UNIVERSITY

Kaplaushenko A.G., Pryakhin O.R., Varinskiy B.A., Iurchenko I.A.,
Shcherbak M.A., Samelyuk Yu.G., Kucheryavyi Yu.N., Hulina Yu.S.

PHYSICS AND CHEMISTRY OF SURFACE PHENOMENA. BASES OF THE ADSORPTIVE THERAPY

Teaching and methodical manual
for foreign student



Zaporozhye, 2016

ЗАПОРІЗЬКИЙ ДЕРЖАВНИЙ МЕДИЧНИЙ УНІВЕРСИТЕТ

Каплаушенко А.Г., Пряхін О.Р., Варинський Б.О., Юрченко І.О.,
Щербак М.О., Самелюк Ю.Г., Кучерявий Ю.М., Гуліна Ю.С.

ФІЗИКО-ХІМІЯ ПОВЕРХНЕВИХ ЯВИЩ. ОСНОВИ АДСОРБЦІЙНОЇ ТЕРАПІЇ

Навчально-методичний посібник
для студентів англомовної форми навчання

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Authors:
Kaplaushenko A.G., Pryakhin O.R., Varinskiy B.A., Iurchenko I.A.,
Shcherbak M.A., Samelyuk Yu.G., Kucheryavyi Yu.N., Hulina Yu.S.

Reviewers:
Parchenko V.V., Dr.hab., Professor of the Department of Toxicology and Inorganic Chemistry, Zaporozhye State Medical University;
Gladychev V.V., Dr.hab, Professor, Head of the Department of Medicinal Preparations Technology, Zaporozhye State Medical University.

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Каплаушенко А.Г., Пряхін О.Р., Варинський Б.О., Юрченко І.О.,
Щербак М.О., Самелюк Ю.Г., Кучерявий Ю.М., Гуліна Ю.С.

Рецензенти:
Парченко В.В., професор кафедри токсикологічної та неорганічної хімії Запорізького державного медичного університету, д. фарм. н..
Гладишев В.В., зав. кафедри технології ліків Запорізького державного медичного університету, д.фарм.н..

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CONTENTS

PREFACE

Medicinal Chemistry is one of the most rapidly developing areas within the discipline of Chemistry, both globally and locally. It is the study of the design, biochemical effects, regulatory and ethical aspects of drugs for the treatment of disease.

The aim of this discipline is to produce graduates with an appropriate background in biology and pharmacology, built upon a strong chemistry foundation.

Methodical recommendation of Medicinal Chemistry is designed to equip students with strong grounding in biological and chemical technique which is relevant to the pharmaceutical world.

The discipline gives an in-depth coverage of the chemical techniques required and relates these to the relevant pharmacology, anatomy, biochemistry and molecular biology.

The whole course of Medical chemistry which consists of ten topics is studied by students-physicians during the first year. Lecturer staff of department has prepared an educational and methodical recommendation in which the theoretical material is stated in the concise and available form.

The distribution of material on each of ten topics that are studied is set according to training program, the thematic plan of lectures and practical training.

The material of each topic is stated in such way that performance of practical work and the solution of situational tasks are preceded by theoretical part in which questions of medicine and biological value and also connection with other disciplines (biological chemistry, normal physiology, pathophysiology and others) are included.

Offered laboratory works and situational tasks will give students the chance to understand theoretical material fully and to use this knowledge in practice.

The experience of teaching medical chemistry shows that it is not always possible to coordinate an order of laboratory works realization with sequence of lecture course statement. That is why students usually have to prepare for practical work performance independently before the lesson. Therefore the theoretical part (in which the necessary volume of knowledge for conscious performance of experiment is given) precedes to each section of these Methodical recommendations.

Increasing of level of seminar and laboratory works is reached by use of such forms of occupations which open and consolidate theoretical knowledge, train scientific thinking, develop creative initiative and impart skills of handling devices and chemicals, chemical ware.

The structures, figures and schemes are clear and easy to follow and color is used well, highlighting main points without being distracting.

Chapters are helpfully signposted throughout, informing the reader how topics are related, which is especially important in such a multidisciplinary subject.

Topics are also presented clearly and with a logical progression culminating in the main points, questions and reading sections at the beginning of each chapter.

An assortment of case studies is provided and the authors work through each one in great detail, giving an overall perspective on the science.

Finally, very useful and informative appendices and a glossary are provided together with a comprehensive index that is good enough to rival any search engine!

There are many books that describe medicinal chemistry and its uses, but these methodological recommendations present medicinal chemistry and its related topics in a clear, informative and interesting way that really demonstrates the application and impact of this fundamental subject in society.

INTRODUCTION

Purpose: To study bases of the physical and chemical processes proceeding in a surface level – concepts about a surface tension and surface activity, sorption processes, including adsorption on surfaces liquid-gas, liquid-liquid, adsorption on firm sorbents. To master bases the chromatographic of methods of the analysis and the adsorptive therapy.

Target tasks:

- to study bases of physical and chemical processes proceeding in a surface level;
- to study to make calculations of a surface tension, surface activity, adsorption value, to build graphic regularities of the above parameters from concentration;
- to study to operate with formulas and to use them for the solution of situational tasks on an occupation subject;
- to receive practical skills of experimental work on determination of value of adsorption on border liquid-gas, and also with use of firm sorbents.
- to learn to give an assessment of reliability of the received results;
- to acquire a test material on an occupation subject.

The student has to know:

- the main theoretical questions connected with the surface phenomena and their importance in biology and medicine: surface tension of liquids and solutions; isotherm of a surface tension; surface activity; surface-active and surface and inactive substances; Traube's rule;
- sorption processes: adsorption on border liquid-gas and liquid-liquid undressed; Gibbs's equation; orientation of molecules of surface-active substances in a surface layer;

- structure of biological membranes; adsorption bases on limit of the section a firm body gas; Lengmyur's equation; adsorption from solution on a surface of a solid body; regularities of adsorption of the dissolved substances, vapors and gases; Freundlich equation;
- hysical and chemical bases of the adsorptive therapy (haemosorption, plazmosorbtion, limfosorbtion, enterosorbtion, application therapy); immunoadsorbents.

The student has to be able:

- to use scales and chemical ware correctly;
- to use an aspirator and to measure pressure with the help of the manometer;
- to determine concentration of substance by titrimetric method;
- to make calculations of a surface tension and surface activity;
- to build graphics of dependence of value of a surface tension from concentration;
- to define graphically and to calculate adsorption value.

CONCISE THEORETICAL MATERIAL

Every living organism contains a huge number of heterogeneous systems on which interface there are major biochemical processes. All surface phenomena are characterized by small energy of activation. For this reason biochemical reactions proceed on an interface with a high speed at environment temperature.

The majority of the reactions proceeding in an organism is made with direct participation of enzymes catalysts. Every enzyme at the first stages of the action adsorbs a substratum on a surface of a fermentative complex and than shows specific catalytic action.

The main function of blood is an oxygen carrier from lungs to all tissues and organs. It is realized effectively thanks to big specific surface of erythrocytes that allows them are saturated very quickly with oxygen in lungs and also quickly are got rid from excess of carbon dioxide. For the same reason there is also a fast poisoning of an organism at inhalation of toxic fumes and gases. On a surface of erythrocytes also medicinal substances are transferred which then are adsorbed with current of blood to bodies and issues.

The adsorptive processes are used for elimination of toxic substances from an organism. For this purpose through an adsorbent layer (absorbent carbon is now used mainly) pass blood, plasma and a lymph. These processes are called according to haemo - plazmo- and a limfosorbtion. The technique of haemosorption is rather simple: the integral blood taken from arterial system, pass through a column with adsorbent and return in an organism. Lack of haemosorption is direct contact of adsorbent with cellular particles of blood (erythrocytes, platelets, leukocytes). Therefore some types of adsorbents can destroy them. Sorption nature of cleaning remains if through a sorbent pass not integral blood but the acellular environment is plasma.

Works are widely conducted on improvement of properties of enterosorbents for extraction radionuclides from an organism (generally strontium and caesium), and also toxic heavy metals. In this case processes of adsorption are accompanied by formation of complex compounds and reactions of an ionic exchange.

Whole chemistry branch of creation of the surface-active substances was appeared on the basis of ideas about the surface phenomena, because they are necessary components of cosmetic and hygienic detergents.

1. Structure features of an interface of phases. Surface energy and surface tension

All interfaces in accordance with the aggregate state of adjoining phases are divided into two types:

1) mobile interfaces: between liquid and gas (l–g) and two immiscible liquids (l–l);

2) motionless interfaces: between a solid body and gas (b-g), a solid body and liquid (b –l), a solid body and a solid body (b-b).

The surface phenomena are called the processes happening on interphase boundary. Their reason is special condition of particles (molecules, atoms, ions) in layers of liquids and the solid bodies which are directly adjacent to interfaces. These layers sharply differ on many physical and chemical properties (to specific energy, density, viscosity, electric conductivity, etc.) from layers in the depth of the volume of phases. Differences are caused by a certain orientation of particles in surface layer and their special power state in comparison with particles in volume. Gibbs's general energy of G two-phase heterogeneous systems equals to the sum of Gibbs energy of the volume phases G_{v1} and G_{v2} and Gibbs's energy of an interface of phases (surface energy of G_s):

$$G_{system} = G_{v1} + G_{v2} + G_s \qquad (1).$$

Gibbs's surface energy of system is proportional to the area of an interphase surface:

$$Gs = \sigma \cdot S, \qquad (2)$$

where Gs is Gibbs's surface energy of system, J; σ is coefficient of proportionality and is called a surface tension, J/sq.m, S – area of an interphase surface, sq.m.

We will consider the mechanism of emergence of Gibbs surface energy on the example of two-phase system water – water vapor (l-g). The intermolecular forces operating on a molecule of water (A), settling down in the depth of liquid and surrounded from all directions similar molecules, are shown evenly from the next molecules. Equally effective these forces it is equal to zero. On the molecule of B which is on an interface, from adjoining phases forces of different value as total forces of an attraction of unit of volume of liquid it is much more, than gas units of volume because of its sparseness work. Therefore for surface molecules equally effective molecular forces it isn't equal to zero, and it is directed in liquid in this connection surface molecules seek to be involved in a liquid phase (fig. 1).

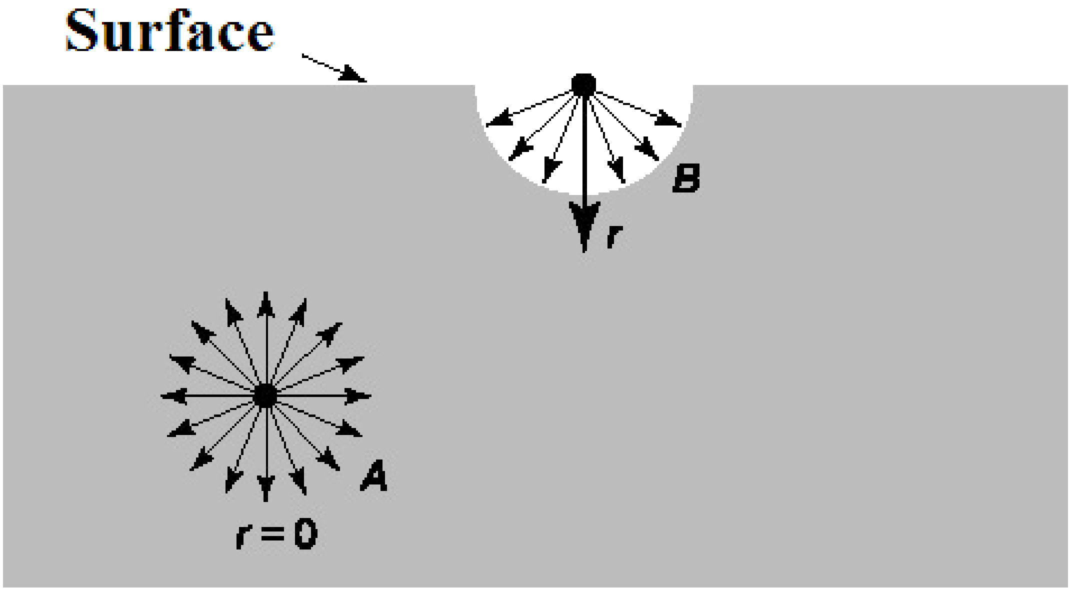


Fig. 1 Intermolecular forces operating on molecules in a blanket (B) and in volume of liquid (A)

Thus, molecules of a blanket have uncompensated forces of an attraction and therefore possess excess surface energy. From the thermodynamic point of view such state is energetically unprofitable. Therefore molecules of a blanket seek to leave in a liquid phase that leads to reduction of surface area of the section of phases. The spherical form of small droplets and ideally smooth surface of liquid in a wide vessel is explained by it. Process of transition of molecules of liquid depth on a surface demands energy expense for overcoming of forces of intermolecular interaction. The work directed on increase in a surface turns into potential energy of molecules of a blanket – in surface energy. The surface energy having per unit area to a surface (specific surface energy), is called as a surface tension (σ).

$$\sigma = Gs / S. \qquad (3)$$

Units of measure of a surface tension in SI: J/m^2 or N/m, as J = N·m.

