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PHYSICAL CHEMISTRY OF REAL AND COLLOID SOLUTIONS

Minsk BSMU 2018

МИНИСТЕРСТВО ЗДРАВООХРАНЕНИЯ РЕСПУБЛИКИ БЕЛАРУСЬ
БЕЛОРУССКИЙ ГОСУДАРСТВЕННЫЙ МЕДИЦИНСКИЙ УНИВЕРСИТЕТ
КАФЕДРА ОБЩЕЙ ХИМИИ

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ФИЗИЧЕСКАЯ ХИМИЯ РЕАЛЬНЫХ И КОЛЛОИДНЫХ РАСТВОРОВ

PHYSICAL CHEMISTRY OF REAL AND COLLOID SOLUTIONS

Практикум

Минск БГМУ 2018

УДК 544(076.5)(075.8)-054.6
ББК 24.5я73
Х95

Рекомендовано Научно-методическим советом университета в качестве практикума 20.12.2017 г., протокол № 4

Р е ц е н з е н т ы: канд. фарм. наук, доц., зав. каф. фармацевтической химии Н. Д. Яранцева; канд. физ.-мат. наук, доц., зав. каф. медицинской и биологической физики М. В. Гольцев

Хрусталёв, В. В.

Х95 Физическая химия реальных и коллоидных растворов = Physical and colloid chemistry of real and colloid solutions : практикум / В. В. Хрусталёв, О. В. Контява, С. Р. Казюлевич. – Минск : БГМУ, 2018. – 138 с.

ISBN 978-985-567-929-6.

Содержит теоретический материал, задачи и протоколы лабораторных работ по физической и коллоидной химии. Представлен материал к занятиям по темам: термодинамика растворов, буферные системы, электрохимия, поверхностные явления, коллоидные и грубодисперсные растворы, растворы биополимеров.

Предназначен для иностранных студентов 2-го курса, обучающихся на английском языке по специальности «Фармация».

УДК 544(076.5)(075.8)-054.6
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ISBN 978-985-567-929-6

PREFACE

This book is on the physical chemistry of solutions. Since our bodies may be likened to the systems of interconnected vessels, future pharmacists should know all the specific properties of water solutions.

The book starts from ideal solutions of nonelectrolytes and ends up with colloid and coarsely dispersed systems, as well as with real solutions of proteins. Each chapter includes sufficient mathematical, thermodynamic and kinetic apparatus that is necessary for calculations, explanations and conclusions on the mechanisms and consequences of processes happening in solutions.

Experimental works are designed to get future pharmacists ready for investigations and quality tests. The material explained in this book is the basis necessary for future understanding of such important disciplines, as Pharmaceutical Chemistry, Pharmaceutical Technology and Biochemistry.

CHAPTER 1
THERMODYNAMICS OF WATER SOLUTIONS

Main topics of the chapter:

1. *Ideal solution as a perfect model.*
2. *Heat effects of the dissolving.*
3. *Solubility of solid substances.*
4. *Colligative properties of ideal solutions.*
5. *Real solutions of strong electrolytes.*
6. *The rule of ionic strength.*

Ideal solution is a useful model that works well if we describe the behavior of rather dilute real solutions. There are several distinctive properties of ideal solutions. First of all, particles of a solute in the ideal solution interact with particles of a solvent in the same manner as particles of a solute interact with each other, and as particles of a solvent interact with each other. Schematically, we can show it as follows: A + B = A + A = B + B. Other properties of ideal solutions are the consequences of the first property: the heat effect of the dissolving is equal to zero ($\Delta H_{dissolving} = 0$); the final volume of a solution made from two liquids is equal to the sum of the initial volumes of a solvent and a solute ($V_{solution} = V_{solvent} + V_{solute}$); Raoult's law perfectly obeys in ideal solutions (the vapor pressure of a given substance upon a solution is equal to the multiple of its vapor pressure upon a pure substance and its mole fraction in a solution).

Heat is neither released, nor absorbed in the process of ideal solution formation. The heat required to break bonds between the same particles is completely compensated by the heat released during the formation of new bonds between different particles. For the formation of real solution the enthalpy is never equal to zero.

There are several types of heat effects observed during the process of dissolving. The first heat of the dissolving is the enthalpy of formation of a solution made from 1 mole of a solute and the largest possible amount of a solvent (at the infinite dilution). In figure 1.1 the value of the first heat of the dissolving (ΔH^0) is situated on the Y-axis. The complete heat of the dissolving (ΔH_S) is the enthalpy of formation of a solution made from 1 mole of a solute and the amount of a solvent required to make a saturated solution. In figure 1.1 it is shown by the rightmost point. The complete heat of the dissolving is much lower than the first heat of the dissolving. Indeed, the higher the amount of solvent, the higher the number of interactions between the molecules of solute and the molecules of solvent, and the higher the heat effect of hydration. Notice that in figure 1.1 the heat effect relative to the environment is plotted against the molality of a solution. That is why the value of ΔH (relative to the environment) is positive. The process illustrated in figure 1.1 is exothermic. However, if it were endothermic, the direction of the plot would be the same, while the X-axis would be situated higher than the value of ΔH^0.

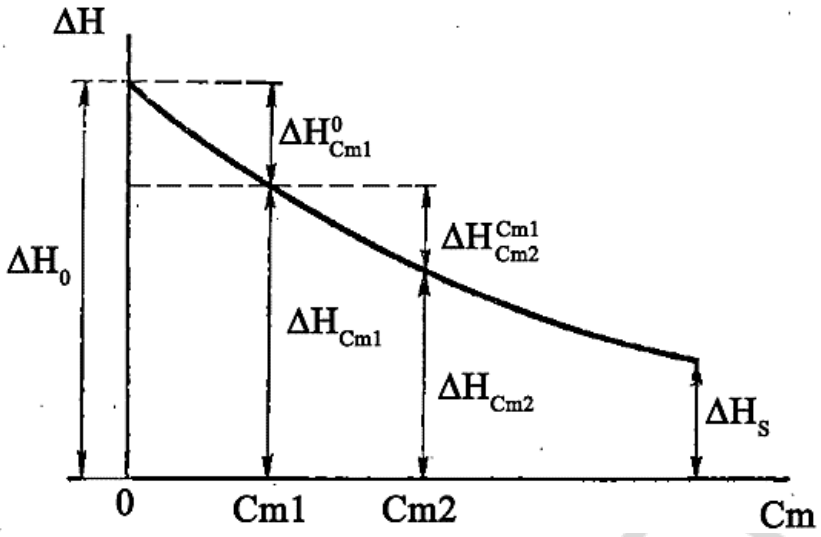

Figure 1.1. Heat effects of the dissolving

Using the graph from figure 1.1 one can explain such terms as the intermediate heat of the dissolving (when you put more solute in the solution of the same substance) and the intermediate heat of the dilution (when you put more solvent in the solution). The integral heat of the dilution is the heat effect of the dilution of a solution containing 1 mole of a solute in the largest possible amount of solvent. The differential heat of the dissolving is the heat effect of the dissolving of 1 mole of a solute in the largest possible amount of the saturated solution.

The higher the amount of solvent, the more exothermic is the process of the dissolving. In general, the heat effect of the dissolving of any solid ionic substance in water is a sum of the heat effect of the destruction of the crystal lattice and the heat effect of hydration. The first process is the same as melting, but it proceeds at lower temperature and with the help of water molecules. Usually the heat effect of the destruction of the crystal lattice during the dissolving is thought to be equal to the heat effect of melting. This heat effect doesn't depend on the amount of water, unlike the heat effect of hydration.

$\Delta H_{dissolving} = \Delta H_{melting} + \Delta H_{hydration}$

Salt hydrates are usually thought to be solid substances in which ions are already hydrated. If it is true, then the heat of the dissolving of a dry salt ($CuSO_4$) is the sum of the heat of the dissolving of a salt hydrate ($CuSO_4 \cdot 5H_2O$) and the heat of hydration.

$\Delta H_{dry\ salt} = \Delta H_{salt\ hydrate} + \Delta H_{hydration}$

As one can understand from figure 1.1, the last equation is not completely true. In the salt hydrate ions are not completely hydrated, like they would in the largest possible amount of water. By the way, the first heat of the dissolving (in the largest possible amount of a solvent) cannot be measured directly. The point on the Y-axis of the graph from figure 1.1 is always plotted with the help of approximation (one has to continue the line until it will cross the Y-axis).

According to the first and the second laws of thermodynamics, real solution is formed spontaneously in isobaric and isothermic conditions, in case if the free energy of Gibbs is negative.

$\Delta G_{dissolving} = \Delta H_{dissolving} - T\Delta S_{dissolving}$

Since the heat effect of the ideal solution formation is equal to zero, the sign of the Gibbs free energy of its formation is determined by the sign of the entropy of its formation only. It means that an ideal solution of any solid or liquid substance in liquid solvent is formed spontaneously, because of the increase of entropy.

For ideal solutions we can derive the equation that determines the solubility of a substance in any solvent. To start with, we should write the equation of the chemical potential of a solute in a solution.

$\mu_{solute} = \mu^0_{solute} + RT\ln\chi_{solute}$

The chemical potential depends on the molar Gibbs free energy in standard conditions (μ^0_{solute}) and the mole fraction (χ_{solute}) of a solute in a solution. The lower the concentration, the more negative is the "$RT\ln\chi_{solute}$" value.

In the system with a precipitate and a saturated solution upon it there is a chemical equilibrium between the process of the dissolving and the process of the precipitation.

$\mu_{solute\ in\ a\ saturated\ solution} = \mu_{precipitate\ (solid\ substance)}$

We know that the chemical potential of a solute in a saturated solution is equal to its standard chemical potential plus RT multiplied by natural logarithm of its mole fraction in a saturated solution.

$\mu_{solute\ in\ a\ saturated\ solution} = \mu^0_{solute\ (liquid\ substance)} + RT\ln\chi_{solute\ in\ a\ saturated\ solution}$

The standard chemical potential of a solute in a solution is equal to its chemical potential in a melted (liquid) state. That is why we can re-write the equation again and see that "$-RT\ln\chi_{saturated}$" is the Gibbs free energy of melting for a given solute.

$\mu^0_{solid\ substance} = \mu^0_{liquid\ substance} + RT\ln\chi_{saturated}$

$\mu^0_{liquid\ substance} - \mu^0_{solid\ substance} = -RT\ln\chi_{saturated}$

$\Delta G_{melting} = -RT\ln\chi_{saturated}$

Then we should use the differential form of Gibbs–Helmholtz equation and substitute ΔG by "$-RT\ln\chi$" in that equation.

Gibbs–Helmholtz equation itself is derived from the equation of the derivative of a ratio between Gibbs energy and temperature.

$d(G/T) = (TdG - GdT)/T^2$

Since $dG = Vdp - SdT$, we can substitute dG in the previous equation.

$d(G/T) = (TVdp - STdT - GdT)/T^2 = (TVdp - [G + ST]dT)/T^2$

$d(G/T) = (TVdp - HdT)/T^2$

In isobaric conditions $dp = 0$, and the equation becomes much simpler. The last thing is to divide both sides by ∂T.

$\partial(G/T) = -H\partial T/T^2$ and $\partial(G/T)/\partial T = -H/T^2$

For the process of melting we use the value of ΔG instead of overall Gibbs energy.

$\partial(\Delta G_{melting}/T)/\partial T = -\Delta H_{melting}/T^2_{melting}$

$\partial(-R\ln\chi_{saturated})/\partial T = -\Delta H_{melting}/T^2_{melting}$

$\partial(\ln\chi_{saturated})/\partial T = \Delta H_{melting}/(R\cdot T^2_{melting})$

Different solid substances demonstrate different solubility values. To calculate a solubility one should integrate the previous equation from mole fraction in a saturated solution to 1, and from the temperature of dissolving to the temperature of solute melting.