The concept about a surface tension (specific surface energy) is fair for any heterogeneous systems, including for system liquid – liquid, and also for the solid body adjoining on gas or liquid.

The surface tension at different liquids variously also depends by nature liquids, the nature of an adjoining phase, temperature, pressure (if an adjoining phase gas), and also by nature and concentration of the dissolved substances.

Table 1

Surface tension of various liquids on to border with air at 293 K

Liquid	**Surface tension σ , mJ/ m^2**	**Liquid**	**Surface tension σ , mJ/ m^2**
Water	72,8	Chloroform	27,1
Glycerin	64,7	Ethanol	22,3
Acetic acid	27,6	Methanol	22,6
Olive oil	33,0	Blood serum	45,4
Benzene	29,4	Phenol	42,3

Surface tension on border liquid-air (the nonpolar gaseous environment) depends on polarity of liquid. For example, at low-polar liquids (benzene) the surface tension is less, and polar liquids (water) – have more.

The surface tension on border liquid-liquid also depends by nature adjoining phases: if more a polarity difference of phases, than more surface tension on limit of their section.

The surface tension of liquids decreases with temperature growth. It means that at a critical temperature the limit of the section between phases disappears and system gas-liquid turns from the heterogeneous into the homogeneous. Therefore the value of a surface tension is a measure of heterogeneity of system, and not only gas-liquid, but also liquid-liquid.

With increasing of pressure interaction of surface molecules of liquid with molecules of a gas phase is increased to and excess of molecule energy is decreased too. Therefore with pressure increasing in system liquid-gas the surface tension is decreased.

The dissolved substances depending on the nature can influence a surface tension of liquids differently. Ability of the dissolved substances to change a surface tension of solvent is called as surface *activity*. All substances on ability to change a surface tension of solvent share on three groups:

1. *The Surface-active Substances (SAS)* lower a surface tension of solvent. In relation to water the SAS are many organic compounds: alcohols, acids of an aliphatic series and their salt (soap), esters, amines, proteins, etc.

2. The Surface Inactive Substances (SIS) – slightly raise a surface tension of solvent. In relation to water the SNS are inorganic acids, the bases, salts, and also such organic compounds, as glycine (aminoacetic acid).

3. The Surface Nonreactive Substances (SNS) – practically don't change a surface tension of solvent. In relation to water the SNS is a sucrose and some other substances.

Dependences of surface tension change of water solutions of the specified substances classes on their concentration are represented in Fig. 2 (isotherms of a surface tension, T = const). From Fig. 2 it is visible that at increase in concentration of the SAS the surface tension of solution decreases to the minimum limit value; at increase in concentration of SIS the surface tension of solution increases, and at increase in concentration of SNS the surface tension of solution doesn't change.

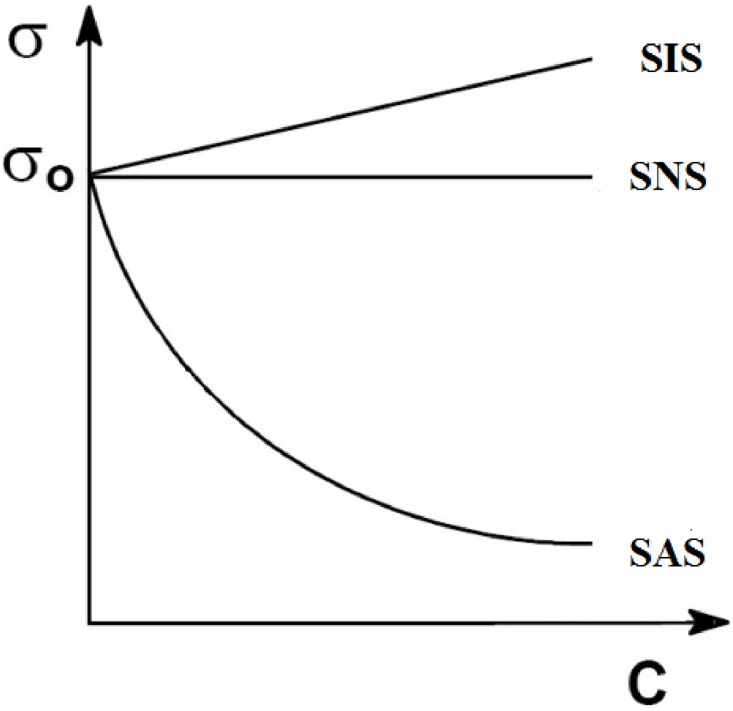
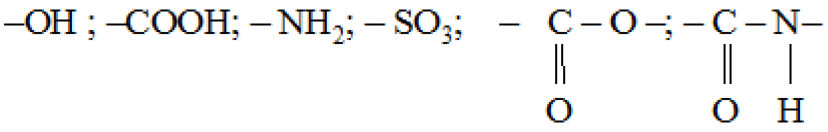


Fig. 2. Dependences of surface tension change a of water solutions SAS, SNS and SIS on their concentration.

2. Structure and classification of the SAS.

We will consider a structure of the SAS in view of their great biological importance. Ability of substance to lower a surface tension of solvent is caused by existence in its molecule of nonpolar (hydrophobic) hydrocarbonic part ("tail") and polar hydrophilic group ("head"). To polar groups belong:



$$-OH;\ -COOH;\ -NH_2;\ -SO_3;\quad -\underset{\underset{O}{\|}}{C}-O-;\ -\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-$$

Such substances are called diphilic. Diphilic molecules of SAS are designated by the standard symbol ———o, where a circle is polar group, and a hyphen is the nonpolar radical.

Length of the hydrocarbonic radical of a SAS molecule strongly affects it's surface activity. According to Traube's rule:

Surface activity of substances of the same homological series increases approximately by 3 times with increasing of a hydrocarbonaceous chain at group –CH_2– (for the diluted water solutions). The surface tension of their solutions decreases.

This rule is well illustrated by family of the curves represented in Fig. 3.

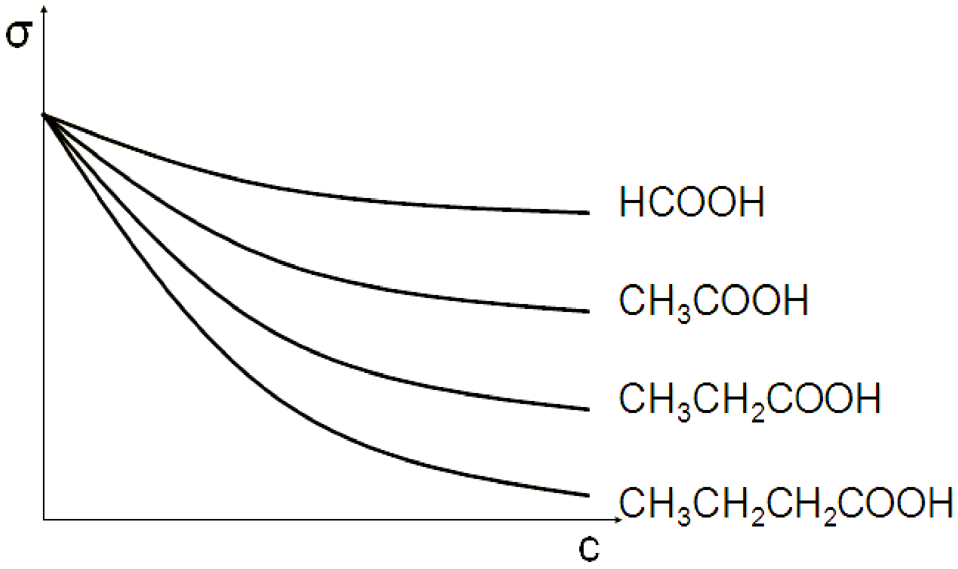


Fig. 3. Dependence of a surface tension of various SAS of one homological series

In some cases biological activity (for example, narcotic action, bacterial action, etc.) substances of the same homological series increases with increasing of their surface activity.

Depending on ability to dissociation in the SAS water solutions share on ionogenic (electrolytes) and nonionic (nonelectrolytes). In turn ionogenic SAS are subdivided into anion, cationic and ampholytic (amphoteric).

Anion SAS dissociate in water with formation of surface-active anion. To SAS of this type making the most part of world production of all surface-active substances, belong:

a) carbonic acids and their salts (soap) of the general formula RCOOM (where M – metal), for example , sodium palmitate $C_{15}H_{31}COONa$, sodium stearate $C_{17}H_{35}COONa$, sodium oleate $C_{17}H_{33}COONa$;

b) alkylsulfates $ROSO_2OM$;

c) alkylaryl sulfonates $RArSO_2OM$ and ect.

As SAS broad practical application is found by salts of synthetic fatty acids of C_{10} fraction – C_{17}, replacing acids of a vegetable and animal origin.

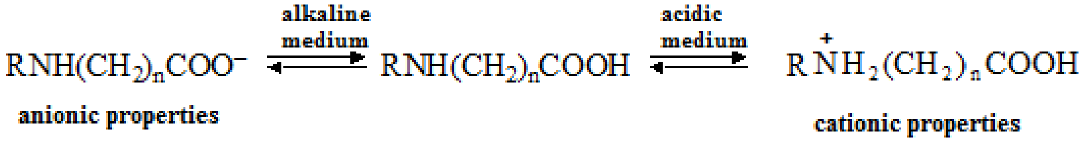
Cationic SAS dissociate in water with formation of a surface-active cation. Among these are :

a) salts of primary, secondary and tertiary aliphatic and aromatic amines;

b) salt of the alkyldisplaced ammonium bases.

Cationic SAS are the most toxic and least biologically decomposed of all SAS. They are often use as bactericidal, fungicide, disinfecting substances, corrosion inhibitors.

Ampholytic SAS have two functional groups (one of them has acidic character and another contain the alkaline character), for example, carboxyl and aminogen groups. Depending on pH media amfolitic SAS show anion-active or cation-active properties:



$$\underset{\textbf{anionic properties}}{RNH(CH_2)_nCOO^-} \overset{\textbf{alkaline medium}}{\rightleftarrows} RNH(CH_2)_nCOOH \overset{\textbf{acidic medium}}{\rightleftarrows} \underset{\textbf{cationic properties}}{R\overset{+}{N}H_2(CH_2)_nCOOH}$$

Nonionic SAS don't dissociate in solutions on ions. They usually represent mix of homologs with various length of a polyoxyethylene chain of the general formula $RO(OCH_2CH_2)_nH$ where R is a hydrocarbonic radical.

3. Importance of the surface phenomena in medicine.

Water is the most often being applied solvent. It possesses a big surface tension (72,75 mJ/м^2 at 20 ^{o} C), therefore in relation to it many substances are surface-active.

The surface tension of biological liquids (for example, blood serums – see tab. 1) is less than water owing to SAS existence of various nature in them (acids of a fat row, steroids, etc.). As a result these substances spontaneously collect (are adsorbed) at walls of vessels, cellular membranes that facilitates their penetration through these membranes.

Change of a surface tension of biological liquids is used in the diagnostic purposes. For example, the surface tension of plasma of blood considerably changes at various diseases (anaphylactic shock, a cancer, etc.). With age the person the surface tension of serum of blood decreases.

From numerous methods of measurement of a surface tension at biochemical, physiological and clinical trials most often use a stalagmometric method and a method of breakdown of vials of air.