$\ln\chi_{saturated} = (\Delta H_{melting}/R) \times (1/T_{melting} - 1/T)$

According to the last equation (Shredder equation), the higher the enthalpy of melting, and the higher the temperature of melting, the lower the solubility of a given substance in any solvent. Since the melting is always an endothermic process, the higher the temperature, the higher the solubility of a substance. Indeed, the temperature of melting for a solid substance is always higher than the temperature at which it dissolves in water: in brackets we always got a negative number that becomes more negative with the growth of $T_{melting}$. This equation shows that the mole fraction of a solute in a saturated solution is changing with the temperature: the higher the temperature of the dissolving, the less negative is the number in brackets. It works for every solid substance in any liquid, if they make an ideal solution. In other words, the stronger the bonds between particles of a substance in a solid state, the lower its solubility. In ideal solutions solubility of solid substances does not depend on the nature of a solvent. There are also so-called colligative properties of solutions, that do not depend on the nature of a solute, if a solution is ideal.

We can list four colligative properties:

– vapor pressure decrease;

– boiling point elevation;

– freezing point depression;

– osmotic pressure.

All these properties in ideal solutions occur because of the increase in entropy because of the dissolving only. Heat effects (i. e. the process of hydration) are not even considered in the formulas that describe colligative properties.

The first way to express the first Raoult's law is arithmetical. The total vapor pressure upon a solution is equal to the sum of vapor pressures for two components (solute and solvent). Both of them are calculated according to the following formula.

$P_1 = P^0_1\cdot\chi_1$ $\quad$ $P_2 = P^0_2\cdot\chi_2$ $\quad$ $P_{total} = P_1 + P_2$

If the first component is not volatile at all, then the vapor pressure upon it is equal to zero. In this case the total vapor pressure upon a solution is only because of the vapor pressure of a solvent. The last one follows the Raoult's law. Finally, we can write the following equation.

$P_{total} = P^0_{solvent}\cdot\chi_{solvent}$

Since the mole fraction of a solute is equal to "$1 - \chi_{solvent}$", and the decrease of vapor pressure is the difference between $P^0_{solvent}$ and P_{total}, we can re-write the last equation.

$\Delta P / P^0_{solvent} = (P^0_{solvent} - P_{total}) / P^0_{solvent} = (P^0_{solvent} - P^0_{solvent} \cdot \chi_{solvent}) / P^0_{solvent}$

$\Delta P / P^0_{solvent} = P^0_{solvent} (1 - \chi_{solvent}) / P^0_{solvent} = 1 - \chi_{solvent} = \chi_{solute}$

$\Delta P = P^0_{solvent} \cdot \chi_{solute}$

The decrease of the vapor pressure upon a solution is equal to the multiple of vapor pressure upon a pure solvent and the mole fraction of a nonvolatile solute. This law is explained by the increase of entropy in the solution of nonvolatile substance. Other explanations that can be found in different sources are not applicable to ideal solutions. To make it clear, follow the thermodynamic derivation of the same Raoult's law.

In the state of equilibrium in a pure solvent, chemical potentials of liquid and gaseous solvent are equal to each other. The last one depends on the partial pressure of a solvent.

$\mu^0_{pure\ solvent} = \mu^0_{gaseous\ solvent} + RTlnP^0_{solvent}$

For the chemical potential of a solvent in a solution we can write the same equation, but the actual partial vapor pressure will be different (P_1).

$\mu^0_{solvent} = \mu^0_{gaseous\ solvent} + RTlnP_1$

The chemical potential of a solute in a solution is expressed in the following way.

$\mu^0_{solvent} = \mu^0_{solvent} + RTln\chi_1$

Since chemical potentials of liquid and gaseous solvent are identical in the state of equilibrium, we can write the following.

$\mu^0_{gaseous\ solvent} + RTlnP_1 = \mu^0_{solvent} + RTln\chi_1$

The chemical potential of a pure liquid solvent is equal to "$\mu^0_{gaseous\ solvent} + RTlnP^0_{solvent}$".

$\mu^0_{gaseous\ solvent} + RTlnP_1 = \mu^0_{gaseous\ solvent} + RTlnP^0_{solvent} + RTln\chi_1$

Finally, we can cross out repeating expressions from the equation.

$ln\chi_1 = lnP_1 - lnP^0 = ln(P_1/P^0)$

$\chi_1 = P_1/P^0$ that is the same as $P_{total} = P^0_{solvent} \cdot \chi_{solvent}$

Notice that this formula has no variables that depend on the nature of a solute.

Water solution starts its freezing (crystals of pure water are starting to appear) at the temperature that is lower than 0 °C. This observation in a generalized form is as follows: the difference in the freezing temperature (the temperature of the start of crystallization) of a solution of a nonvolatile substance is proportional to the molality of that solution. The first part of the second Raoult's law is expressed by a simple formula.

$\Delta t_{freezing} = K \cdot C_m$

The coefficient of proportionality (K) is known as the cryoscopic constant ("cryo" means frost). The dependence between $\Delta t_{freezing}$ and C_m is linear, according to the equation. One may be surprised, but this simple equation works for ideal solutions only, and it can be derived from the Shredder's equation. To make the derivation, one should consider water as

a solute, and a dissolved substance as a solvent. In this case the process of freezing is considered as the process of precipitation of water.

$\ln\chi_{\text{solute in saturated solution}} = (\Delta H_{\text{melting of solute}}/R) \times (1/T_{\text{meting of solute}} - 1/T)$

$\ln\chi_{\text{water}} = (\Delta H_{\text{melting of water}}/R) \times (1/T_{\text{melting of water}} - 1/T)$

$\ln\chi_{\text{water}} = (\Delta H_{\text{melting of water}}/R) \times ((T - T_{\text{melting of water}}) / (T_{\text{melting of water}} \times T))$

$\ln\chi_{\text{water}} = -(\Delta H_{\text{melting of water}} \times \Delta T) / (R \times T_{\text{melting of water}} \times T)$

$-\ln(1 - \chi_{\text{solute}}) = (\Delta H_{\text{melting of water}} \times \Delta T) / (R \times T_{\text{melting of water}} \times T)$

$\Delta T = (-\ln(1 - \chi_{\text{solute}}) \times R \times T_{\text{melting of water}} \times T) / \Delta H_{\text{melting of water}}$

This equation should be simplified with the help of three assumptions. First assumption: the natural logarithm of "1 – x" is approximately equal to "x". The lower the value of "x", the higher the accuracy of this approximation. Second assumption: we can assume that the difference between the temperature of freezing for pure water and for a solution is not very big. Because of this, $T_{\text{melting of water}} \times T$ is approximately equal to $T^2_{\text{melting of water}}$. Third assumption: the mole fraction of a solute is almost equal to the multiple of molality and the molar mass of a solvent divided by 1000 (since molality is expressed in mol/kg). We assume that the number of moles of solute is much lower than the number of moles of water.

After the rearrangements we come to the following equation.

$\Delta T = (R \times T^2_{\text{melting of water}} \times M_{\text{water}} \times C_m) / (1000 \times \Delta H_{\text{melting of water}}) = K \times C_m$

Notice that all the three assumption work good if the solution is rather dilute. So, the linear dependence between $\Delta t_{\text{freezing}}$ and molality of a solution exist when the molality itself is rather low. The nature of the cryoscopic constant is clear now: it is everything from the right part of the above written equation, except molality. So, the formula for the calculation of the cryoscopic constant is as follows.

$K = (RT^2_{\text{freezing}} / \Delta H_{\text{melting}}) \cdot (M_{\text{solvent}} / 1000)$

The higher the temperature of freezing (=melting) for a solvent, the higher the cryoscopic constant. The higher the enthalpy of melting (it always has a positive sign), the lower the cryoscopic constant. The higher the molar mass of a solvent, the higher the cryoscopic constant.

For water the cryoscopic constant is equal to 1.86 K·kg/mol. Using this constant one can predict the freezing temperature for a solution of any substance with known molality. One also can find the molality of a solution after the experimental determination of the freezing point of a solution. From the molality one can calculate the molar mass of a substance. This way of molar mass determination is known as cryoscopy. This method can give just an approximate molar mass, since there are several approximations mentioned above in the derivation of a simple $\Delta t_{\text{freezing}} = K \cdot C_m$ equation.

The second part of the second Raoult's law is about the boiling point elevation. The process of boiling of a solution cannot be compared with the precipitation at all (unlike the process of freezing). So, we need to derive an equation that is similar to the Shredder's

equation, from the very beginning. In the moment of boiling the chemical potential of the vapor is equal to the chemical potential of the solvent in a liquid solution. So, we can write the following equation.

$\mu_{vapor} = \mu^0_{liquid\ solvent} + RT\ln\chi_{solvent}$

$\mu^0_{liquid\ solvent} - \mu_{vapor} = -RT\ln\chi_{solvent}$

$\Delta G_{boiling} = -RT\ln\chi_{solvent}$

The molar Gibbs energy of the boiling of a solvent is expressed through the mole fraction of the solvent now. This expression is used for the modification of the Gibbs–Helmholtz equation for the process of boiling.

$\partial(\Delta G_{boiling}/T)/\partial T = -\Delta H_{boiling}/T^2_{boiling}$

$\partial(-RT\ln\chi_{solvent}/T)/\partial T = -\Delta H_{boiling}/T^2_{boiling}$

$\partial(-R\ln\chi_{solvent})/\partial T = -\Delta H_{boiling}/T^2_{boiling}$

$\partial(\ln\chi_{solvent})/\partial T = \Delta H_{boiling}/(R\cdot T^2_{boiling})$

This equation should be integrated: the left part is integrated from the given mole fraction to the mole fraction equal to 1; the right part is integrated from the temperature of boiling of a solvent to the temperature of boiling of a solution. The resulting equation is as follows.

$\ln\chi_{solvent} = (\Delta H_{boiling}/R) \times (1/T_{boiling} - 1/T)$

Using the same three assumptions that we used before, we can convert this equation to the familiar look ($\Delta T_{boiling} = E\cdot C_m$).

$\Delta T = (R \times T^2_{boiling} \times M_{boiling} \times C_m) / (1000 \times \Delta H_{boiling}) = E \times C_m$

$E = (R \times T^2_{boiling} \times M_{boiling}) / (1000 \times \Delta H_{boiling})$

E is an ebullioscopic constant. For water this constant is equal to 0.52 K·kg/mol. Notice that the value of cryoscopic constant (K) for water (1.86 K·kg/mol) is 3.58 times higher than the value of ebullioscopic constant (E). Because of this reason ebullioscopy gives less accurate results than cryoscopy when it is used for the molar mass calculation.

The overall second Raoult's law tells that both the freezing point depression and the boiling point elevation are proportional to the molality of a solution. Notice that the freezing point goes down, while the boiling point goes up for a solution of a nonvolatile electrolyte (figure 1.2), making the area of liquid solvent existence wider from both sides. It happens simply because of the increase in entropy in any solution. If a liquid boils, the entropy in a system increases (because of the conversion of that liquid to a gas). The entropy inside a solution is higher than the entropy in a pure solvent. So, the difference in entropy is lower when a solvent boils in the presence of a solute. If we consider that the difference in enthalpy is the same for both processes, then to reach the same $\Delta G = 0$, we need to increase the temperature to make "$T\Delta S$" equal to "ΔH". In the same manner, when solid solvent melts and forms a solution, the increase in entropy is higher than if that solid solvent just melts. To reach the equilibrium state (when $\Delta G = 0$) one needs to decrease

the temperature to make "TΔS" equal to "ΔH" of melting. In other words, a solvent is more stable if it forms a solution, than if it exists as a pure liquid.

If a vapor pressure decreases, the line of liquid and gas co-existence for water making a solution is situated below the same line for a pure water in the state diagram. As a consequence, that line crosses the isobar of 1 atmosphere at higher temperature (figure 1.2). One more consequence is that the line of liquid and gas co-existence for water from a solution crosses the line of solid and gas co-existence at a lower temperature. So, the triple point for water being a solvent is situated at lower temperature and pressure than that for pure water. The line of solid and liquid co-existence starts from the triple point and crosses an isobar of 1 atmosphere at a lower temperature, if we deal with water from a solution, than if we deal with pure water. Since the vapor pressure upon liquid in a solution is decreased, it becomes equal to the vapor pressure upon solid at a lower temperature (liquid boils when the vapor pressure upon it is the same as upon the corresponding solid).

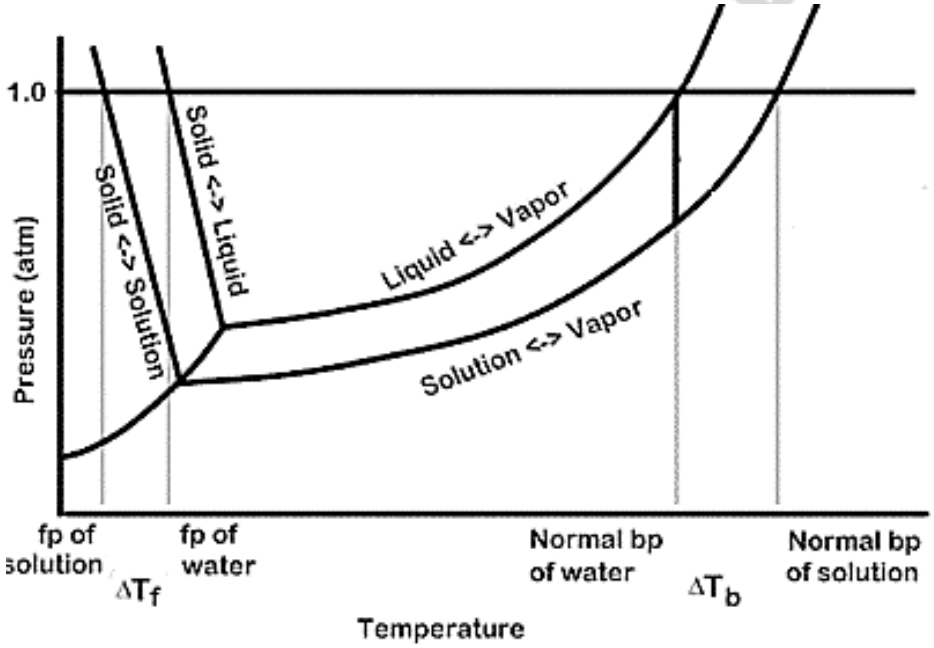

Figure 1.2. Schematic phase diagram of pure water and water as a solvent in a solution of a nonvolatile solute

The fourth colligative property is known as osmotic pressure. To define the osmotic pressure one needs to define osmosis first. Osmosis is the process of the diffusion of a solvent through the semipermeable membrane from the area with the lower content of a solute to the area with the higher content of a solute. Solute itself cannot pass through the semipermeable membrane. Generally speaking, osmosis occurs because solvent tends to be distributed equally in both parts of a system separated by a membrane. The entropy in the whole system must reach its highest possible value. So, when a solvent flows through the membrane, the entropy decreases in the area of a lower concentration of solute, and it is increasing in the area of a higher concentration of solute. Until the overall ΔS is positive, the process will continue.

Osmotic pressure is the pressure that one needs to apply to the semipermeable membrane (from the side of more concentrated solution) to stop the process of osmosis. This definition came from the experiment with the U-shaped vessel. There is a semipermeable membrane in the bottom of such vessel (figure 1.3, *a*). If one puts a solute in the right cylinder, the level of liquid inside it starts to grow because of osmosis. However, soon that growth stops: a system reaches the equilibrium (figure 1.3, *b*). Then one applies a pressure on the surface of liquid from the right cylinder, and the water starts to flow back to the left cylinder. When the levels of liquid are at the same point in the both cylinders again, a physical pressure applied to the liquid from the right cylinder is nothing but the osmotic pressure (figure 1.3, *c*). Let us perform thermodynamical description of the final system.

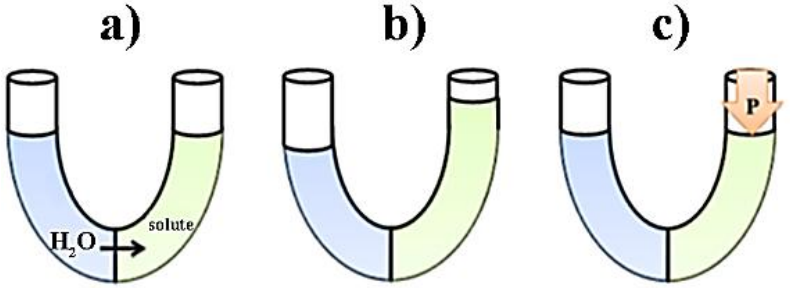

Figure 1.3. Experiment with U-shaped vessel. Two tubes are separated by a semipermeable membrane

The chemical potential of a solvent in both cylinders is identical. In the left one it is equal to μ^0 of a solvent, while in the right one it is equal to the sum of μ^0, "RTlnχ" and the change of it caused by the increased external pressure. The last value is equal to the integral of $(\partial\mu^0_{solvent}/\partial p)_T dp$ from the atmospheric pressure to the final external pressure. As we know, the partial derivative of Gibbs energy per pressure at the constant temperature is nothing but the volume. Since the chemical potential is the molar Gibbs energy, then the whole expression is equal to the molar volume of a solvent (V_m^0).

$$\mu^0_{solvent} = \mu^0_{solvent} + RT\ln\chi_{solvent} + \int_{p\ atmospheric}^{p\ final} (\partial\mu^0_{solvent}/\partial p)_T\, dp$$

$$\mu^0_{solvent} = \mu^0_{solvent} + RT\ln\chi_{solvent} + \int_{p\ atmospheric}^{p\ final} V_m^0 dp$$

Molar volume of water does not depend on pressure at room temperature. Because of this reason, the integral becomes equal to $V^0 \cdot P_{osmotic}$. The next step shows that this expression is equal to $RT\ln\chi_{solvent}$ with an opposite sign.

$$-RT\ln\chi_{solvent} = V_m^0 \cdot P_{osmotic}$$

Then one has to change the mole fraction of a solvent by the "$1 - \chi_{solute}$" and use the approximation that tells that "ln(1 – x)" is almost equal to "–x".

$$RT\chi_{solute} = V_m^0 \cdot P_{osmotic}$$

Osmotic pressure can be calculated from that formula.

$$P_{osmotic} = (RT\chi_{solute})/V_m^0$$

One more approximation is needed to convert this formula to the familiar expression. Mole fraction is equal to the number of moles of a solute over the sum of numbers of moles for a solute and a solvent. If we assume that the last sum is almost equal to the number of moles of a solvent, and this number of moles (according to the mathematics) is equal to 1, then this value will be crossed out together with the denominator of the molar volume. That is how "χ_{solute}/V_m^0" is almost equal to the molarity (C) of the solution.

$P_{osmotic} = CRT$

This expression reminds the gas law ($pV = nRT$ easily converts to $p = CRT$). Because of this reason there is another definition of osmotic pressure. The osmotic pressure is equal to the pressure of an ideal gas in a closed container at a given temperature: the concentration of an ideal gas is equal to the molar concentration of a solute, the volume of a container is equal to the volume of a solution.

Osmotic pressure of an ideal solution does not depend on the properties of a dissolved substance. Approximations mentioned above show that the linear dependence between the molarity and the osmotic pressure is expected for dilute solutions only. In case if two solutions have the same osmotic pressure, they are called isotonic relative to each other. A solution with higher osmotic pressure is called hypertonic relative to the one with lower osmotic pressure that is called hypotonic. Osmotic pressure can be measured experimentally. From the osmotic pressure one can calculate the molar mass of a solute.

In real solutions there is a difference between theoretically predicted values of all the colligative properties and their experimentally determined values. For each concrete substance one may use a coefficient (the multiple) that makes theoretical results equal to experimental results. This coefficient is known as an isotonic coefficient (i). There are many factors that influence the value of an isotonic coefficient. However, the most influential factor for dilute solutions of electrolytes is the dissociation. Strong electrolytes dissociate completely, and the number of real particles in a solution becomes several times higher than the number of units of a solute. Weak electrolytes dissociate incompletely, but still the total number of particles (molecules and ions) in their solutions is higher than the number of units.

If we assume that the only one cause of the deviation of the behavior of a solution of weak electrolyte from the theoretically predicted one is its partial dissociation, then we can calculate the value of the dissociation degree (α) from the value of isotonic coefficient.

$i = P_{osmotic\ real} / P_{osmotic\ predicted} = P_{osmotic\ real} / (CRT)$

$\alpha = (i - 1) / (n - 1)$

In the last equation "i" is an isotonic coefficient, and "n" is the number of ions that one unit of a given electrolyte can produce during the dissociation. In the same manner one can calculate "i" from the temperature of melting, the temperature of boiling and the difference in vapor pressure.

Surprisingly, solutions of strong electrolytes never show isotonic coefficients exactly equal to numbers of ions they form during the dissociation. This phenomenon cannot be

explained by the partial dissociation (since those electrolytes are strong). That is why it is explained by the partial association. In a water solution ions of strong electrolytes interact with each other, but they do not form crystals. They just make associates kept together by electrostatic attraction. Moreover, those ions in associates are hydrated. The higher the concentration of an electrolyte, the higher the percentage of ions included in associates, and the higher the order of those associates. So, solutions of strong electrolytes demonstrate weaker colligative properties than they should.

The activity of an ion is less than its real concentration. To convert the concentration (C) into activity (a) one needs to multiply it by the factor of activity (f_a).

$a = f_a \cdot C$

Usually an average activity is used for both the cation and the anion of the same electrolyte, since they are usually introduced together in the solution. The average activity is the geometric mean of the activities of cation and anion in powers equal to their subscripts in a formula of a salt. For example, for a salt A_mB_n the average activity is calculated as follows.

$$a_{\pm} = \sqrt[m+n]{a^m_A \cdot a^n_B}$$

Average activity can be calculated from the molarity (or molality) of a salt with the help of an average coefficient of activity.

$a_{\pm} = f_{a\pm} \cdot C$

To calculate an average coefficient of activity one may use the formula of Debye and Huckel written below.

$$-\log f_{a\pm} = 0.509 \cdot \left| Z_+ \cdot Z_- \right| \cdot \sqrt{I}$$

In this formula Z_+ is the charge of a cation, Z_- is the charge of an anion, I is the ionic strength of a solution. Notice that the module of the multiple of charges is used in that formula. The number 0.509 is an empiric constant for water at the temperature of 25 °C that is determined by its density and dielectric properties. According to this formula, the higher the ionic strength of a given solution, the lower the factor of activity, the lower the activity of ions.

Ionic strength is a half sum of the multiples of molalities and the squares of the charges of all the ions in a solution. According to this definition, the higher the concentration of an ion, and the higher the charge of an ion, the higher the ionic strength of the whole solution.

$$I = {}^1/_2 \Sigma C_{mi} \cdot Z_i^2$$

The subscript “i” in the formula above shows that we deal with the “i-th” ion: all the ions in the solution must be considered in the calculation of ionic strength.

Different solutions may have the same ionic strength. In other words, two solutions of different substances made from different ions may have the same value of ionic strength. If it is true, then the average coefficient of activity is the same for a given strong electrolyte in all the solutions of the same ionic strength. Ions of the same charge have the same coefficient of activity in all the solutions of the same ionic strength. These two statements

are known as the rule of the ionic strength. This rule works good if we deal with dilute solutions (with an overall molality of all ions less than 0.02 mol/kg), and it still works relatively good in solutions with an overall molality from 0.02 to 0.2 mol/kg. All the reactions in human body proceed at the constant ionic strength of approximately 0.15 mol/kg. In the physiological solution (saline) ionic strength is close to that value: it is equal to exactly 0.15 mol/kg.

Colligative properties are used for the determination of the hydration (coordination) number of an ion. For example, for Ca^{2+} ions the hydration number is 12 according to the freezing point depression, and it is equal to 7 according to the boiling point elevation. The vapor pressure decrease measurements confirmed that the higher the temperature, the lower the hydration number.

Problems

1. Calculate the vapor pressure over the solution containing 13.68 g of sucrose $C_{12}H_{22}O_{11}$ in 90 g of water at 65 °C if the pressure of saturated vapor over pure water at the same temperature is 25.0 kPa.