4. Adsorption on mobile limit of the section of phases.

Any system according to the second beginning of thermodynamics seeks to pass into such state at which it possesses the minimum stock of Gibbs energy spontaneously. Therefore, she aspires to a minimum of surface Gibbs energy

($\boldsymbol{G_s = \sigma \cdot S}$). Therefore the system formed by one component, for example pure solvent (σ = const при T = const), can lower a stock of the surface Gibbs energy in these conditions only one way – to take the form at which the interface of phases is minimum.

The system consisting more than of one component, besides surface area reduction, can lower Gibbs's surface energy and by reduction of a surface tension (σ), that is by redistribution of the dissolved substance between the volume of a liquid phase and a blanket. We will consider chances of distribution of the dissolved substance in water solution (fig. 4).

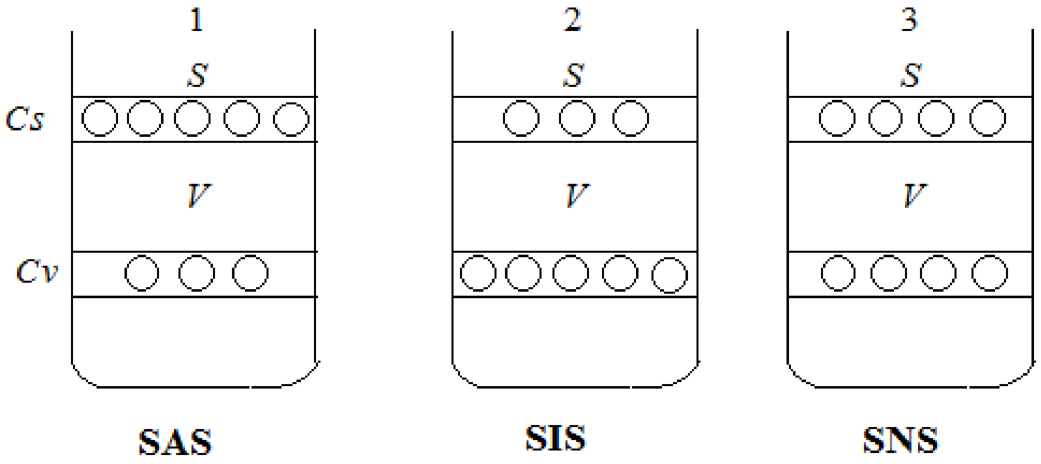


Fig.4 . Chances of distribution of the dissolved substance between a surface layer and volume of a liquid phase (water).

Cs – concentration of the dissolved substance in a blanket;

Cv – concentration of the dissolved substance in volume of a phase

1. SAS reduce a surface tension of solvent (water) therefore collect in a blanket (*Cs*>*Cv*), in this connection in system the stock of surface energy of Gibbs decreases. SAS have to possess: a) surface tension smaller in comparison with a surface tension of solvent, differently accumulation of substance in a blanket thermodynamic would be unprofitable; b) rather small solubility (if they were well lysed, liquids would seek to leave from a surface deep into).

2. SIS increase a surface tension of solvent (water) therefore collect in volume of a phase ($Cs<Cv$), as only in this case the stock of surface energy of Gibbs in system relatively decreases. SIS have to possess the following properties: a) their surface tension has to be more surface tension of solvent; otherwise they will spontaneously seek to collect in a blanket; b) their solubility has to be high as only provided that they will seek to go from a surface to volume.

3. SNS don't change a surface tension of solvent (water), therefore their concentration in a blanket same, as well as in volume of a phase ($Cs=Cv$).

Process of spontaneous redistribution of the dissolved substance on limit of the section of phases concerning the volume of solution is called as adsorption (Γ), and quantitatively it measure in mol/sq.m or mmol/cm^2. To measure excess amount of the adsorbed substance directly on borders liquid-gas and liquid-liquid hardly because of its small amount on limit of the section of phases in comparison with quantity in volume. Therefore adsorption value usually calculate by means of Gibbs's equation which is removed on the basis of the second beginning of thermodynamics:

$$\Gamma = -\frac{d\sigma}{dC}\cdot\frac{C}{RT}, \qquad (4)$$

where Γ – amount of the substance adsorbed by unit of an interface of phases, mol/sq.m; C – equilibrium molar concentration of the dissolved substance, mol/l; R – gas constant equal to 8,314 J / mole*K; $-\frac{d\sigma}{dC}$ – the first derivative of a surface tension on the concentration, taken with a minus sign.

At narrow intervals of concentration the derivative in Gibbs's equation can be replaced with the relation of final changes:

$$\Gamma = -\frac{\Delta\sigma}{\Delta C}\cdot\frac{C}{RT}, \qquad (5)$$

where $\Delta\sigma = \sigma_2 - \sigma_1$ is change of a surface tension at increase in concentration of solution on $\Delta C = C_2 - C_1$.

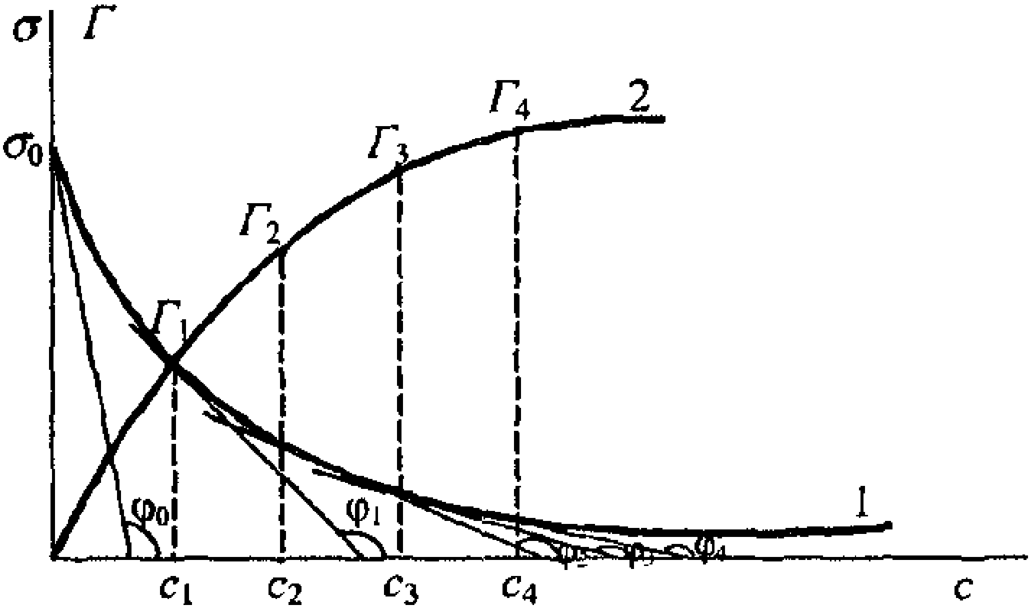


Fig. 5. Isotherm of a surface tension of SAS water solution, $\sigma = f\,(C)$*;*
isotherm of Gibbs adsorption, $\Gamma = f\,(C)$

Gibbs's equation reflects the following dependence: the more strongly the surface tension with increase in concentration of adsorbed substance, the more its surface activity decreases. It testifies that the minus sign indicates inverse relationship between the value of adsorption Γ and a surface tension σ.

If $\Delta\sigma / \Delta C < 0$, то $\Gamma > 0$, i.e. adsorption is positive (the substance collects on an interface of phases), and it is characteristic for surface-active substances. If $\Delta\sigma / \Delta C > 0$, то $\Gamma < 0$, i.e. adsorption is negative (the substance collects in volume) and it is characteristic for surface inactive substances.

For calculation of adsorption value for Gibbs's equation measure a surface tension for several solutions of surface-active substance with different concentration C_1, C_2... at a certain temperature and according to experience build a curve $\sigma = f\ (C)$ as shown in fig. 5. In the points of this curve corresponding to concentration C_1, C_2..., carry out tangents and define tangents of angle of their inclination of α to abscissa axis:

$$\mathrm{tg}\alpha_1 = \left(\frac{\Delta\sigma}{\Delta C}\right)_1; \qquad \mathrm{tg}\alpha_2 = \left(\frac{\Delta\sigma}{\Delta C}\right)_2.$$

Values $(\frac{\Delta\sigma}{\Delta C})_1$ and $(\frac{\Delta\sigma}{\Delta C})_2$, corresponding to concentration C_1, C_2..., multiply on $-\frac{C_1}{RT}, -\frac{C_2}{RT}$, ..., receive values Γ_1, Γ_2..., put them on the schedule $\Gamma = f(C)$ also receive a curve of an isotherm of adsorption of Gibbs (fig. 5).

Results of inspections of the Gibbs equation carried out by various methods, practically coincided with the value of the adsorption defined experimentally and calculated on the equation of Gibbs (tab. 2).

Table 2

The values of adsorption defined experimentally and theoretically

Substance	**Adsorption**	
	$\Gamma_{exp} \cdot 10^7$, mol/sм^2	**$\Gamma_{theor} \cdot 10^7$, mol/sм^2**
Phenol	4,1	4,8
Capronic acid	6,2	6,3
Hydrocinnamic acid	5,6	5,1

Substance adsorption is the reversible process which ends with establishing of the adsorptive balance where the speed of adsorption is equal to the speed of the return process is desorption.

Dependence of adsorption on balance concentration of the dissolved substance at a constant temperature is called adsorption isotherm.

The schedule of a typical experimental isotherm is represented in Fig. 6. With increasing of balance concentration of the dissolved substance the value of adsorption grows directly proportionally (OA segment). With the further growth of equilibrium concentration of substance the increase of adsorption has parabolic character (AB segment). At big concentration of the dissolved substance adsorption reaches the limit value (Γ_∞) which isn't changing with further increase of concentration and is graphically represented by a horizontal straight line (BC segment).

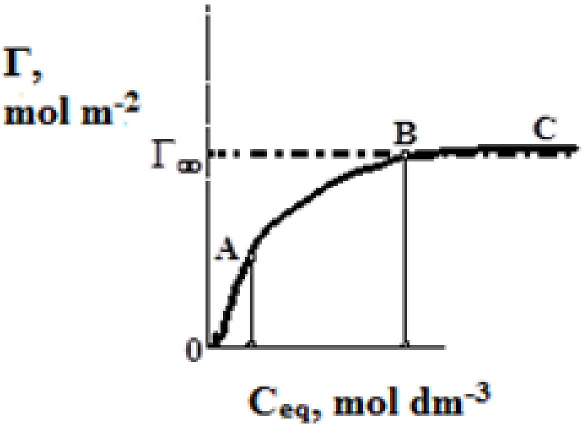


Fig. 6. Isotherm of adsorption of surface-active substance on limit of the section water solution – gas

Adsorption of surface-active substances of the same homological series changes according to Traube's rule: adsorption of substance increases with growth of length of an hydrocarbonaceous radial of SAS molecules (Fig. 7)

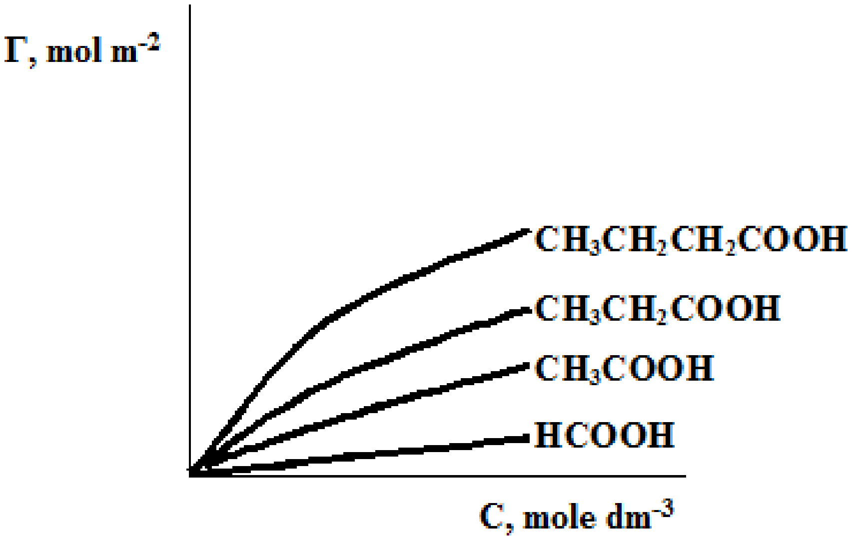


Fig. 7. Adsorption isotherms for water solutions of a homological number of fatty acids

Besides the nature and concentration of the dissolved substance, its adsorption also depends on temperature on a liquid surface: adsorption decreases with temperature growth.