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2. The osmotic pressure of the solution containing 2.8 g of a biopolymer in 200 ml of the solution is equal to 0.70 kPa at 25 °C. Find the relative molecular mass of the solute.

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3. Calculate the osmotic pressure of the solution containing 16 g of sucrose $C_{12}H_{22}O_{11}$ and 350 g of water at 293 K (density of the solution should be taken as 1 g/cm^3).

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4. Determine the saturated vapor pressure of water over 1 % urea solution ($CO(NH_2)_2$) at 298 K. The saturated vapor pressure over pure water at the same temperature is 2.34 kPa.

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5. 100 g of water contains 2.3 grams of an electrolyte. The solution has an osmotic pressure of 618.5 kPa at 25 °C. Determine the molar mass of the non-electrolyte. The density of the solution is assumed to be equal to 1 g/cm^3.

6. Calculate the boiling point of the solution containig 9 g of glucose $C_6H_{12}O_6$ in 100 g of water?

7. At what temperature will the 20 % ethyl alcohol solution (in water) freeze if the freezing point of water is 0 °C ?

8. How many grams of sucrose $C_{12}H_{22}O_{11}$ should be dissolved in 100 g of water in order to: a) lower the freezing temperature of the solution by one degree? b) increase the boiling temperature of the solution by one degree?

9. Apparent degree of dissociation of 0.1 M potassium chloride solution is 0.80. What is the osmotic pressure of this solution at the temperature of 17 °C?

10. Calculate the molar mass of the electrolyte (KA) if the decrease in the freezing point of a solution containing 5.85 g of this substance in 1000 g of water is 0.353 degrees. The apparent degree of dissociation of the electrolyte is 0.9 (E (H_2O) = 1.86 kg·deg/mole).

CHAPTER 2
BUFFER SOLUTIONS

The main topics of the chapter:

1. *pH and acidity.*
2. *pK of acids and bases.*
3. *Hendersson–Hasselbach equation.*
4. *Types of buffer systems.*
5. *The usage of buffer systems.*
6. *Buffer systems of human body.*

Buffer solution (buffer system) is a solution that keeps pH at approximately the same level after the addition of small amount of strong acid or strong base. This definition explains that buffer system is something that can neutralize both acids and bases. To understand this definition properly we must come back to the material on acids, bases and pH in water solutions.

According to the Arrhenius theory, acids are electrolytes that produce only one type of cation in water solution. That cation is H^+ more correctly represented as H_3O^+ known as hydronium ion. Bases are electrolytes that produce only one type of anion in water solution. That anion is OH^- known as hydroxide ion. Water itself partially dissociates into both H^+ and OH^- ions. Electrolytes may be strong or weak. Strong electrolytes dissociate completely and irreversibly. Weak electrolytes dissociate partially and reversibly: the equilibrium of the dissociation can be described by a standard equation (according to the law of mass action).

$K_{diss} = ([H^+]\cdot[Anion^-]) / [Acid]$ and $K_{diss} = ([OH^-]\cdot[Cation^-]) / [Base]$

According to the law of dilution, the lower the concentration of an electrolyte, the higher the degree of its dissociation. This statement can be approved mathematically. For example, for HF dissociation at a given temperature K_{diss} is constant, the concentration is equal to “C”, the degree of dissociation is equal to “α”.

$HF \leftrightarrow H^+ + F^-$

If the fraction of HF molecules that really dissociated is equal to α, then the concentration of H^+ is equal to $C\cdot\alpha$, and the concentration of F^- is also equal to $C\cdot\alpha$. The concentration of remaining molecules of HF is equal to $C(1 - \alpha)$. The equation for K_{diss} calculation is as follows.

$K_{diss} = (C\cdot\alpha\cdot C\cdot\alpha) / C(1 - \alpha) = C\cdot\alpha^2/(1 - \alpha)$

If the degree of dissociation is rather law, we can assume that “1 – α” is almost the same as “1”.

$K_{diss} \approx C\cdot\alpha^2$

Weak electrolytes behave as strong electrolytes if their solutions are extremely dilute. Strong electrolytes behave like weak electrolytes if their solutions are extremely concentrated.

Water is weak electrolyte. Its constant of dissociation is rather low: $1.8 \cdot 10^{-16}$ at 25 °C. So, we can write the equation about this process.

$K_{diss} = ([H^+] \cdot [OH^-]) / [H_2O] = 1.8 \cdot 10^{-16}$

The above written equation includes the concentration of water in pure water. We can calculate it for 1 L of water: the density of water is 1 g/ml, the mass of water is 1000 g, the molar mass is 18 g/mol, and the number of moles is 55.6 mol. So, the concentration of water in pure water is equal to 55.6 mol/L, and we can re-write the equation with this concrete number.

$K_{diss} = ([H^+] \cdot [OH^-]) / 55.6 = 1.8 \cdot 10^{-16}$

$K_{water} = K_{diss} \cdot [H_2O] = 55.6 \cdot 1.8 \cdot 10^{-16} = 1 \cdot 10^{-14}$

$[H^+] \cdot [OH^-] = 1 \cdot 10^{-14}$

The multiple of concentrations of H^+ and OH^- in water solution is always equal to the same number at the same temperature. At 25 °C that constant of water (water ion product) is equal to $1 \cdot 10^{-14}$. It means that if we know the concentration of H^+, we can calculate the concentration of OH^-, and vice versa.

To avoid the usage of low numbers, it was suggested to use negative decimal logarithm of the concentration of H^+ ions to describe the level of acidity in water solution. For example, if the concentration of H^+ is equal to 0.01 mol/L, pH is equal to 2, if the concentration of H^+ is equal to 0.00001 mol/L, pH is equal to 5.

$pH = -\log[H^+]$ $pOH = -\log[OH^-]$ $pH + pOH = 14$

In the same manner we can calculate pOH from the concentration of OH^- ions. Since the ion product of water is 10^{-14}, the sum of pH and pOH is equal to 14. Using this simple equation we can get pH from the concentration of alkali in water solution.

The level of pH in the solution of weak acid is calculated with the help of the degree of dissociation (α). In each step of dissociation the concentration of H^+ is equal to the multiple of concentration of a weak acid and the degree of its dissociation. The level of pH in the solution of strong acid is calculated from the activity of H^+ ions that is equal to their concentration multiplied by the coefficient of activity (f_a). For alkali you need to calculate the activity of OH^- ions, convert it to pOH, and then minus the resulting number from 14.

Since the most of the constants of dissociation are expressed by very low numbers, it is better to use their negative decimal logarithms to compare them with each other. In the similar manner to pH and pOH, pK_a is equal to the negative decimal logarithm of the constant of dissociation for an acid, while pK_b is equal to the decimal logarithm of the constant of dissociation for a base.

$pK_a = -\log K_{diss}$ for an acid

$pK_b = -\log K_{diss}$ for a base

Notice that the reaction of deprotonation for an acid is a reversed reaction for the process of protonation for a base. The sum of pK_a for an acid and pK_b for its conjugate base is equal to 14.

acid + base ↔ conjugate base + conjugate acid

$H_2PO_4^- + H_2O \leftrightarrow HPO_4^{2-} + H_3O^+$

Buffer system contains two components: either a weak acid and its conjugate base, or a weak base and its conjugate acid. In this definition we mean an acid or a base in terms of Bronsted–Lowry theory. According to that theory, acid is a particle that loses a proton, while base is a particle that gains a proton. So, an acid becomes deprotonated and thus turns to a base (conjugate base). A base becomes protonated and thus turns to an acid (conjugate acid). If we convert the definition in terms of Bronsted–Lowry theory to the Arrhenius theory, then we will classify buffer systems into four types.

1. Acidic buffer systems made from weak Arrhenius acid and its salt.
2. Basic buffer systems made from weak Arrhenius base and its salt.
3. Salt buffer system made from two salts of the same acid (one of them is more acidic than the other).
4. Protein buffer system.

There are two processes in the acidic buffer system. Both of them are in the equilibrium state. Weak acid is partially dissociated. Anion of the weak acid is partially hydrolyzed. If we consider these processes from the point of view of protolytic theory, we will see that they are mutually connected with each other. The product of the first one (anion of weak acid) is the reactant for the second one, while the product of the second one (weak acid) is the reactant for the first one.

Dissociation: $CH_3COOH + H_2O \leftrightarrow CH_3COO^- + H_3O^+$

Hydrolysis: $CH_3COO^- + H_2O \leftrightarrow CH_3COOH + OH^-$

Water acts as a reactant in both reactions. As the products of these two processes we have H_3O^+ and OH^- ions that are connected with water by the equation of its dissociation (autoprotolysis).

Autoprotolysis of water: $H_2O + H_2O \leftrightarrow H_3O^+ + OH^-$

Since the buffer system is based on three equilibrium processes (including the dissociation of water), it is rather stable. When H^+ ions are added to the buffer system, they shift the first equilibrium to the left (anion of weak acid is protonated), they shift the second equilibrium to the right (OH^- ions form water with the excess of H^+), and the last process is described by the third equilibrium. Finally, the concentration of weak acid is growing, while the concentration of its anion is decreasing. Buffer system exchanges a strong acid by a weak acid. If one adds OH^- ions to the acidic buffer system, they react with weak acid and form water and a corresponding anion. Anion is a weak base (according to protolytic theory). So, buffer system exchanges a strong base by a weak base.

If we come back to Arrhenius theory, we will see that three equilibriums may be described by a single equilibrium equation of electrolytic dissociation.

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

$K_{diss} = ([H^+]\cdot[CH_3COO^-]) / [CH_3COOH]$

According to this equation, the concentration of H^+ is determined by the ratio of concentrations of weak acid and its salt (anion), since K_{diss} is constant at a given temperature.

$[H^+] = (K_{diss}\cdot[CH_3COOH]) / [CH_3COO^-]$

If we take a negative decimal logarithm of this equation, it transforms to the Hendersson–Hasselbach equation for the calculation of pH in buffer solution.

$-\log[H^+] = -\log((K_{diss}\cdot[CH_3COOH]) / [CH_3COO^-])$

$-\log[H^+] = -\log K_{diss} - \log([CH_3COOH] / [CH_3COO^-])$

Since $-\log[H^+]$ is equal to pH and $-\log K_{diss}$ is equal to pK_a, we can re-write this equation.

$pH = pK - \log([CH_3COOH]/[CH_3COO^-])$

To remove minus from this equation it is enough just to change positions of concentrations under the logarithm.

$pH = pK_a + \log([CH_3COO^-] / [CH_3COOH])$

In general, Hendersson–Hasselbach equation is written as follows (for an acidic buffer system and for a basic buffer system, respectively).

$pH = pK_a + \log([salt] / [acid])$ and $pH = 14 - pK_b - \log([salt] / [base])$

Hydrolysis of an anion of a weak acid is already considered in the Hendersson–Hasselbach equation, since the constant of hydrolysis can be derived from the constant of dissociation.

$CH_3COO^- + H_2O \leftrightarrow CH_3COOH + OH^-$

$K_{eq} = ([CH_3COOH]\cdot[OH^-]) / ([CH_3COO^-]\cdot[H_2O])$

Such value, as $[OH^-]$ can be expressed from the equation of water dissociation (autoprotolysis).

$K_{diss} = ([H^+]\cdot[OH^-]) / [H_2O]$, so $[OH^-] = (K_{diss}\cdot[H_2O]) / [H^+]$

The multiple of K_{diss} for water and $[H_2O]$ is known as K_w, that is equal to 10^{-14}. The multiple of K_{eq} for hydrolysis and $[H_2O]$ is known as the constant of hydrolysis (K_h).

$[OH^-] = K_w/[H^+]$

The combined equation includes the reversed expression of the constant of dissociation (acidity constant) for an acid.

$K_h = ([CH_3COOH]\cdot K_w) / ([CH_3COO^-]\cdot[H^+])$

$K_h = K_w / K_a$

The stronger the acid, the higher the K_a, and the lower the K_h for its anion. The weaker the acid, the lower the K_a, the higher the K_h for a corresponding anion.

As one can notice, pH in a buffer system depends on pK and on the ratio between concentrations of two components. pK itself depends on temperature (the higher the temperature, the higher the constant of dissociation, the lower the pK). So, pH should not depend on exact concentrations of two components (on the molarity of buffer), but just on the ratio between them. However, some small changes of pH are expected during the dilution of buffer system. They are caused by the difference between the constant of dissociation and the constant of hydrolysis. From the dilution law we know that the lower the concentration of an acid, the higher the degree of its dissociation (α), the higher the amount of H^+ ions in the solution. In the same manner, the lower the concentration of a salt, the higher the degree of its hydrolysis (h), the lower the amount of H^+ ions in the solution. So, the presence of both acid and its salt in the same solution prevents drastic changes of pH during the dilution, but the higher the difference between K_a and K_h, the stronger the deviation.

$K_a \approx C\alpha^2$ and $\alpha \approx \sqrt{K_a/C}$, but $K_h \approx Ch^2$ and $h \approx \sqrt{K_h/C}$

What happens with pH if we add a small amount of strong base to the acidic buffer? One can calculate the resulting pH using the same equation of Hendersson–Hasselbach. The amount of acid in the solution will decrease, while the amount of salt will increase. As a result, the ratio between two components of the buffer will become different, but the final change in pH will be relatively small. If we add a small amount of strong acid tom the acidic buffer, the amount of weak acid will increase, while the amount of salt will decrease.

$pH = pK_a + \log([salt] + [strong\ base] / [acid] – [strong\ base])$

$pH = pK_a + \log([salt] – [strong\ acid] / [acid] + [strong\ acid])$

In basic buffer systems we use modified equations to estimate a new level of pH.

$pH = 14 – pK_a – \log([salt] – [strong\ base] / [base] + [strong\ base])$

$pH = 14 – pK_a – \log([salt] + [strong\ acid] / [base] – [strong\ acid])$

If the amount of added strong acid is higher than the amount of salt in acidic buffer system, the buffer will be destroyed. So, the higher the amount of salt in such system, the higher the amount of acid it can neutralize. To characterize the ability of buffer system to neutralize strong acids one can use the buffer capacity against an acid. It is equal to the amount of H^+ ions that decreases pH by 1 point in 1 L of a given buffer solution. Buffer capacity against a base is calculated in the similar way, but for $OH^–$ anions. So, buffer capacity can be determined experimentally: one has to measure the change in pH occurred after the addition of a certain volume of strong acid (or base) with known normality and use the formulas written below.

$B_{acid} = (C_{N\ acid} \cdot V_{acid}) / (V_{buffer\ solution} \cdot \Delta pH) = n_{eq\ acid} / (V_{\ buffer\ solution} \cdot \Delta pH)$

$B_{base} = (C_{N\ base} \cdot V_{base}) / (V_{buffer\ solution} \cdot \Delta pH) = n_{eqbase} / (V_{\ buffer\ solution} \cdot \Delta pH)$

Buffer capacity can also be calculated mathematically using the same Hendersson–Hasselbach equation. The change in pH is calculated easily.

$\Delta pH = pK_a + \log([salt] / [acid]) - pK_a - \log([salt] - [strong\ acid] / [acid] + [strong\ acid])$

$\Delta pH = \log([salt]\cdot([acid] + [strong\ acid]) / [acid]\cdot([salt] - [strong\ acid])$

Then just calculate ΔpH after the addition of any small amount of acid (or base) and insert it in the formula for buffer capacity calculation.

It is known that the highest buffer capacity is established when the ratio between two components of buffer system is equal to 1:1. This experimental observation can be easily approved mathematically using the same Hendersson–Hasselbach equation. However, one should understand that the ratio of 1:1 is optimal for buffer capacity only if we compare buffers of the same overall molarity. The same amount of added acid (or base) will change pH of the 1:1 system much less than that of the system with a biased ratio between components, but with the same sum of concentrations for those two components. Because of this fact it is better to use buffer system with pK_a of an acid that is as close to pH in a solution as it is possible (to increase the buffer capacity). Recommended variations are as follows: pH should be in the rage of ±1 from pK_a. For effective basic buffer systems pH should be in the rage of ±1 from $14 - pK_a$.

To prepare a buffer solution one may use the Hendersson–Hasselbach equation. You know the needed pH level, you know the molarity of buffer solution, you know the volume, while pK_a (or pK_b) of the weak acid (or base) can be found elsewhere. You should start from the determination of the ratio between two components of buffer system. Let us try acidic buffer again.

$[salt]/[acid] = 10^{pH - pKa}$

Once you know the molar ratio, find the total number of moles (n) for both components (from final volume and molarity of buffer system). Then compose an equation like this.

$x/(n - x) = molar\ ratio$

In this equation x is the number of moles of salt. Find the number of moles of an acid. After that convert amounts to masses, weigh those masses of components and dissolve them in a volumetric flask of a needed volume.

Once you did these actions and prepare your buffer solution, don't be surprised if pH value is different than the desired one according to the pH-meter. In a real life initial pH of distilled water is lower than 7, since carbon dioxide (and other substances) dissolve in it. So, the best empirical way to make buffer solution is to pour together two solutions of the same molarity: solution of a salt and solution of an acid. If you mix them at any ratio, the final molarity for two components together will stay the same. Under the control of pH-meter add the solution of component 2 to the solution of component 1 until pH will reach the desired point. Then take the volume you need from the resulting solution.

The level of pH in our blood is kept at the same level with the help of buffer systems. Blood itself can be represented as the real solution of electrolytes, organic nonelectrolytes

and biopolymers that contains white blood cells, red blood cells and platelets as well. The solution without cells is called plasma. One can separate plasma from cells with the help of centrifugation. Before this operation blood clotting should be prevented. So, the most important contribution into the maintenance of pH in blood plasma is made by bicarbonate buffer system (it is made from carbon dioxide and bicarbonate anions). Average pH of human blood is equal to 7.4. If one considers real average concentrations of carbon dioxide and bicarbonate ions in our blood and insert them into the Hendersson–Hasselbach equation, the result will be equal to exactly 7.4. Other buffer systems from blood plasma that must be mentioned are: phosphate buffer system and protein buffer system (all the blood proteins contribute to it).

Red blood cells (erythrocytes) make significant contribution into the maintenance of pH in blood because of the hemoglobin/oxyhemoglobin buffer system. That system works in a mutual connection with bicarbonate buffer.

In tissues carbon dioxide moves from cells into the blood stream, and from blood plasma to red blood cells because of the gradient of its concentration. In red blood cells an enzyme called carbonic anhydrase catalyzes the reaction between carbon dioxide and water. Resulting species of that reaction are bicarbonate anion and hydronium cation. The last one protonates hemoglobin (namely, nitrogen atom from histidine side chain that coordinates Fe^{2+}). As a result, the complex made from heme, oxygen and histidine residue from globin becomes unstable and releases oxygen. In the same time, oxygen gets to tissues and pH in blood stays almost the same after the enrichment with carbon dioxide. Indeed, the range of pH variations in venous blood (7.32–7.42) is just a little lower than the rage of pH variations in arterial blood (7.35–7.45).

In lungs oxygen moves from alveoli to capillary, and from plasma to red blood cells. Inside red blood cells oxygen binds protonated hemoglobin. The resulting complex, as we already mentioned, is unstable. So, it breaks down into oxygenated but deprotonated hemoglobin and hydronium cations. Last ones react with bicarbonate anions under the control of carbonic anhydrase and form carbon dioxide and water. Carbon dioxide, thus, leaves capillary and moves in alveoli to be exhaled from lungs. That is how bicarbonate buffer system helps us to “breathe out” carbon dioxide and to release oxygen from hemoglobin in tissues.

Problems

1. Calculate the pH of 0.02 M solution of ammonium hydroxide. The ionization constant of $NH_3 \cdot H_2O$ is $1.8 \cdot 10^{-5}$.

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2. Calculate the pH of a buffer solution 1 L of which contains 18.4 g of formic acid and 68 g of sodium formate if $pK_a(HCOOH) = 3.75$.

3. Calculate the pH of the acetate buffer prepared from 100 mL of 0.1 M CH_3COOH solution and 200 mL of 0.2M CH_3COONa solution if $K_a(CH_3COOH) = 1.75 \cdot 10^{-5}$. How will the pH of this buffer solution change after the addition of 30 mL of 0.2 M NaOH solution?

4. Calculate the pH of a buffer solution prepared from 20 ml of 0.1 M formic acid solution and 30 ml of 0.2 M solution of sodium formate, pK(HCOOH) = 3.75.

5. 0.01 M NaOH was added to 1 liter of a buffer solution containing 0.1 mole of $NH_3 \cdot H_2O$ and NH_4Cl. Calculate the pH of the solution after adding alkali if $pK(NH_3 \cdot H_2O) = 4.75$.

6. To change the pH of 100 ml of blood from 7.36 till 7.00 we have to add 36 mL of· 0.05 M HCl solution. Calculate the buffer capacity of blood against the addition of acid (mol/L pH).

7. To change the pH to 100 ml of blood from 7.32 to 7.42 we have to add 3.6 ml of 0.1 M hydrochloric acid. Calculate the buffer capacity of blood against the addition of acid.

CHAPTER 3
ELECTROCHEMISTRY

Main topics of the chapter:

1. *Electric conductivity.*
2. *Mobility and the rate of movement of ions in water solution.*
3. *Kohlrausch law.*
4. *Applications of conductometry.*
5. *Electrode processes.*
6. *Standard hydrogen electrode.*
7. *Thermodynamics of galvanic element.*
8. *pH-meter.*
9. *Redox potentials.*

What happens when we pass electricity through water? If we apply direct electric current (DC) to the water solution, it results in the process of electrolysis. During the electrolysis redox reactions happen on two electrodes: oxidation happens on the anode (positively charged electrode), while reduction proceeds on the cathode (negatively charged electrode). If we apply alternating electric current (AC) to the water solution, electrolysis is not happening, and we are able to measure the conductivity of water solution without any changes in its content caused by the measurement.

Conductivity is the opposite value to resistance. Resistance (R) is measured in Ohm, while conductivity (L) is measured in Siemens. There are two types of conductors: metals and melts or water solutions of ionic substances. In metals electricity is transferred by free electrons, while in melts of ionic substances electricity is transferred by ions. In water solutions of ionic substances electricity is also transferred by ions, but those ions are hydrated by water molecules.

$L = 1/R$

For the first type of conductors (imagine a piece of wire) resistance is equal to the multiple of the specific resistance (ρ) and the ratio between the length (l) and the area of the transverse section (S). The longer the length, the higher the resistance, the wider the wire, the lower the resistance. So, specific resistance is the resistance of a given type of material with the length of 1 m and the area of the transverse section equal to 1 m^2.

$R = \rho \cdot (l/S)$

From the two equations we can make a single one. In this equation we will replace the expression of "$1/\rho$" by κ that is specific conductivity. In what units should we express specific conductivity?

$L = (1/\rho) \cdot (S/l) = (\kappa S)/l$ and $\kappa = (L \cdot l)/S$

According to the equation, κ should be measured in $S \cdot m/m^2$. We can cross out meters from this expression and leave just S/m. What is the sense of this definition for water

solutions? Imagine that electrodes are quadratic (1 meter per 1 meter), and that they are situated on a distance that is equal to 1 m. In this case the conductometer will measure the conductivity of exactly 1 cubic meter (m^3) of a solution. The intensity of continuous electric field must be equal to exactly 1 volt per meter.

The rate of movement of an ion in the electric field (ω) is defined as the distance (in meters) that an ion will travel during 1 second if the intensity of electric field is equal to 1 V/m and the distance between electrodes is 1 m. Different ions demonstrate different rates of movement. If we multiply the rate of movement for an ion by Faraday constant, we will calculate the mobility (U) of an ion. The rate of movement is measured in $m^2/(V \cdot sec)$, while ion mobility is measured in $(m^2 \cdot S)/mol$.

$U = F \cdot \omega$

Faraday constant is equal to the multiple of Avogadro's number and the elementary charge of one electron. In other words, Faraday constant is equal to the charge (measured in coulomb) of 1 mole of electrons.