5. Orientation of SAS molecules at the surface layer. Structure of biological membranes

Existence of the minimum value of a surface tension at SAS solutions and limit value of adsorption (Γ_∞) allowed I. Langmuir (1881-1957) to make assumption about orientation of the adsorbed molecules at surface layer. Molecules of SAS consist of two parts: polar (hydrophilic) and nonpolar (hydrophobic). At adsorption the polar group has big affinity with a polar phase (for example, with water) to contact it. At the same time the nonpolar group is pushed out in an nonpolar phase (Fig. 8).

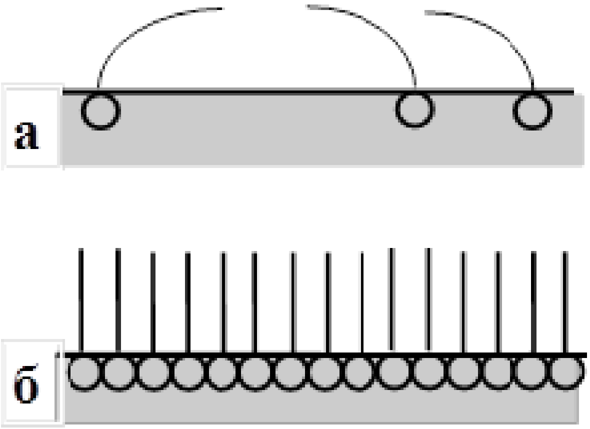


Fig. 8. Structure of Langmuir's monolayer

At small concentration of SAS hydrocarbonaceous radicals "lie" on a surface of polar liquid, and polar groups are immersed in it (Fig. 8).

The number of the molecules increases at surface layer with increase of SAS concentration in solution. It lead to formation of a saturated monomolecular adsorptive layer on a boundary surface (Fig. 8). The molecules of SAS are extremely focused on layer. This layer figuratively is called as Langmuir's molecular stockade. Constancy of limit adsorption of Γ_∞ at organic substances of the same homological row is explained by existence of a monomolecular saturated layer.

Ideas of orientation of SAS molecules in a saturated adsorptive layer played an important role in doctrine development about structure of biological membranes (Fig. 9).

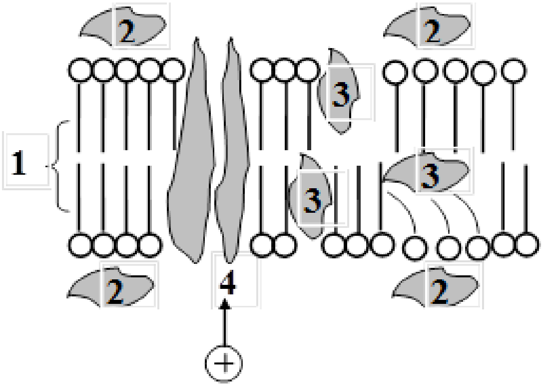


Fig.8.9. Mosaic model of the structure of biological membranes:
1 - lipid bilayer;
2 - surface proteins;
3 - integral proteins;
4 - ion channel.

Fig.9. The structure of biological membranes

Cellular membranes are formed mainly by molecules of two types:

- ✓ lipids
- ✓ proteins.

Lipids are insoluble in water, but they are liquefiable in organic solvents. Feature of membrane lipids is existence of polar groups at one end of their molecule (for example, – COON), which have hydrophilic properties. The other its end is represented a long hydrocarbonaceous chain with hydrophobic properties. Lipids form bimolecular pellicle (thickness about 70 ^{0}A). The polar groups of pellicle present on both surfaces of a membrane, and nonpolar are shipped in it.

Molecules of protein can present near external and internal surfaces of a membrane, and also get through all its thickness partially or completely.

Cellular membranes are very strong and usually possess properties of an electric insulator. Biological membranes aren't rigid structures.

For example, in many cases of a proteins and lipids in membranes are in continuous movement.

6. Adsorption on motionless interface (on a surface of solid substance)

Adsorption on motionless interface of phases is accumulation of one substance on a surface of another.

The solid substance on which surface other substance collects, is called **adsorbent**, and absorbed substance is an ***adsorbate.***

In the energetic relation sites of a surface of a solid body aren't equivalent. Surface sites with the greatest local stock of surface Gibb’s energy are called active centers on which an adsorption is occurred.

Adsorption can be considered as interaction of molecules of an adsorbate with the active centers of adsorbent surface. This interaction can be various. There are physical and chemical adsorption as a consequence of that.

During physical adsorption adsorbent and an adsorbate interact at the expense of Van der Waals's forces. Physical adsorption proceeds spontaneously, is reversible and a little specific. The physical adsorption decreases with increasing of temperature.

During chemical adsorption (hemosorption) adsorbate the chemical bond is formed between adsorbent and everyone loses its identity. Hemosorption is similar to chemical reaction and is usually accompanied by formation at interface of phases. For example, CO_2 adsorption on slaked lime leads to formation of a thin layer of a calcium carbonate on its surface.

$$CO_2(g) + Ca(OH)_2(s) = CaCO_3(s) + H_2O(g)$$

Energy of interaction at a hemosorption makes 40–400 kJ/mol, i.e. is on 1-2 orders more than this value for physical adsorption (10 – 40 kJ/mol). As a rule hemosorption is monomolecular. If it happens with small thermal effect, it often indicates about of the parallel process demanding expenses of energy (for example, dissociation of molecules of an adsorbate on a surface).

Hemosorption is characterized by specificity of interaction and is often irreversible. During chemical adsorption instead of the adsorbed substance another substance can desorb into. The specified types of interaction are shown at various stages of process of adsorption. So, during adsorption of gases by surfaces of solid bodies at the initial stage of process chemical forces of interaction participate in the basic.

For example, CO_2 and O_2 absorption by activated carbon with a low pressure is accompanied by formation of chemical bonds between molecules of an adsorbate and an adsorbent surface. A significant amount of energy is thus allocated. At later stages of adsorption process (with high pressures of gases) physical forces come into effect.

Process of adsorption is usually reversible. Some particles can come off a surface of adsorbent and go to surrounding space. This process is called as a desorption. Over time both processes bring system into a condition of the adsorptive balance: adsorption ⇄ desorption.

Most often adsorption process is exothermic. According to the principle of Le-Chatelier it is favorable to carry out it at rather low temperatures. With temperature increase owing to increase in fluctuations of the particles adsorbed by a surface, balance moves towards desorption process.

Depth of adsorption course is characterized by specific adsorption which is called quantity of the adsorbate adsorbed on unit of a adsorbent surface:

$$\Gamma = n / S, \ \text{mol/ m}^2, \qquad (6)$$

where n – amount of the adsorbate, mole; S – square of the adsorbent, m^2.

Most often specific adsorption on a surface of strong substance express in moths on 1 kg (or mmol on 1 g) adsorbent, as measurement of surface area of any adsorbent – quite labor-consuming operation:

$$\Gamma = n / m, \text{ mol/kg}, \qquad (7)$$

where n – amount of the adsorbate, mol; m – mass of the adsorbent, kg.

Small energy of activation and, therefore, a high speed is characteristic for adsorption except reversibility and exothermicity.

Adsorption depends by nature adsorbent and an adsorbate, on temperature, on a specific surface of adsorbent, on adsorbate pressure (for adsorption of gases), by nature solvent and concentration of an adsorbate in solution (for adsorption from solutions).

Nonpolar adsorbents, for example, the graphitized soot or absorbent carbon, adsorb nonpolar organic compounds better. Polar adsorbates are better adsorbed on a surface of polar adsorbents, such, for example, as silica gel, aluminum oxide, cellulose, etc. With the same mass of adsorbent adsorption increases with increase in a specific surface (i.e. crushing) of adsorbent.

Gibbs's equation is used universally for calculation of adsorption value , i.e. is applicable both for mobile limits of the section, and for the motionless. But in practice it is impossible to measure the value of a surface tension on a surface of solid substance.

For the description of experimentally obtained data of adsorption on a surface both solid substance, and liquid, the large number of the equations is offered, but Lengmuir and Freundlich equations are more often used.

7 . Monomolecular theory of adsorption. Lengmyur's equation

The monomolecular theory of adsorption was offered in 1915 by the American physicist-chemist I. Lengmuir and includes the following provisions:

1. Particles of adsorbed substance located only on the active centers representing separate atoms or atom groups, acting over an adsorbent surface, and being characterized the greatest non saturation of chemical bonds.

2. Each particle of adsorbed substance (adsorbate) occupies one active center of adsorbent.

3. Adsorption ends as soon as the monomolecular layer is formed. At this moment all active centers are occupied and the surface of adsorbent is covered with an adsorbate one thick layer a molecule.

4. The adsorbed molecules are kept by the active centers only during a certain period then leave a surface (are desorbed) and their place is taken by other molecules, i.e. adsorption has dynamic character. At balance of adsorption and a desorption speeds are equal.

5. Interaction between the adsorbed molecules is absent. It means that stay of molecules on the active centers doesn't influence adsorption process on the next active centers that is incorrectly.

Proceeding from the provisions given above, Lengmuir could give the general equation of an isotherm of adsorption:

$$\Gamma = \Gamma_{\infty} \frac{C}{K + C}, \tag{8}$$

Where Γ_{∞} is the limit adsorption observed at extent of filling of a surface the adsorption equal 1, mol/m^2 ; K is a constant is equal to a half of limit adsorption; C is equilibrium concentration of solution, mol/dm^3.

In case of adsorption of gases and vapors in the equation (8) equilibrium concentration of solution is replaced with value of equilibrium partial pressure of gas or vapor (p):

$$\Gamma = \Gamma_{\infty} \frac{P}{K + P}. \tag{9}$$

The analysis of the Lengmuir equation shows that depending on equilibrium concentration (pressure) of an adsorbate it can take various forms. At very small concentration ($C << K$) value C in a denominator of the equation

(8) can be neglected, and then this equation takes the linear form: $\Gamma = (\Gamma_\infty / K) \cdot C$,

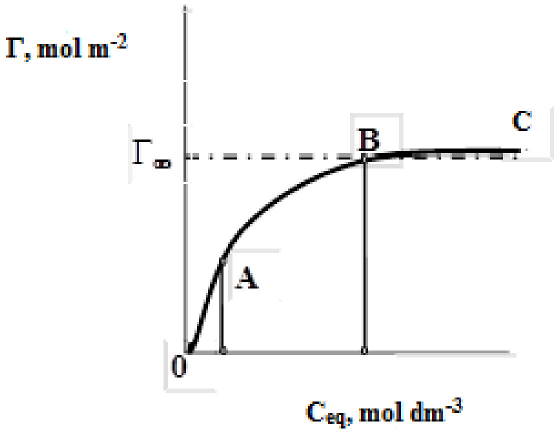


Fig. 10. Langmuir adsorption isotherm.

I.e. dependence between concentration and adsorption is represented by the straight line passing through the beginning of axes of coordinates (Fig. 10, OA segment).

If concentration is great (C>>K), value K in a denominator can be neglected, and then $\Gamma = \Gamma_\infty$, i.e. dependence between concentration and adsorption is represented by the straight line passing through the beginning of axes of coordinates (fig. 10, OA segment).

If concentration is big (C >> K), value K in a denominator can be neglected, and then $\Gamma = \Gamma_\infty$, i.e. the amount of the adsorbed substance reaches the maximum size and on concentration doesn't depend any more (BC segment).

At average concentration Lengmuir equation can give a look which answers a parabolic site of an isotherm of adsorption (segment AB).

When $K = C$, so $\Gamma = 1/2\ \Gamma_\infty$. It follows from this that the constant K in the equation of Lengmuir is equal to such equilibrium concentration at which one half of the active centers on a surface of adsorbent is occupied with molecules of adsorbate, and another remains free.