F = 96485.33 C/mol

We can convert 1 coulomb (a unit of electric charge) into "(second·Volt)/Ohm", so the multiple of Faraday constant and the rate of the movement of an ion is really expressed in "$(m^2 \cdot S)/mol$".

As one can see in table 3.1, the most mobile cation in water solution is H^+. This unique property of H^+ is explained by its ability to travel through the solution by the way of the changing of water molecules that form H_3O^+ cation together with a proton. Water molecules are connected with each other by hydrogen bonds, as do H_3O^+ cations. Protons from these cations are connected to their own oxygen atom by covalent polar (dative) bonds, and to neighboring oxygen atoms by hydrogen bonds. Protons may "jump" from one oxygen to another: hydrogen bond appears in the place of covalent polar one, and covalent polar one appears in the place of hydrogen bond. This process acquires certain direction in the electric field. The most mobile anion is OH^-. However, it moves slower than H^+. Negatively charged oxygen from OH^- group and not just a proton should move through the water. Other cations and anions are moving much slower than H^+ and OH^- ions.

Among cations one can observe a clear trend: the higher the charge density on a cation, the slower its rate of movement. The charge density is the ratio between the charge and the radius of a cation. If the radii of two cations are identical, the one with the higher charge will be hydrated better, and its hydration radius will be larger. The larger the hydration radius (the higher the number of water molecules that hydrate a given cation), the slower the rate of its movement through the water (because of the big size of a moving particle). If charges of two cations are identical, the one with the higher radius will be more mobile in water solution, since it will have smaller charge density and smaller radius of hydration. In other words, if you move from top to bottom of the IA group from the Periodic Table (from lithium to rubidium), the mobility of cations will be increasing.

Mobility of anions show similar trends: the higher the charge, the higher the mobility; the lower the atomic radius for monoatomic anions, the higher the hydration radius, the lower the mobility (see F^-, Cl^- and Br^- in table 3.1). Notice that for I^- mobility is lower than that for Br^-. The mobility of ions in the electric field also depends on the charge density itself, and not just on the hydration radius. It is known that sulfate anions have large radius of hydration, and so their mobility demonstrates rather low level.

Table 3.1

The rate of movement and mobility of certain cations and anions in water solution

Cations	**$\omega \cdot 10^{-8}$, $m^2 \cdot V^{-1} \cdot sec^{-1}$**	**$U \cdot 10^{-4}$, $m^2 \cdot S \cdot mol^{-1}$**	**Anions**	**$\omega \cdot 10^{-8}$, $m^2 \cdot V^{-1} \cdot sec^{-1}$**	**$U \cdot 10^{-4}$, $m^2 \cdot S \cdot mol^{-1}$**
H^+	36.3	349.8	OH^-	20.6	199.2
Li^+	4.0	38.7	F^-	5.7	55.4
Na^+	5.2	50.3	Cl^-	7.9	76.3
K^+	7.6	73.5	Br^-	8.1	78.4
Rb^+	8.0	77.5	I^-	8.0	76.9
Cs^+	8.0	77.5	NO_3^-	7.4	71.5
NH_4^+	7.6	73.5	CH_3COO^-	4.2	40.9
Mg^{2+}	5.5	106.1	CO_3^{2-}	7.2	138.6
Al^{3+}	6.5	183.2	SO_4^{2-}	8.3	159.6

The higher the temperature, the lower the viscosity of a solvent, the lower the radius of hydration, and so the higher the mobility of ions. The increase in temperature also affects such processes as dissociation and association. The higher the temperature, the higher the constant of dissociation (and dissociation degree) for weak electrolytes, and the higher the coefficient of activity of ions from strong electrolytes.

Interestingly, anomalous conductivity of H^+ and OH^- ions is achieved only in water solutions. Other ions are also not so mobile in solvents with lower dielectric constant than that for water. Indeed, the lower the dielectric constant, the lower the constant of dissociation for an electrolyte. Another factor that determines the conductivity is the viscosity: in more viscous solvents mobility of all the ions becomes lower. It is known that the multiple of viscosity of a solvent and the mobility of an electrolyte is constant.

The dependence between the dilution and the specific conductivity has the ascending part and the descending part. Dilution is the value that is opposite to concentration ($V = 1/C$). So, for weak electrolytes the dependence is described by Ostwald's law ($\alpha \approx \sqrt{K_{diss}/C}$). First, specific conductivity is increasing because of the increase of the degree of dissociation, but sooner or later α reaches its maximal point (100 %). After that moment specific conductivity is decreasing because of the decrease of concentration of the completely dissociated electrolyte. For strong electrolytes the ascending part of the dependence between specific conductivity and dilution (figure 3.1) is explained by the increase of the factor of activity (f_a) because of the decrease of the ionic strength ($-\log f_a = 0.509 \cdot |Z^+ \cdot Z^-| \sqrt{I}$). One should remember that in solvents other than water

substances may demonstrate unexpected chemical properties: for example, they can form specific complexes that affect the dependence between concentration and electric conductivity of a solution.

Molar conductivity (λ_m) is the ratio between the specific conductivity and the molar concentration of a given electrolyte. Molar concentration in this case must be expressed in mol/m^3.

$\lambda_m = \kappa/C$

We can define molar conductivity as the conductivity of 1 m^3 of a solution that contains exactly 1 mole of a given electrolyte in a continuous electric field with the intensity of 1 V/m. It is interesting to highlight that the size of both electrodes must be quadratic and equal to 1 m per 1 m. Of course, there are no such electric conductometers. Because of this reason, each conductometer requires calibration with the aim to find out its specific constant. Actually, one should determine the conductivity (or the resistance) of a solution with known electric conductivity (or resistance) with a given conductometer. Then the ratio between the real conductivity and the number appeared on a screen of a conductometer will become a specific constant. To get the real conductivity of a solution one needs to multiply that machine-specific constant by the number from the screen.

The formula for the conversion of the rates of ion movement for cation and anion of a given weak electrolyte into molar conductivity of the solution of a corresponding salt is given below.

$\lambda_m = (F \cdot C \cdot \alpha(\omega_{cation} + \omega_{anion}))/C = F \cdot \alpha(\omega_{cation} + \omega_{anion}) = \alpha(U_{cation} + U_{anion})$

In the same manner, we use either the rates of ion movement, or mobilities of ions, to calculate the molar conductivity of the solution of a strong electrolyte.

$\lambda_m = (F \cdot C \cdot f_a(\omega_{cation} + \omega_{anion}))/C = F \cdot f_a(\omega_{cation} + \omega_{anion}) = f_a(U_{cation} + U_{anion})$

To use those two formulas written above one needs to know the values of the degree of dissociation (for weak electrolytes) or the factor of activity (for strong electrolytes).

If we dilute a given solution of weak electrolyte, its dissociation degree increases, and so the molar conductivity is growing. Then the value of α becomes equal to 100 % and molar electric conductivity does not show any dependence on the dilution anymore (see horizontal line in plots from figure 3.1). The maximal possible molar electric conductivity (limiting molar conductivity) is a constant value for a given electrolyte at a given temperature. In a similar manner, molar conductivity of a strong electrolyte is growing until the moment when the factor of activity reaches 100 %. Then molar conductivity (λ_m) will be equal to the maximal possible molar conductivity (λ^0_m) that is known as limiting molar conductivity (at the limit of the infinite dilution).

Each dependence represented in figure 3.1, *b* can be described by a following equation.

$\lambda_m = \lambda^0_m - K/\sqrt{V}$

In this equation K is an empiric constant, and V is the dilution. At an infinite dilution the value of "$K/\sqrt{V}$" becomes infinitely low.

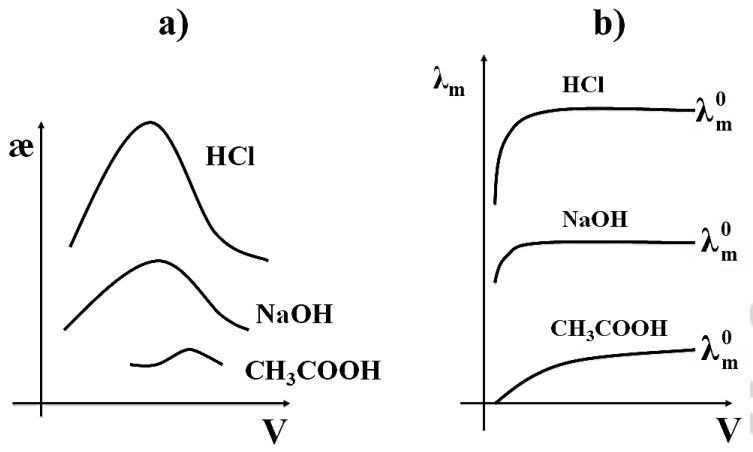

Figure 3.1. The dependence between specific conductivities (a) and molar conductivities (b) on the dilution for weak and strong electrolytes

According to Kohlrausch's law, at infinite dilution ions are not interacting with each other, and the limiting molar conductivity is equal to the sum of mobilities of ions.

$\lambda^0_m = U_{cation} + U_{anion}$

Using this equation we can calculate the degree of dissociation and the factor of activity for weak or strong electrolyte, respectively, at a given concentration.

$\alpha = \lambda_m/\lambda^0_m$ and $f_a = \lambda_m/\lambda^0_m$

Since $\alpha \approx \sqrt{K_{diss}/C}$, we can also find the constant of dissociation with the help of conductometry. The value of mobility for a given ion can be found in a specific handbook or in electronic data base. Frequently mobilities of ions are go under the names: limiting molar conductivity for a cation ($\lambda^0_{cation\ m}$) and limiting molar conductivity of an anion ($\lambda^0_{anion\ m}$).

Except the degree of dissociation and the constant of dissociation, one can estimate pH in the solution of a weak acid or base using conductometry. Actually, with this technique one can determine the dissociation degree. Then the concentration of H^+ ions is calculated with the help of known value of K_{diss} and converted into pH. Of course, it is possible to determine pH in this way in solutions with just a single acid or base.

One can also calculate the constant of solubility of hardly soluble electrolyte using conductometry. If we assume that the factor of activity for a given electrolyte is equal to 100 %, then the only factor that makes real molar conductivity lower then limiting molar conductivity is the solubility of electrolyte, and it can be calculated easily.

$\chi_{dissolved} = n_{dissolved} / n_{initial} = \lambda_m/\lambda^0_m$ and $\lambda_m = \kappa/C$

The combination of these two equation gives the following one.

$(n_{dissolved} \cdot C)/n_{initial} = \kappa/\lambda^0_m$

The left part of the equation is equal to the solubility (measured in mol/L). So, finally:

$S = \kappa / \lambda^0_m$

In the equations written above "C" means the concentration of electrolyte that would be achieved if the whole amount of that substance has been dissolved. If the solubility of

a given electrolyte is rather low, its specific conductivity may become comparable with the specific conductivity of water. In this case one should minus specific conductivity of water from the conductivity of a solution.

$$\kappa_{electrolyte} = \kappa_{solution} - \kappa_{water}$$

Specific conductivity of highly purified water is equal to $5.5 \cdot 10^{-6}$ S/m, or 0.055·μS/cm.

More information can be obtained from the conductometric titration. In this technique titrant is added to the vessel with a probe under the control of conductometer. After the addition of each drop of a titrant, conductivity is measured. If one titrates strong acid by strong base, then before the point of equivalence the conductivity is decreasing, and after the point of equivalence it is growing at a less steep slope (figure 3.2). If one titrates strong base by strong acid, then ascending part of a curve is steeper than the descending part. Indeed, the mobility of H^+ ions is higher than the mobility of OH^- ions.

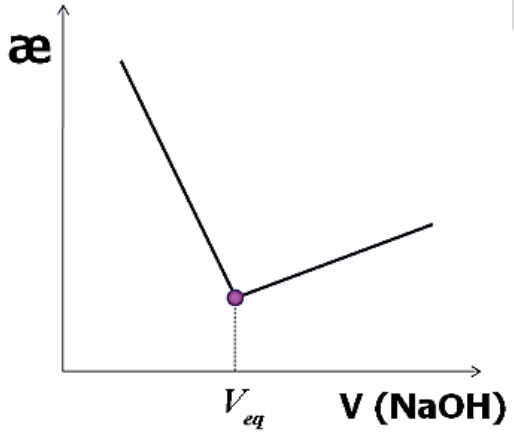

Figure 3.2. The curve of conductometric titration of a strong acid by a strong base

If one titrates weak base by strong acid, mobility of resulting cations and anions cannot be ignored. If base is rather weak, there will be no minimum on the titration curve, but just a point at which the slope of the dependence between the volume of added acid and conductivity becomes steeper. The same type of a plot is observed when one titrates weak acid by strong base (figure 3.3).

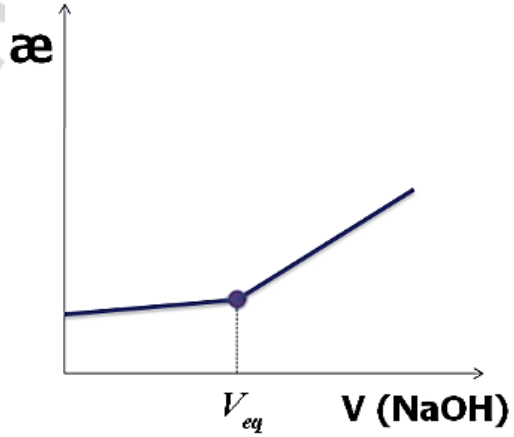

Figure 3.3. The curve of conductometric titration of a weak acid by a strong base

Another application of conductometric titration is in the detection of precipitation point. If one titrates salt of a weak base and strong acid (like $ZnSO_4$) by strong base, then after the growth of conductivity, it decreases until the point at which all zinc sulfate is converted into insoluble zinc hydroxide ($Zn(OH)_2$). After that point the conductivity is starting to grow again: zinc hydroxide reacts with the excess of strong base and forms soluble complex anions $[Zn(OH)_4]^{2-}$.

Conductometry may be used for indirect measurement of the rate of some biochemical reactions. For example, the products of the enzymatic hydrolysis of lipids are salts of fatty acids that increase specific conductivity of a solution. So, one can monitor the activity of lipase with the help of conductometer. The same technique can be used to monitor the activity of cholinesterase that hydrolyses acetylcholine into choline and acetic acid, that leads to the increase of specific conductivity of a solution.

In medicine and biology conductometry may be used with the aim to check the content of electrolytes in biological fluids (in blood plasma and serum, in gastric juice, in urine). Reography is a method that allows to monitor the blood flow in a given organ or muscle: the conductivity of tissues decreases when the blood flow through it decreases. That is how one can find evidences of thrombosis using conductometry. Moreover, one can measure the conductivity of a certain area of a body to monitor the process of local inflammation that causes the increase of the amount of liquid in tissues. The higher the amount of liquid, the better the conductivity. In the same manner one can approximately estimate the amount of fat tissue in an organism. The higher the amount of fat, the lower the conductivity (table 3.2).

Table 3.2

Specific conductivity of some organs and tissues

Biosubstrate	æ, S/m
Urine	2.00
Cerebrospinal fluid	1.80
Blood plasma	1.55
Gastric juice	1.15
Muscles	0.70
Whole blood	0.54
Neural tissue	$4 \cdot 10^{-2}$
Adipose tissue (fat)	$2 \cdot 10^{-2}$
Skin	$3 \cdot 10^{-4}$
Bones	$5 \cdot 10^{-7}$

Notice that neural tissue is a bad conductor of electricity, even though its function is to provide electric signals. The explanation is in the fact that axons of neurons are isolated by myelin coats. That is why nerve fibers are resistant to external electric field.

In pharmacy conductometric titration may be used in the quality control of weak acids (phenobarbital, sulfadimesine, thymol) and bases (caffeine, amydopirine), as well as salts if weak bases (dibazole, papaverine).

The quality of purified water can also be checked with the help of conductometry. For drinking water the level of specific conductivity varies from 50 to 500 μS/cm, while for purified water it should vary from 2 to 50 μS/cm.

Electrodes in conductometers are quite inert: usually they are made from platinum. So, metal ions are not getting into water solution. However, other electrodes participate in so-called electrode processes.

If metal electrode is omitted in a water solution that contains its own cation, two processes proceed simultaneously. Cations of a metal get from the piece of metal into the water solution, and cations from water solution get into the metal electrode. These processes exist in the state of equilibrium. The process of the transfer of metal cation into water solution can also be separated into two steps. First, water molecules cover the metal plate and enhance the ionization of metal atoms. Then, water molecules hydrate metal cations and newly formed hydrated cations get into the water solution. Initially there are both cations and neutral atoms in the metal plate, as well as common free electrons. In water solution the equilibrium between neutral atoms and cations is shifted towards cations (because of ionizing properties of water and the transfer of cations into water solution). Other products of this process (electrons) cannot get into water solution. So, the amount of free electrons is growing in a metal plate that has just been omitted into water. The surface of a metal electrode becomes negatively charged. Positively charged particles (cations of metal) are attracted to the negatively charged metal surface. That is how double electric layer is formed. Electrode potential is formed because of the existence of double electric layer. An electrode omitted into the solution of its own salt is called half-element. The scheme of such electrode is written in the following manner: $Me \mid Me^{n+}$. Vertical line symbolizes the border between two phases: in the solid phase there are metal atoms, while in the liquid phase there are metal cations.

If we connect two electrodes together by a wire, and if we connect two cells (two vessels with water solutions) by a salt bridge, electricity will start to circulate in a system. Electrons will travel through the wire from the more negatively charged electrode to the less negatively charged electrode, while anions will travel from the last one to the first one through the salt bridge. Salt bridge is necessary to complete the electric circle, and not to let the cations of more electronegative metal to be reduced directly on an opposite electrode. So, salt bridge may be represented by a tube with agarose and the solution of strong electrolyte that cannot react with electrodes and ions from corresponding solutions. We can measure the electromotion force (voltage) in this system with a voltmeter. The system itself produces electricity. Actually, it is nothing but a single cell of a battery also known as galvanic cell (chemical source of a direct electric current).

The values of electrode potentials for different electrodes are measured in a galvanic element with the standard hydrogen electrode. Hydrogen electrode is actually made of platinum. That peace of platinum is omitted into the 1M solution of HCl. Gaseous hydrogen

(H_2) is continuously passed through the solution at the atmospheric pressure at 298 K. Hydrogen has very low solubility in water, so it dissolves in platinum. Inside the platinum hydrogen exists in an atomic state: those atoms are small enough to get through the crystal lattice of platinum. On the surface between platinum and water some hydrogen atoms are ionized: an atom leaves an electron in the peace of platinum, and resulting proton protonates a water molecule. This process is balanced with an opposite one, when protons from H_3O^+ move from water to platinum and gain back their electrons. Schematically hydrogen electron is written like this: $(Pt)H_2 \mid 2H^+$, even though hydrogen is not molecular inside the platinum.

The potential of hydrogen electrode is taken as zero. If we connect another electrode to the standard one in a galvanic element with a voltmeter, we can measure the voltage of the redox reaction. Actually, that voltage shows us the value of Gibbs free energy for a given process. Let us consider a system made from zinc electrode and hydrogen electrode. The scheme of this system is written as follows: $Pt(H_2)|2H^+||Zn^{2+}|Zn$. Notice that an electrode that is oxidized is written in the right side of a scheme (according to the "right plus" rule). A double vertical line in the middle symbolizes a salt bridge.

Free energy of Gibbs is equal to the useful work of a process in isobaric and isothermic conditions, but with the negative sign. A useful work can be calculated from the electromotion force (EMF) between two electrodes (ΔE). The value of EMF should be multiplied by the Faraday constant (F) and the number of electrons lost by 1 mole of a substance (n). Indeed, the multiple of coulombs and volts gives us joules.

$-\Delta G = nF\Delta E$ and $\Delta G = -nF\Delta E$

Let us modify the combined equation of the first and the second law of thermodynamics with the help of our knowledge of the fact that entropy with a negative sign is the partial derivative of Gibbs energy per temperature ta the constant pressure.

$\Delta G = \Delta H - T\Delta S = \Delta H + T(\partial\Delta G/\partial T)_p$

$A'_{max} = -\Delta H + nFT(dE/dT)$

If the electromotive force of galvanic element is decreasing with the growth of temperature, the temperature coefficient (dE/dT) is lower than zero. In this case electric work has a lower value than the enthalpy, and the process is exothermic.

If the electromotive force of galvanic element is growing with the increase in temperature, the process is endothermic.

The heat effect of the work of galvanic element can be calculated from the same equation.

$nFE = -\Delta H + nFT(dE/dT)$

$\Delta H = -nF(E - TdE/dT)$

Free energy of Gibbs is equal to the sum of chemical potentials for all the components of a system. In this case for the zinc electrode (made from 1 mole of zinc atoms) we can write the following equation.

$\mu(Zn) = \mu(Zn^{2+}) + \mu(2e^-)$

Chemical potential of zinc cations is equal to the sum of their standard chemical potential and "RTlnC".

$\mu(Zn) = \mu^0(Zn^{2+}) + RT\ln[Zn^{2+}] + 2FE_1$

The same equation can be written for 1 mole of hydrogen.

$\mu(H_2) = \mu(2H^+) + \mu(2e^-)$

$\mu(H_2) = 2\mu^0(H^+) + RT\ln[H^+] + 2FE_2$

$2FE_2 - 2FE_1 = \mu(H_2) - 2\mu^0(H^+) - RT\ln[H^+] - \mu(Zn) + \mu^0(Zn^{2+}) + RT\ln[Zn^{2+}]$

Since the potential of a standard hydrogen electrode (E_2) is equal to zero, and the concentration of H^+ is equal to 1M, we can delete corresponding numbers from the equation.

$-2FE_1 = (\mu^0(Zn^{2+}) + \mu(H_2)) - (\mu(Zn) + 2\mu^0(H^+)) - RT\ln[Zn^{2+}]$

Now we have an expression that includes ΔG^0 of the process of oxidation of 1 mole of zinc by hydrogen cations (the difference between total chemical potentials for products and reactants).

$-2FE_1 = \Delta G^0 - RT\ln[Zn^{2+}]$ and $2FE_1 = -\Delta G^0 + RT\ln[Zn^{2+}]$

In the general way:

$-nFE = \Delta G^0 - RT\ln[Me^{n+}]$ and $nFE = -\Delta G^0 + RT\ln[Me^{n+}]$

If the concentration of zinc cations is equal to 1M, the expression that gives us the value of ΔG from the value of ΔE will be derived: $\Delta G = -nF\Delta E$. However, if the concentration of zinc cations is not equal to zero, the value of electrode potential will be different. Let us divide both parts of the equation by nF.

$E = -\Delta G^0/(nF) + (RT/nF)\ln[Me^{n+}]$

The value of $-\Delta G^0$ divided by Faraday number and the number of electrons participated in the reaction is equal to the standard potential of a given electrode φMe^{n+}. The resulting equation (Nernst equation) relates the exact electrode potential and the concentration of corresponding (potential determining) cations in the solution around the electrode.

$E = \varphi(Me^{n+}) = \varphi^0(Me^{n+}) + (RT/nF)\ln[Me^{n+}]$

If one prefers to use decimal logarithm instead of natural one, the equation may be re-written using the value of R and standard temperature. So, "RT/F" is equal to 0.059.

$\varphi(Me^{n+}) = \varphi^0(Me^{n+}) + (0.059/n)\log[Me^{n+}]$

Exactly for zinc electrode the standard potential is equal to –0.76 V. If the concentration of potential determining cations is higher than 1M, the number under the logarithm is positive, and the potential is getting closer to zero. Physically, high concentration of cations in the solution prevents ionization of zinc atoms, and makes the module of the negative charge of the electrode lower: the excess of electrodes in zinc electrode becomes low. In contrast, if the concentration of zinc cations in solution is very low, the number under the logarithm becomes negative, and the resulting potential of zinc electrode becomes rather negative: zinc atoms are getting in the solution fast and produce a big excess of electrons in the metal electrode.