When we know Γ_∞ , we can calculate the surface which is occupied with one molecule of the adsorbed substance on surfaces and molecule length, assuming that its length is equal to thickness of a monomolecular pellicle. On the 1 cm^2 is adsorbing Γ_∞ moles of the substance; multiplying Γ_∞ on the Avogadro's constant N_A we will receive number of molecules on 1 $см^2$. From this calculate the surface which is occupied with one molecule S_o , is:

$$S_o = 1/(\Gamma_\infty \cdot N_A). \qquad (10)$$

The mass of substance falling on unit of a surface of a saturated adsorptive layer, is equal to work of limit adsorption of Γ_∞ on molar mass (M) of the substance:

$$m = \Gamma_\infty \cdot M. \qquad (11)$$

In that case molecule length in the saturated adsorptive layer is equal to thickness of this layer (ℓ), it is possible to calculate by means of the equation:

$$\ell = m/\rho = (\Gamma_\infty \cdot M)/\rho, \qquad (12)$$

where ρ is substance density, kg/m^3 ; Γ_∞ is limit adsorption, mol/m^2;
M is molar mass, kg/mol.

As showed numerous measurements, the value (S_o) was constant for the homological series containing the same group, irrespective of number of atoms in a chain. It serves as the proof of vertical orientation of molecules. On a surface there is only this hydrophilic group whereas pellicle thickness (ℓ) increases approximately at the same value when lengthening chain on group $–CH_2–$ on $1{,}4 \cdot 10^{-8}$ cm.

Determination of the area of the cross section (S_o) and length (ℓ) allowed to find out the value and a form of molecules of many organic substances. For the first time in the history of chemistry the molecule value were determined by such method (by Gibbs and Lengmyur's equations), and subsequently are confirmed in other ways.

8. Freundlich equation

The representations developed by I. Lengmuir, substantially idealize and simplify the valid picture of adsorption. Actually the surface of the adsorbent majority is non-uniform, between the adsorbed particles there can be an interaction and adsorption often isn't limited to formation of a monomolecular layer. In this case the equation of an isotherm of adsorption becomes complicated. G. Friendlich assumed the mass of the adsorbed gas or the dissolved substance, having per unit mass adsorbent, has to be proportional to equilibrium pressure (for gas) or equilibrium concentration (for the solid substance adsorbed from solution), built in any fractional degree. Than pressure of gas or the more concentration of the dissolved substance is higher, the more substance will be adsorbed on an adsorbent surface.

However this dependence carries not directly proportional, but parabolic character. This situation is expressed empirical (i.e. removed on the basis of experimental data) G. Freundlich equation:

$$\Gamma = K_f P^{1/n} \quad \text{or} \quad \Gamma = K_f C^{1/n}, \qquad (13)$$

Where P is equilibrium pressure of gas in system; C is equilibrium concentration; K_f and *1/n* is constants.

Freundlich equation represents the equation of a parabola (Fig. 11) and can't explain almost rectilinear increase of adsorption at low concentration, and also the limit value of adsorption which isn't depending on concentration.

The constant 1/n characterizes curvature of an isotherm of adsorption, i.e. an isotherm deviation from a straight line; K_f represents adsorption value at equilibrium concentration адсорбтива, equal 1 mol/l (at C = 1 mol/l and $\Gamma = K_f$). Constant Cf over a wide range the Indicator 1/n usually fluctuates is a proper fraction.

With temperature increase value of K_f has to decrease, and 1/n – to increase. Obviously, almost rectilinear site of an isotherm for small pressure or concentration can be received by means of G. Freundlich equation only if 1/n =

1. In the same way the horizontal rectilinear site of an isotherm corresponding to high pressures or concentration, it is possible to receive only at 1/n = 0.

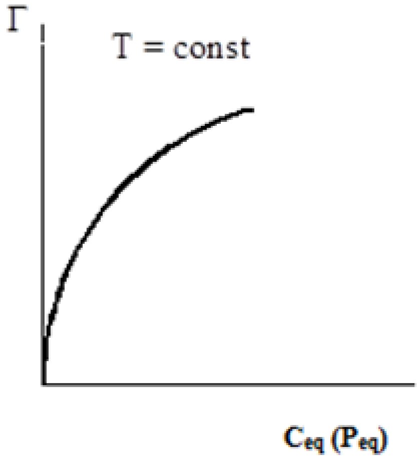


Fig.11. Freundlich isotherm

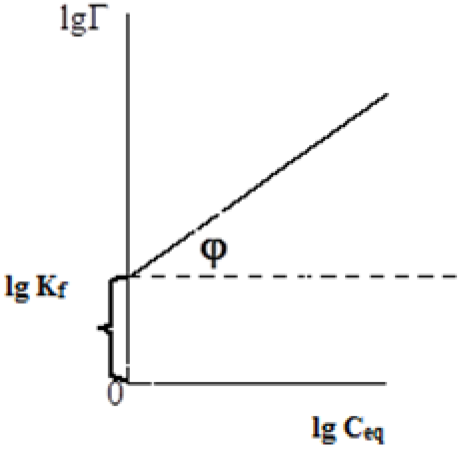


Fig.12. Graphic determination of the constants in the Freundlich equation

Thus, the indicator 1/n in essence itself is function C or P. As 1/n is accepted to the constant number lying within 0,2-1 (for adsorption from the gas environment) or 0,1-0,5 (for adsorption from solutions), Friendlich equation is suitable only for an interval of average pressure or concentration. Analytically the adsorptive isotherms as a whole are much better described by Lengmuir equation.

It is easy to find constants of the equation of Friendlich graphically on the isotherm constructed in logarithmic coordinates (fig. 12). So, for adsorption from solution we have:

$$lg\Gamma = lg\, K_f + 1/n\, lgC\,. \qquad (14)$$

Dependence lgΓ from lgC is expressed by a straight line. The piece cut by a straight line on ordinate axis, is equal to lgK_f , of an inclination of a straight line to abscissa axis is equal 1/n.

It is necessary to notice that when logarithmic the equation (13) Γ it is accepted to express in mol/g, and $C_{eq.}$ in mole / l.

9. Adsorption on limit of the section a solid body – gas

The phenomenon of concoction of gases on border a solid body – gas (adsorption of gases by solid bodies) was opened at the end of the XVIII century independently from each other by the Swedish chemist and the druggist K. Scheele (1742-1786) and the Italian professor F. Fountain (1730-1805).

F. Fontana found out that incinerated charcoal is capable to absorb various gases in the volumes considerably surpassing its own volume.

K. Scheele established that in some cases the process stated above is reversible: at change of conditions the absorbed gas can be allocated.

Gas adsorption on a solid body is the simplest case of adsorption as the system consists of only two components.

Gas adsorption as it was already noted, will depend on temperature, pressure, the adsorbate nature, by nature and a specific surface of adsorbent.

With increase of pressure of gas or couple adsorption by their solid body increases. On a surface of a solid body those gases which are easier condensed in liquid other things being equal are better adsorbed.

For example, absorbent carbon well adsorbs chlorine ($T_{boiling}$ = 239,7 K), ammonia (T_b = 240,0 K), but doesn't adsorb CO_2 (Tb. = 83,0 K), nitrogen (T_b

= 77,0 K), hydrogen (T_b = 20,0 K). Owing to bad adsorption in a fire zone where there is a lot of carbon oxide (II), it is impossible to use a usual gas mask.

10. Adsorption on limit of the section a firm body solution

Adsorption of the dissolved substances by adsorbent pellicle – more difficult process, than adsorption of gases by solid bodies as it becomes complicated a number of factors:

1) presence of the third component is the solvent which molecules can compete with adsorbate molecules for places on an adsorbent surface;

2) interaction between adsorbate and solvent molecules;

3) electrostatic interaction between a surface of adsorbent and adsorbate ions if it is electrolyte.

Adsorption of nonelectrolytes and weak electrolytes. The adsorption phenomenon from solutions solid bodies was open and studied in 1785 by the Russian chemist and the druggist T. E. Lovits (1757-1804).

Nonelectrolytes and weak electrolytes on a surface of adsorbent are adsorbed from solutions in the form of molecules. Such process is called as molecular adsorption.

As a result of adsorption concentration of the dissolved substance in solution decreases. Adsorption value from solution can be determined on a difference of initial and equilibrium concentration of an adsorbate in solution:

$$\Gamma = \frac{(C_0 - C)V}{m}, \qquad (15)$$

where C_0 is initial concentration of an adsorbate, mol·l^{-1};

C – equilibrium concentration of an adsorbate, mol·l^{-1};

V – the volume of solution of an adsorbate from which there was an adsorption, l;

m – mass of adsorbent, kg;

Γ – adsorption, mol·kg^{-1}.

In this case adsorption depends by nature adsorbent and solvent, by nature and concentration of an adsorbate, on temperature, and also on a specific surface of adsorbent.

Physicist and chemist P. A. Rehbinder (1898-1972) formulated the rule of alignment of polarity: *on polar adsorbents polar adsorbates from low-polar solvents are better adsorbed; on nonpolar adsorbents – nonpolar adsorbates from polar solvents.*

For system the adsorbate-adsorbent can be formulated influence of the nature of solvent on adsorption also in the form of the rule: *the better in this solvent this adsorbate is dissolved, the it is worse adsorbed; the it is dissolved worse than better is adsorbed from it.*

These rules can be explained to that process of adsorption of solutions is caused by energy of interaction not only between molecules of an adsorbate and the active adsorptive centers of adsorbent, but also between molecules of solvent and the active adsorptive centers.

With growth of concentration of solution adsorption on limit of the section a firm body solution increases to some limit value.

At adsorption of SAS on limit of the section a solid body-solution as well as on border solution-gas, molecules of an adsorbate are focused variously depending on the adsorbent and solvent nature.

In system nonpolar adsorbent polar solvent the nonpolar part of a molecule of an adsorbate ("tail") is turned to an adsorbent surface, and the polar part ("head") is shipped in solvent (Fig.13 a). In this case adsorption of SAS submits to Traube rule: with growth of length of the hydrocarbonaceous radical adsorption increases.

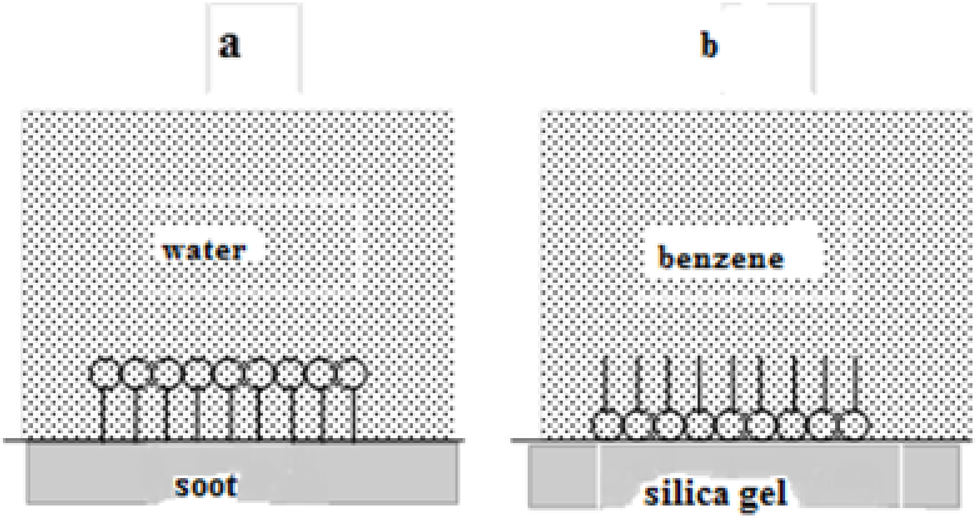


Fig. 13. Orientation of surfactant molecules at the interface.

In system polar adsorbent nonpolar solvent of a molecule of an adsorbate, on the contrary, are turned by polar part to an adsorbent surface, and their nonpolar part is shipped in solvent (fig. 13b), and at adsorption of SAS Traube turned rule is carried out: with growth of length of the hydrocarbonaceous radical adsorption decreases. The circulation of the rule is explained by that with growth of length of a hydrocarbonic chain solubility of SAS grows in nonpolar solvents.

Adsorption of strong electrolytes. In solutions of strong electrolytes the dissolved substance is in completely ionized state.

Therefore for their adsorption a number of features is characteristic, for example, ions are adsorbed generally on polar adsorbents and badly adsorbed on the nonpolar.

The major factors causing specificity of adsorption of strong electrolytes, the sign of a charge of a surface of adsorbent, value and a sign of a charge of an ion of electrolyte, and also its radius and degree of a solvatation (hydration) are. On positively loaded sites of a surface of adsorbent from solution anions, on negatively loaded cations are adsorbed.

$$\mathrm{Cs^+ > Rb^+ > NH_4^+ > K^+ > Na^+ > Li^+}$$

Increasing of cation radius
Decreasing of adsorption

$$\mathrm{NO_3^- > I^- > Br^- > Cl^- > F^-}$$

Increasing of anion radius
Decreasing of adsorption

Fig. 14.Lyotropic series of ions adsorption

It is established that the adsorptive ability of ions (especially cations) on a surface of adsorbent increases with increase in their charge.

The following rule is experimentally also established: at identical charges the adsorptive ability is more at those ions which radius in the solvated (hydrated) state is less. According to this rule, ions on the adsorptive ability settle down in the certain sequence which has received the name the liotropic ranks (fig. 14).

Distinguish the following types of adsorption of strong electrolytes: selective and exchange.

Selective adsorption submits to the rule established by the American physics chemist K. Fajans (1887-1975): on a surface of this adsorbent ions, related to the nature of adsorbent and capable to complete its crystal lattice are adsorbed mainly.

As illustration of the rule of Faience charging of a surface of a crystal deposit of silver iodide, received as a result of the following reaction can serve: $\mathrm{KI(aq) + AgNO_3(aq) = AgI(s) + KNO_3(aq)}$

Deposit surface at equivalent quantities KI and $AgNO_3$ it isn't loaded (Fig. 15 a); at surplus $AgNO_3$ it is loaded positively in a consequence of adsorption of ions Ag^+ (Fig. 15b), and at surplus of KI is loaded negatively because of adsorption of I^- ions (Fig. 15 c).

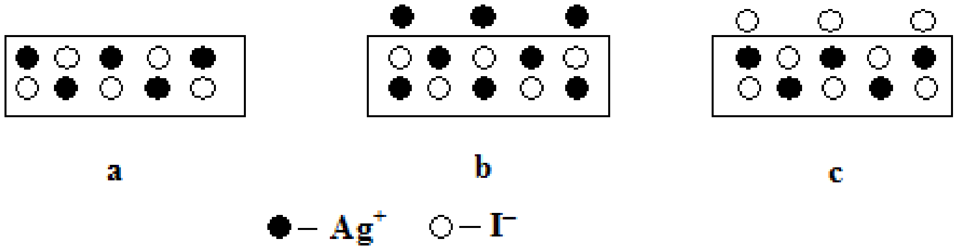


Fig. 15. Charge emergence on an adsorbent surface (AgI crystals) owing to selective adsorption of ions from solution:

a) $C(AgNO_3) = C(KI)$; b) $C(AgNO_3) > C(KI)$; c) $C(AgNO_3) < C(KI)$

Ion-exchange adsorption represents process at which adsorbent and solution exchange among themselves the same loaded ions in equivalent quantities. The adsorbents capable to an exchange of ions, are called as ionites.

Ionites in medicine and biology. Ionites are new effective therapeutic remedy for regulation of water-salt balance.

For example, pH gastric juice in norm 1,7–3,5, and at the increased acidity pH< 1,7. To decrease in acidity of gastric juice at various diseases apply ionites in OH^- – a form (anion exchange resin).

Action anion exchange resinis explained by course of reaction of an exchange of anions: $R–Kt^+OH^- + Cl^- \rightleftarrows R – Kt^+Cl^- + OH^-$. Being formed in this reaction OH^-–ions neutralize H^+–ions ($OH^- + H^+ = H_2O$),therefore concentration of free acid in gastric juice goes down.

The second important task solved in principle with use cation exchange resin, is a removal from an organism of excess ions of sodium, and in certain cases is excess ions of potassium.

In an organism ions of sodium are in the basic in intercellular liquid and according to the content in it among other electrolytic components win first place (136-145 mmol/l).

Sodium ions are one of regulators of osmotic pressure of intercellular liquid. Their delay in an organism at cardiovascular diseases, kidney insufficiency leads to a water delay and by that causes hypostases and dropsy. Ions of sodium arrive to the gastrointestinal highway directly with food, and also get from blood into intestines and back through an intestinal wall.

Removal of ions of sodium and prevention of their receipt with food (a saltless diet) at treatment, for example, hypertensions is very hard transferred by the patient because of monotony of food. If together with usual food to accept anion exchange in H^+–form, that ions of sodium containing in food is occluded by it cation exchange resin ($R–An^-H^+ + Na^+ \rightleftarrows R–An^-Na^+ + H^+$) and with it are brought out of an organism. But application cation exchange resin can cause undesirable acidosis.

Except sodium ions, cation exchange resin can occlude ions of potassium, calcium, magnesium and by that to cause change of their level in an organism. Therefore apply mixes cations exchange resin in H^+– and $К^+$–forms, H^+– and NH_4^+– forms.

The developed systems of rendering the urgent help and treatment of radiation injuries included measures for the prevention of absorption of radioactive materials and acceleration of their removal from an organism. Among these measures the important place is taken by application of ion-exchange materials (organic ionites, dioxide of the titan, carboxymethyl cellulose, clays). They are a part of the compositions applied to deactivation of intact integuments. In these compositions the ion-exchange material plays a role of the firm additives improving mechanical cleaning of skin.

Besides, it facilitates ion-exchange sorption of radionuclide. At pollution of integuments of wounds and grazes radioactive strontium they are recommended to be processed not only physiological solution, but also Vokatsit (a preparation of the high-oxidized cellulose) – it is capable to absorb strontium.

For removal from an organism of radionuclides: К, Ca, Li, Na, Ag it is recommended to use cation exchange resinКУ–2 (as rule, inH^+–for).

For strontium removal at poisoning ^{90}Sr, uranium or plutonium fission products as a result of which are formed ^{89}Sr,^{90}Sr,^{140}Ba it is expedient to apply cation exchange resin – polyantimon – it is recognized as the most effective in such cases.

Along with application of molecular sorbents in hemosorption (a way of purification of blood from toxic substances of various origin) ions exchange resin for sorption of the ionized substances, generally electrolytic components – K^+, by Na^+, Ca^{2+} are used also.

The sorption method with use of ions exchange resin can be applied also to purification of other biological liquids: lymph, plasmas after its separation from uniform elements.

Ions exchange resin carry out important functions in biological researches: they are applied to isolation, allocation and partial cleaning of viruses at production of virus vaccines. For conservation and stabilization of donor blood use phosphate and other derivative cellulose.

The premature fibrillation is warned by removal from plasma of salts of calcium and their replacement by means of an ionic exchange of potassium salts. The product of oxidation of cellulose monocarboxycellulose (MCC) – is used in surgery as hemostatic, bactericidal and resolving means, and also the carrier of medicinal connections.

Ionic exchange in biological systems.

Properties of the catalytic center of many enzymes are defined by the cation which was in it (metalloenzymes) or anion which keep both electrostatic forces, and coordination bonds. These ions can be replaced with other ions. When replacing an ion change structure and properties of the catalytic center, are weakened or catalytic properties of enzyme are completely lost.

It is established that the ionic exchange is important and for transfer of various ions through biological membranes – not only passive (due to diffusion), but also active, directed against a concentration gradient. Active transfer is carried out by proteins – the carriers possessing in various states unequal selectivity to exchanging ions (in case of the so-called sodium pump – to ions Na^+ and K^+).

An important role in live systems is played by educations like gams. Basis gem of hemoglobin makes a porphyrin ring with the ions of H^+ replaced on an ion of Fe^{2+}. The similar ring with Mg^{2+} represents a chlorophyll basis.

In the tooth enamel which main part makes calcium hydroxyphosphate – $Ca_5(PO_4)_3OH$, also there can be reactions of an ionic exchange. Ions of hydrogen of organic acids (pyruvic, latic, etc.), being in a saliva, react to enamel surfaces with hydroxyphosphates calcium. Thus there is an exchange of ions. Dissolution of tooth enamel as a first approximation can be described the following equation:

$$2Ca_5(PO_4)_3OH + 2H^+ \rightleftharpoons 3Ca_3(PO_4)_2 + Ca^{2+} + 2H_2O$$

If concentration of ions of hydrogen increases more considerably, calcium ions (Ca^{2+}) completely will pass into solution (i.e. into a saliva) and there will be the dissolution of tooth enamel promoting emergence of caries:

$$2Ca_5(PO_4)_3OH + 8H^+ \rightleftharpoons 10Ca^{2+} + 6HPO_4^{2-} + 2H_2O$$

To fight against caries apply compounds of fluorine. Fluorine ions differently, depending on their local concentration, react with calcium of tooth enamel. If it isn't enough of them, they partially replace hydroxyl ions in a crystal lattice calcium hydroxyphosphate:

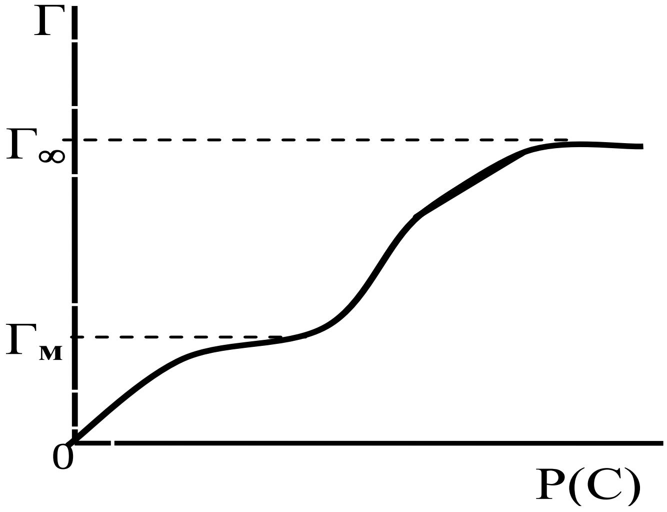
$$Ca_5(PO_4)_3OH + F^- \rightleftharpoons Ca_5(PO_4)_3F + OH^-$$

If it is more than fluorine, at first not too strong integumentary layer of fluoride of calcium which can serve as the long-term tank of fluorine for layers lying more deeply calcium hydroxyphosphate is formed.

Durability of calcium fluorinephosphate is increased in comparison with calcium hydroxyphosphate is explained by that fluorine ions "sit" in a crystal lattice, than hydroxyl ions more strongly.

11. Polymolecular adsorption. Polanyi's theory and BET

Often process of adsorption comes to an end with education on an adsorbent surface not one layer of molecules of adsorbate, and a polymolecular adsorptive layer. In this case the isotherm of adsorption differs from Lengmuir and has more difficult appearance (Fig. 16)



Type of an isotherm for polymolecular adsorption

Γм - monolayer saturation

Γ∞ - limit saturation

Possibility of formation of polymolecular layers is considered in M. Polanyi's theory (1915). Which basic position is that adsorption allows existence on a surface of firm adsorbents of the adsorptive forces operating at distance, considerably exceeding diameter of molecules of adsorbate. By the nature the adsorptive forces are Van-der-Waals's forces. Gas molecules, getting to the adsorptive field, are attracted by an adsorbent surface therefore the polymolecular layer which density decreases in process of removal from an adsorbent surface is formed.

Polanyi's theory doesn't give mathematical expression of an isotherm of adsorption, but its representations were cornerstone of the modern theory of volume filling of a time of adsorbent molecules of adsorbate.

S. Brunauer, P. Emmett and E. Teller created most the general theory of polymolecular adsorption is called BET theory (1935-1940).

Its basic provisions are:

1. On a surface of adsorbent there is a certain number equivalent in the power relation of the active centers.

2. Each molecule of the previous layer represents the possible active center for adsorption of the following adsorptive layer.

3. Interactions of the next adsorbed molecules in the first and last layers are absent.

4. It is supposed that all molecules in the second and farther layers behave like liquid molecules.

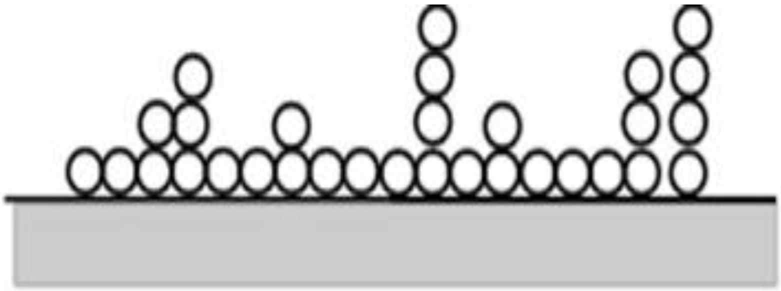


Fig. 17 The sheme of structure of the adsorbed layer on the BET theory

Thus, the adsorbed phase can be presented as set of the adsorptive complexes are chains of molecules, first of which it is connected with an adsorbent surface. All these chains energetically don't interact with each other. The scheme of a structure of the adsorptive layer according to the theory of BET is submitted in Fig. 17.

QUESTIONS FOR SELF-PREPARATION

1. Features of a power condition of interfaces of phases. Surface energy and surface tension.

2. Surface-active and surface inactive substances. Isotherms of a surface tension. Dyuklo-Traube's rule. Stalagmometric method of measurement of a surface tension of liquids.

3. Adsorption on an interface liquid-gas and liquid-liquid. Gibbs's equation, his analysis. Orientation of molecules in a blanket; structure lipidic bilayer of biological membranes.

4. Adsorption on an interface a firm body gas and a firm body liquid. Isotherms of adsorption of Lengmyur and Friendlich. Lengmyur and Freundlich equations, their analysis.

5. Adsorption on a surface of firm adsorbent from solution. Ionites in biology and medicine. Ionic exchange in biological liquids.

6. Value of the surface phenomena in biology and medicine. Adsorption use in medicine and medicine and biological researches.

7. Polymoleculararadsorption. BETisotherm.

EXERCISES

Exercise #1

What do the surface tension of an aqueous solution of amyl alcohol equal, if the number of drops of solution flowing from stalagmometry is 72, and the number of water drops is 60? Surface tension of water at a temperature of 293 K equals $172{,}8 \cdot 10^{-3}$J/m^2 (the density of the solution is 1 g/cm3). To solve this problem, see the experimental work 1.

Exercise #2

Surface tension of 0.2 M aqueous solution of SAS at 20^0C is equal to $55 \cdot 10^{-3}$J/m^2. Calculate the value of adsorption (surface tension of water at 20^0 C is $72{,}75 \cdot 10^{-3}$J/ m^2).

Exercise #3

It was established experimentally that the value of maximum adsorption of propionic acid is $3{,}0 \cdot 10^{-3}$mole/g; coefficient K is equal to $6{,}0 \cdot 10^{-2}$mole/l. What was mass of propionic acid adsorbed from the solution, if the balance concentration of the acid is 0,1 mole/l ? The mass of the adsorbent is 1 g.

Exercise #4

Three acetic acid with different concentration are given. To 100 ml of each solution was added 3 g of activated coal. The amount of acid before and after the adsorption was determined using titration with 50 ml each of acid solutions by KOH of 0.1 mole/ l concentration.

a) Determine the amount of adsorption for each solution, using the following data:

Volume of titrant (KOH) before an adsorption, ml	5,50	10,60	23,00
Volume of titrant (KOH) after equilibration, ml	1,22	3,65	10,20

Execise #5

Determine the value of $C_8H_{17}COOH$ acid adsorption on the surface of aqueous solution at 10^0 C if the mass fraction of the acid in solution is 0.02%. The surface tension of pure water and the solution at this temperature are accordingly $74,22 \cdot 10^{-3}$ and $57,0 \cdot 10^{-3}$ J/m^2.

Exercise #6

It was established experimentally that the maximum adsorption of SAS (M = 60 g / mole) is $5,0 \cdot 10^{-3}$ mole/g. The value of K is equal to 0.06 mole / l. How many grams of a substance adsorbed by two grams of this adsorbent from solution if the balance concentration of SAS has became 0.2 mole/l?

STANDARDS FOR SOLVING EXERCISES

Execise 1.

Determine the value of $C_8H_{17}COOH$ acid adsorption on the surface of aqueous solution at 10^0 C if the mass fraction of the acid in solution is 0.005%. The surface tension of pure water and the solution at this temperature are accordingly $74{,}22 \cdot 10^{-3}$ and $57{,}0 \cdot 10^{-3}$ J/m^2.

Given	*Solution*
$\omega C_8H_{17}COOH = 0{,}005\%$ $\sigma H_2O = 74{,}22 \cdot 10^{-3}$ J/m^2 $\sigma\ C_8H_{17}COOH = 57{,}0 \cdot 10^{-3}$ J/m^2 $T = 283K$	1. To calculate the adsorption on the surface of solution use the Gibbs equation: $\Gamma = -\frac{\Delta\sigma}{\Delta C} \cdot \frac{C}{RT} = -\frac{\sigma_2 - \sigma_1}{C_2 - C_1} \cdot \frac{C}{RT}$
Γ – ?	In the Gibbs equation the value of C_2 means molar concentration of acid, $C_1 = 0$ (pure water).

2. Assuming that the density of the dilute acid solution is ≈1 g/ml (i.e., the same as water), using ω% of acid find that 100 ml of the solution contains 0.005 g of the acid. Consequently 1000 ml of solution contains 0.05 g of acid. The molar mass of acid is 158 g / mole, so the molar concentration of the solution will be:

$$C_M = \frac{m}{M_w \cdot V_{solution}} = \frac{0{,}05}{158 \cdot 1} = 3{,}16 \cdot 10^{-4} \text{ (mole / l).}$$

3. In the Gibbs equation substitute the necessary data:

$$\Gamma = -\frac{57{,}0 \cdot 10^{-3} - 74{,}22 \cdot 10^{-3}}{3{,}16 \cdot 10^{-4} - 0} \cdot \frac{3{,}16 \cdot 10^{-4}}{8{,}314 \cdot 283} = 7{,}3 \cdot 10^{-6} \text{ (mole/m}^2\text{).}$$

Answer: $7{,}3 \cdot 10^{-6}$ mole/m^2

Exercise 2.

It was established experimentally that the maximum adsorption of SAS (M = 60 g / mole) is $5{,}0 \cdot 10^{-3}$ mole/g. The value of K is equal to 0.06 mole / l. How many grams of a substance adsorbed by two grams of this adsorbent from solution if the balance concentration of SAS has became 0.1 mole/l?

Given	*Solution*
$\Gamma_\infty = 5{,}0 \cdot 10^{-3}$ mol/g M_{SAS}= 60 mol/g $K = 0{,}06$ mol/l $C_{equal.} = 0{,}1$ mol/l m(adsorbent) = 2 g	1. Calculate the value of SAS adsorption with the Langmuir's equation: $\Gamma = \Gamma_\infty \frac{C}{K+C}$; $\Gamma = 5{,}0 \cdot 10^{-3} \frac{0{,}1}{0{,}06+0{,}1} = 3{,}125 \cdot 10^{-3}$ (mol/g).
M_{SAS} – ?	2. The amount of adsorbed on the adsorbent mass 2 g will be twice more: $N_{SAS} = 3{,}125 \cdot 10^{-3}$ mol/g $\cdot 2$ g $= 6{,}25 \cdot 10^{-3}$ mol.

3 .Mass of adsorbed material will be equal to:

$M_{SAS} = n \cdot M = 6{,}25 \cdot 10^{-3} \cdot 60 = 0{,}375$ (g).

Answer: m of adsorbed SAS is equal to 0,375 g.

Exercise 3.

To 60 ml acetic acid solution at a concentration of 0.1 mol/l was added 2 g of the adsorbent and shaken up. When equilibration was became the solution sample of 10 ml sodium hydroxide was titrated with a 0.05 mol/l. Was taken 15 ml of titrant on titration. Calculate the value of the adsorption of acetic acid.

Given

$V_{\text{initial}}(CH_3COOH)$ = 60 ml = 0,06 l $C_{initial.}(CH_3COOH)$=0,1 mol/l

M_{SAS} = 60 g/mol

m(adsorbent) = 2 g

$V(CH_3COOH$ on titration) =10 ml

V(NaOH) = 15 ml

C(NaOH)= 0,05 mol/l

Γ (CH_3COOH) – ?

Solution

1. Find the balance concentration of the acetic acid solution by titration:

$$C_{\text{equil.}}(CH_3COOH) = \frac{C(\text{NaOH})\cdot V(\text{NaOH})}{V(\text{CH}_3\text{COOH})};$$

$$C_{\text{equil.}}(CH_3COOH)=\frac{0{,}05\cdot 15}{10}$$

=0,075(mol/l)

2. Calculate the value of the adsorption of acetic acid by the formula:

$$\Gamma(CH_3COOH) = \frac{n\,(CH_3COOH)}{m\ adsorbent} = \frac{(C_{initial.} - C_{equil.})\cdot V_{initial}}{m} = \frac{(0{,}1 - 0{,}075)\cdot 0{,}06}{2} =$$

$$= 7{,}5\cdot 10^{-4}\ (\text{mol/g}) = 0{,}75\ (\text{mmol/g})$$

Answer: $\Gamma(CH_3COOH)$ = 0,75 mmol/g

EXEPERIMENTAL PART

Laboratory work: Determination of alcohol adsorption on the interface liquid-gas

Fill aspirator with water and substitute glass under it.

Using volumetric pipettes pour the distilled water into a test tube in amount such that when the capillary tip of a tightly closed tube touching a surface of the liquid.

Check the tightness before the measurements. When the upper crane of aspirator is closed, open the lower crane until the water begin to drip and util the air bubbles begin to stand out in a test tube. Then close the lower crane.

Make sure that the vacuum created in the flask is kept constant for 1-2 min, when the bubbles will stop to stand out.

Need to adjust the small speed of bubble generation (not less than 30 sec) to get the correct results when we measure the maximum pressure.

Produce at least three measurements of the maximum pressure (P_0) by a manometer. Find the average value and write in table.

Remove the capillary and cork from the test tube and pour instead of water the test solution of alcohol with the lowest concentration.

Wash the capillary with a new solution and measure the maximum pressure of the air bubble (P_x) as previously described.

Measurement is made in sequence from less to more concentrated solution for all given concentrations of alcohol. The data are entered into the table.

Capillary constant ($K_{\text{capillary}}$) calculated according to the value of the surface tension of distilled water at a temperature of the experiment by the formula: $K = \sigma_0/P_0$.

Values (σ) at various temperatures for water are given in the reference book, for example, 20° C - $72{,}75 \times 10^{-3}$ N/m; 25° C - $71{,}97 \text{-} \times 10^{-3}$ N/m.

Calculate σ of the solutions by the formula $\sigma_0 = K \cdot P_{x^2}$ and write to the table:

molar concentration of the solution, mol/m^3						
maximum pressure, P, mm	1. 2. 3.	1. 2. 3.	1. 2. 3.	1. 2. 3.	1. 2. 3.	1. 2. 3.
average maximum pressure, P_A, mm						
surface tension of solutions, N/m						
surface activity, $\frac{d\sigma}{dC}$						
adsorption, Γ, mole/m^2						

К $_{\text{capillary}}$=

$\sigma_{x1} =$ $\sigma_{x3} =$ $\sigma_{x5} =$

$\sigma_{x2} =$ $\sigma_{x4} =$

Build graphs of dependence σ from C.

Determine by graph $\frac{\Delta\sigma}{\Delta C}$

1) $\frac{\sigma_2 - \sigma_1}{C_2 - C_1} =$ 2) $\frac{\sigma_3 - \sigma_2}{C_3 - C_2} =$

3) $\frac{\sigma_4 - \sigma_3}{C_4 - C_3} =$ 4) $\frac{\sigma_5 - \sigma_4}{C_5 - C_4} =$

Use the Gibbs equation to calculate the adsorption: $\Gamma = -\frac{C^{`}}{RT}\frac{\Delta\sigma}{\Delta C}$

$C_1 = \frac{C_1 + C_2}{2} =$

$C_2^{'} = \frac{C_3 + C_2}{2} =$

$C_3^{'} = \frac{C_4 + C_3}{2} =$

$C_4^{'} = \frac{C_5 + C_4}{2} =$

Γ_1=

Γ_3=

Γ_2=

Γ_4=

Build graph $\Gamma = f(C')$

TESTS

How the adsorption of gases on temperature depends?

a) *Is moderated with growth of temperature;
b) Is augmented with growth of temperature;
c) Is not changed.

In how many of times the surface activity of acetic acid differs from a surface activity of formic?

a) *3,5;
b) 10;
c) 6,3;
d) 8,5;
e) 1,8.

On what the separation of reductants in elution analysis is based?

a) *On discrepancy of distribution ratios;
b) On miscellaneous speed of advance;
c) On different dissolubility;
d) On discrepancy of activity ratios;

In what the principle guard rope of phases in chromatography consists?

a) *Discrepancy of distribution ratioes;
b) Good dissolubility of phases in each other;
c) High dissolubility of agents in mobile and fixed phases.

Constant of an equation of Freindlich allows to determine the schedule constructed in coordinates:

a) *lg x/m - lgC.
b) G-T;
c) G-C;

d) x/m-C;
e) s-C;

What is an explanation of difficulties of idealized account of an adsorption on solid surfaces in comparison to an adsorption on a liquid?

a) *By impossibility of measuring of boundary tension and specific surface;
b) By heterogeneity of a surface;
c) By absence of methods of variation of boundary tension;

In the field of what concentrations the equation of Lengmure passes in an equation of Freindlich?

a) *Average;
b) High;
c) Low.

How the magnitude of boundary tension of solution of SAA is changed during formation of a monomolecular layer?

a) *Is moderated and becomes to equal boundary tension of SAA;
b) Is not changed;
c) Increases and becomes to equal boundary tension of water;

What explains persistence of a limiting adsorption in a homologous line?

a) *By an identical amount of molecules placing on unit of an interface;
b) By the identical size of molecules of SAA;
c) By magnification of dissolubility of SAA in water in a homologous line;

What statement for small concentrations of SAA is correct?

a) *Hydrocarbon chains floats on a surface of water, and the polar groups are loaded in water;

b) Hydrocarbon radicals are in water, and the polar groups are reversed in air;
c) Molecular <palings> will be derivated;
d) The polar groups are disposed in air in bridge surfaces of phases.

What possibility gives the equation of the Gibbs?

a) *To place intercoupling between an adsorption, concentration and boundary tension;
b) To construct an isotherm of boundary tension;
c) To construct an isotherm of an adsorption;
d) To place(install) intercoupling between an adsorption and concentration.

Whether the following statement is correct: The adsorption is positivegoing, if the surface activity is more than zero point ?

a) *No;
b) Yes.

Whether the following statement is correct: The adsorption is positive going, if the surface activity is less than zero point?

a) *Yes;
b) No.

What statement is correct for surface-inactive agents?

a) *The adsorption is less than zero point;
b) The adsorption is more than zero point;
c) The adsorption is equal to zero point.

What explains a positive adsorption of SAA?

a) *By weaker coupling of dipoles of water with molecules of SAA, than one with another;

b) By small dissolubility of SAA in water;
c) By stronger coupling of molecules of SAA with water, than molecules of water among themselves.

What equation describes dependence of an adsorption on concentration?

a) *Lengmure equation;
b) Equation of Shishkovsky;
c) Equation of Nernst;
d) Equation of Ostwald.

What is a measure of an adsorption on border the liquid - gas?

a) *Surplus of number of moles on unit of a surface in comparison to the volume of a phase;
b) Mass of agent;
c) Number of moles of agent;
d) Number of moles on unit of a surface;

What kind has the schedule of an isotherm of boundary tension?

a) *Hyperbola;
b) Parabola;
c) Direct rakish downwards;
d) Direct rakish hill up;
e) Direct, parallel to an abscissa axis.

What adsorption from the following definitions strictly corresponds to concept?

a) *Increase of concentration of matter in surface layer;
b) Concentrating of one agent by another;
c) Upbuilding of agent of volume of other matter;
d) Variation of concentration of agent.

What from the listed dependences is expressed with an isotherm of boundary tension?

a) *Boundary tension - function from concentration;
b) Adsorption - function from concentration;
c) Adsorption - function from boundary tension;
d) Boundary tension - function from temperature;

What statement is correct: “At dissolution of a molecule of SAA...“

a) *The non-polar radical is in air;
b) They are completely placed inside water;
c) Only hydrocarbon radical is loaded into water;
d) The polar part of SAA is in a gas phase.

For what from alternatives of a location of molecules Traube rule is valid?

a) *The molecules Of SAA are disposed in bridge surfaces;
b) The molecules of SAA are under an arbitrary angle to a surface;
c) The molecules of SAA will derivate “ a palings of Lengmure “;
d) The molecules of SAA are chaotically distributed inside a liquid.

Among the listed matters please indicate surfactant.

a) *C_2H_5OH;
b) NaCl;
c) H_2SO_4;
d) $K_4Fe(CN)_6$.

What from the listed values is a surface activity?

a) *ds/dC;
b) A;
c) ds;
d) C/RT;

What is a boundary tension?

a) *Specific surface energy;
b) Margin of energy of an interface;
c) A surface energy;
d) Equal in effect attractive forces.

What equation determines dependence of boundary tension on concentration of SAA?

a) *By an equation of Shishkovsky;
b) By an equation of the Gibbs;
c) By an equation of Lengmure;
d) By an equation of Nernst.

In how many of times (maximum) a surface activity of SM will increase at growth a hydrocarbon radical on group - CH_2?

a) *In 3.5 times;
b) In 2 times;
c) In 7 times;
d) In 3 times;
e) In 0.3 times;

What rule institutes dependence of a surface activity on length of a hydrocarbon radical?

a) *A rule of Traube;
b) A rule of Rebinder;
c) A rule of Faience;
d) A rule of Schultz-Hardy.

Who has instituded dependence of a surface activity on length of a hydrocarbon radical?

a) *Traube
b) Gibbs;
c) Shishkovsky;
d) Vant-Hoff;

Please select the valid statement: “The surface-active agent calls matter...”

a) *Diphile matter;
b) Organic matter;
c) The matter, includes hydrophilic group into its structure;
d) The matter containing non-polar group.

Please select the valid statement: “The surface activity depends from...”

a) *The length of a non-polar hydrocarbon radical;
b) Amount of hydrophilic groups;
c) Affinities SAA to water.

From the list of matters select matter having surfactant properties:

a) *Acetic acid;
b) Water;
c) Caustic soda;
d) aluminiumsulphate;
e) Hydrogen nitrate;

Please select the valid statement: “The surface-active agent calls matter, which one at attachment to solution...”

a) *Moderates boundary tension;
b) Augments a surface energy;
c) Augments boundary tension.

How it is possible to diminish a surface energy of solution?

a) *By decreasing of boundary tension;
b) By decreasing of an interface;
c) By increasing of boundary tension.

What to explain confluence of small-sized drops of water in larger by?

a) *Decreasing of a surface energy;
b) Decreasing of boundary tension;
c) Increasing of the floor space of the surface unit.

What method a surface energy of clean matters is decreased by?

a) *Integration of fragments;
b) Crushing of fragments;
c) Decreasing of boundary tension.

Please mark a method which is not being a method of an abatement of a surface energy.

a) *Heat transfer;
b) Decreasing of an interface;
c) Decreasing of boundary tension.

In the list of physicochemical methods of testing please mark a method which is not being a method of determination of boundary tension of liquids.

a) *Gravimetric;
b) Stalagmometric;
c) Method of capillary ascent;
d) Method of break off of a ring;
e) Rebinder method.

There is a water and solution of alcohol in water. Please compare boundary tension of these liquids.

a) *The boundary tension of water is greater, than of solution;
b) The boundary tensions are equal;
c) The boundary tension of solution is greater, than of water.

What method it is possible to determine boundary tension by?

a) *Stalagmometric
b) Titrimetric;
c) Potentiometric;

In what units the boundary tension is metered?

a) *Newton/meter.
b) Centimeter;
c) Kilogram;
d) Newton;

What from the following four statements is correct?

a) *The surface energy is greater than boundary tension;
b) The surface energy is equal to boundary tension;
c) The surface energy is less than boundary tension;
d) These values cannot be compared.

What from the following three statements is correct?

a) *Surface energy - work on formation of an interface;
b) Surface energy - full margin of energy of a phase boundary;
c) Surface energy - energy of transition of matter from one phase in other;

What is the direction of equal in effect ofall forces on border liquid - gas?

a) *To the side of solution;

b) To the side of a gas phase;
c) In bridge interfaces.

What is the value of equal in effect of all forces inside a fluid phase?

a) *Is equal to zero point;
b) Is more than zero point;
c) Is less than zero point.

Sollubilization is:

a) *Dissolution of organic matters in hydrocarbon part of SAA;
b) Association of particles;
c) Dissolution of organic agents in polar parts of SAA.

The adsorption will be directly proportional concentrations in the field of concentrations of SAA:

a) *Small;
b) Average;
c) Large.

The equation A=C/RT*ds/dC is called:

a) *An equation of Gibbs;
b) An equation of Lengmure;
c) An equation of Freindlih.

The equation d = B ln (1+AC) ia called:

a) *An equation of Shishkovsky;
b) An equation of Gibbs;
c) An equation of Lengmure;
d) An equation of Freindlih.

The equation $G = G_0 P / (A+P)$ is called:
a) *An equation of Lengmure;
b) An equation of Gibbs;
c) An equation of Shishkovsky.

The equation $x/m = B P_1/n$ is called:
a) *An equation of Freindlich;
b) An equation of Gibbs;
c) An equation of Lengmure;
d) An equation of Shishkovsky.

SAA in comparison to resolvent has boundary tension:
a) *Smaller;
b) Greater;
c) Equal.

Does the adsorption of gases depend on temperature?
a) *Yes
b) No

What statement is correct for surface-active agents?
a) *The adsorption is less than zero point;
b) The adsorption is more than zero point;
c) The adsorption is equal to zero point.

In the field of what concentrations the equation of Lengmure passes in an equation of Freindlich?
d) *Average;
e) High;
f) Low.

Among the listed matters please indicate surfactant.

a) *C_3H_7OH;
b) KCl;
c) H_2SO_4;
d) $K_3Fe(CN)_6$.

The adsorption is positive going, if the surface activity:

a) is more than zero point
b) *is less than zero point

The adsorption is positive going, if the surface activity is more than zero point?

a) *No
b) Yes

At dissolution of a molecule of SAA:

a) *The non-polar radical is in air;
b) They are completely placed inside water;
c) Only hydrocarbon radical is loaded into water;
d) The polar part of SAA is in a gas phase.

Surface activity of SM will increase in 3,5 times at growth a hydrocarbon radical on group:

a) *- CH_2
b) – CH_3
c) - NH_2

The surface-active agent calls matter:

a) *Diphile matter;
b) Organic matter;
c) The matter, includes hydrophilic group into its structure;

d) The matter containing non-polar group.

The surface activity depends from:

a) *The length of a non-polar hydrocarbon radical;
b) Amount of hydrophilic groups;
c) Affinities SAA to water.

From the list of matters select matter having surfactant properties:

a) *Formic acid;
b) aluminiumsulphate;
c) Water;
d) Caustic soda;
e) Hydrogen nitrate;

The surface-active agent calls matter, which one at attachment to solution:

a) *Moderates boundary tension;
b) Augments a surface energy;
c) Augments boundary tension.

What method a surface energy of clean matters is increased by?

d) Integration of fragments;
e) *Crushing of fragments;
f) Decreasing of boundary tension.

Choose Shishkovsky equation from following list:

a) $A=C/RT*ds/dC$
b) *$d = B \ln (1+AC)$
c) $G = G_0 P / (A+P)$
d) $x/m = B P_1/n$

Choose Gibbs equation from following list:

a) *A=C/RT*ds/dC
b) d = B ln (1+AC)
c) $G = G_0 P / (A+P)$
d) $x/m = B P_1/n$

Choose Lengmure equation from following list:

a) A=C/RT*ds/dC
b) d = B ln (1+AC)
c) *$G = G_0 P / (A+P)$
d) $x/m = B P_1/n$

Choose Freindlih equation from following list:

a) A=C/RT*ds/dC
b) d = B ln (1+AC)
c) $G = G_0 P / (A+P)$
d) *$x/m = B P_1/n$

How the adsorption of gases on temperature depends?

d) *Is moderated with growth of temperature;
e) Is augmented with growth of temperature;
f) Is not changed.

In how many of times the surface activity of acetic acid differs from a surface activity of formic?

f) *3,5;
g) 10;
h) 6,3;
i) 8,5;
j) 1,8.

On what the separation of reductants in elution analysis is based?

e) *On discrepancy of distribution ratios;
f) On miscellaneous speed of advance;
g) On different dissolubility;
h) On discrepancy of activity ratios;

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