If we connect zinc electrode with standard hydrogen electrode, we should minus zinc electrode potential from the hydrogen electrode potential: 0 – (–0.76) = 0.76 V. So, the process of the electron transfer from zinc to hydrogen in standard conditions is spontaneous: EMF is higher than zero, and so ΔG is lower than zero.

If we arrange standard electrode potentials for all the metals in a single row, then familiar series of metal activity will be achieved. In this line metals that stand before hydrogen can react with acids (because ΔG of the electron transfer from metal to hydrogen cation is negative), while those situated after hydrogen cannot react with acids (since ΔG of this process is positive).

Hydrogen electrode may theoretically be used for the measurement of pH in the solution, since its potential depends on the concentration of H^+ in a solution.

$\varphi(H^+) = \varphi^0(H^+) + (RT/nF)\ln[H^+]$

Since the standard potential of hydrogen electrode is equal to zero, n=1, and $pH= -\log[H^+]$ we can re-write this equation.

$\varphi(H^+) = -0.059\ pH$ and $pH = -\varphi(H^+)/0.059$

Hydrogen standard electrode requires the supply of gaseous hydrogen that makes pH determination with the help of that electrode rather complicated and expensive. Usually a pair of silver chloride and glass electrode is used for the measurement of pH.

Electrodes are classified into reversible and irreversible. Reversible ones are subdivided into electrodes of the first and the second order. Electrodes of the first order are reversible only in the respect of a cation. That kind of electrode has already been described by us in a sample of zinc electrode. Electrodes of the second order are reversible in the respect of both cation and anion, since they are made from metal covered by its own hardly soluble salt omitted in the solution containing anion of that salt. The most popular electrode of the second order is silver chloride electrode. That electrode is usually used as a standard one in pair with the glass electrode. The last one is sensitive to the concentration of H^+ cations in a solution. Once again, to measure the concentration of certain ions in a solution one needs a system made from two electrodes omitted in the solution. One of those electrodes is sensitive to the concentration of ions of interest (the electrode used for the measurement) and the second one is not (the electrode used for the comparison). The electromotive force in that system depends on the concentration of certain ions and on the temperature of a system. That is why thermometer is also included in each pH-meter.

The scheme of the silver chloride electrode is Ag, AgCl │ KCl. The redox process is as follows: $Ag \leftrightarrow Ag^+ + e^-$. Notice that this process leads to the production of Ag^+ cations in the solution. So, the potential of silver chloride electrode should depend on the concentration of silver cations in the solution.

$\varphi(Ag^+) = \varphi^0(Ag^+) + (RT/nF)\ln[Ag^+]$

The concentration of Ag^+ cations in the solution is determined by the concentration of Cl^- anions through the solubility product equation.

$K_{sp} = [Ag^+]\cdot[Cl^-]$ and $[Ag^+] = K_{sp}/[Cl^-]$

Saturated solution of KCl is used to fill in the cell of silver chloride electrode, so the concentration of Ag^+ in that solution is very low. Now we can replace the concentration of Ag^+ ions by the resulting expression with $[Cl^-]$ and K_{sp}.

$\varphi(Ag^+) = \varphi^0(Ag^+) + (RT/nF)\ln(K_{sp}/[Cl^-])$

Modifications of this equation give us another one.

$\varphi(Ag^+) = \varphi^0(Ag^+) + (RT/nF)\ln K_{sp} - (RT/nF)\ln[Cl^-]$

At standard temperature the potential of Ag^+ electrode is a constant, as well as the solubility product of AgCl. So, we can simplify the equation for standard temperature.

$\varphi AgCl = 0.222 - 0.059\log[Cl^-]$

Finally, the potential of silver chloride electrode at 298 K depends on the concentration of chloride anions only. The higher the amount of Cl^- anions, the lower the amount of Ag^+ cations, and the lower the value of the electrode potential. Do not forget that the standard value of silver electrode potential is +0.8 V. So, with the increase of Cl^- concentration it is getting closer to zero.

The scheme of the glass electrode is as follows: $Ag\,|\,AgCl,\ Cl^-\,|\,glass\,|\,H^+$. The electrode is made from silver wire covered by AgCl situated in a glass tube with HCl or KCl solution. The bulb of the electrode is made from a specific glass that is covered by silica gel. Cations of sodium in that silica gel are mobile: they can be exchanged by H^+ cations from water solution. The process of the exchange of Na^+ and H^+ cations in the silica gel influences the electrode potential of the outer part of the glass. Total potential of the glass electrode is a sum of the potential of silver chloride electrode, the potential of the inner part of glass, and the potential of the outer part of glass.

$\varphi_{glass} = \varphi(Ag^+) + \varphi_{inner\ glass} + \varphi_{outer\ glass}$

$\varphi_{outer\ glass} = \varphi^0_{outer\ galss} + (RT/nF)\ln[H^+]$

If we assume that potentials of inner silver chloride electrode and inner glass surface are constant, as well as the standard potential of outer glass surface, we will be able to simplify the equation with a single constant K.

$\varphi_{glass} = K + (RT/nF)\ln[H^+] = K + 0.059\log[H^+]$

In a system made from silver chloride electrode and glass electrode we can calculate the electromotive force as a function of H^+ activity in a solution.

$E = \varphi(AgCl) - \varphi_{glass} = \varphi(AgCl) - K - 0.059\log[H^+]$

Since $pH = -\log[H^+]$, we can modify the equation.

$pH = (E - \varphi(AgCl) + K)/0.059 = (E - X)/0.059$

The value of X in the equation must be constant at a given temperature. That value is determined by the potential of the individual AgCl electrode, the potential of the AgCl electrode situated inside the glass electrode, and the potential of the inner surface of glass and the standard potential of the outer glass surface. In case if both AgCl electrodes are identical, they give the same potential at any temperature, and the difference between them

is equal to zero. It means that in ideal pH-meter the value of X depends on the nature of glass from the glass electrode. Anyway, the potential of glass electrode depends on temperature, that is considered in calculations.

Before the usage each pH-meter must be calibrated with at least two solutions of known pH. The dependence between the pH and the EMF is linear from –1 to 12.

Using pH-meter one may measure pH in different solutions (including colored and turbid ones). Moreover, one can perform acid-base titration under the control of pH-meter (instead of indicator). This technique goes under the name potentiometric titration together with similar approaches that combine potentiometry and titration.

To measure the EMF in a galvanic element one should minus the potential of one electrode from the potential of another electrode, starting from the more positive one. For an element made from copper and zinc we should follow the equation written below.

$E = \varphi(Cu^{2+}) - \varphi(Zn^{2+})$

$E = \varphi^0(Cu^{2+}) + (RT/nF)\ln[Cu^{2+}] - \varphi^0(Zn^{2+}) - (RT/nF)\ln[Zn^{2+}]$

$E = \varphi^0(Cu^{2+}) - \varphi^0(Zn^{2+}) + (RT/nF)\ln([Cu^{2+}]/[Zn^{2+}])$

As the process goes on, the activity of Cu^{2+} is decreasing, while the activity of Zn^{2+} is increasing. The process will stop when either zinc electrode will be completely dissolved, or the cations of Cu^{2+} in the solution will be over.

Galvanic element may also be composed of two identical electrodes omitted in solutions with different concentrations of the same salt. For example, for concentration galvanic cell made from two silver electrodes we can write the following.

$E = \varphi^0(Ag^+) + (RT/nF)\ln a_2(Ag^+) - \varphi^0(Ag^+) - (RT/nF)\ln a_1(Ag^+)$

$E = (RT/nF)\ln(a_2(Ag^+)/a_1(Ag^+))$

The process is spontaneous only if the activity of Ag^+ in the second solution is higher than its activity in the first solution ($a_2(Ag^+) > a_1(Ag^+)$). So, silver electrode omitted in the first solution is more negative than silver electrode omitted in the second solution: electrons are moving from the first to the second electrode. As the process proceeds, the concentration of Ag^+ in the second solution is decreasing, as cations are moving inside the silver plate and catch electrons. The concentration of Ag^+ in the first solution is, in contrast, growing, since silver atoms are losing their electrons and cations of silver are moving in the solution. Once the concentrations of Ag^+ in both solutions are identical, the EMF becomes equal to zero.

Another type of galvanic element is made from two inert electrodes. The first electrode is omitted in a solution of oxidizer, while the second one is omitted in a solution of reducer. That is how redox reaction can be used to produce some electricity. If we perform such redox process in separate cells, we can measure its ΔG as the function of EMF. For example, the first electrode is omitted in the solution of $FeCl_3$, while the second one is omitted in the solution of KI. Fe^{3+} ions can be adsorbed on a platinum electrode and gain electrons from that piece of metal and turn to Fe^{2+}. In another cell I^- ions can be adsorbed on

a platinum electrode and lose their electrons turning into I_2. Through the outer circuit (the wire) electrons from I^- will be delivered to Fe^{3+}. Is this process spontaneous? It depends on concentrations of reduced and oxidized forms in both cells, as well as on standard redox potentials of substances from both cells.

Standard redox potential for each pair of reducer and oxidizer (for example, for I_2 and I^-) is measured in a galvanic element with the standard hydrogen electrode. Concentrations of reduced (I^-) and oxidized (I_2) forms must be equal to 1 mol/L. For I^- and I_2 the equation is as follows.

$\varphi(I_2/2I^-) = \varphi^0(I_2/2I^-) + (RT/nF)\ln([I_2]/[I^-]^2)$

For the cell with Fe^{3+} and Fe^{2+} the Nernst–Peters equation is given below.

$\varphi(Fe^{3+}/Fe^{2+}) = \varphi^0(Fe^{3+}/Fe^{2+}) + (RT/nF)\ln([Fe^{3+}]/[Fe^{2+}])$

The EMF in that system is equal to the difference between potentials of two electrodes.

$E = \varphi(Fe^{3+}/Fe^{2+}) - \varphi(I_2/2I^-)$

$E = \varphi^0(Fe^{3+}/Fe^{2+}) + (RT/nF)\ln([Fe^{3+}]/[Fe^{2+}]) - \varphi^0(I_2/2I^-) - (RT/nF)\ln([I_2]/[I^-]^2)$

$E = (\varphi^0(Fe^{3+}/Fe^{2+}) - \varphi^0(I_2/2I^-)) + (RT/nF)\ln([Fe^{3+}]/[Fe^{2+}]) - (RT/nF)\ln([I_2]/[I^-]^2)$

$E = +0.77 - 0.54 + (RT/nF)\ln([Fe^{3+}]/[Fe^{2+}]) - (RT/nF)\ln([I_2]/[I^-]^2)$

When concentrations of all participating species are equal to 1 mol/L this process is spontaneous. In general, the higher the amounts of Fe^{2+} and I^-, and the lower the amounts of Fe^{3+} and I_2, the higher the EMF. Theoretically, when the difference between two standard redox potentials is not very high, we may turn the process to the backward direction if we use the excess of oxidizer from the pair with lower standard potential, and the excess of reducer from the pair with higher standard potential. In general, redox reactions proceed in the direction from stronger oxidizer and stronger reducer towards weaker oxidizer and weaker reducer.

Notice that under the logarithm we use powers upon concentrations that come from half reactions. So, for $KMnO_4$ in acidic medium the redox potential is as follows.

$\varphi(MnO_4^-/Mn^{2+}) = \varphi^0(MnO_4^-/Mn^{2+}) + (RT/nF)\ln([MnO_4^-]\cdot[H^+]^8/[Mn^{2+}])$

According to the equation written above, the redox potential (and so the oxidizing properties) of $KMnO_4$ strongly depends on the concentration of H^+ ions in a solution (on pH).

Standard redox potentials are available in numerous chemistry handbooks and in data bases. Using those values one can estimate the direction of a redox reaction in standard conditions (when concentrations of all participating species are equal to 1 mol/L). To find out how the given redox reaction proceeds at different concentrations one should use Nernst–Peters equation. In the general form it is written like this.

$\varphi_{redox} = \varphi^0_{redox} + (RT/nF)\ln(a_{oxidizer}/a_{reducer})$

Since $\Delta G^0 = -nFE$, one can calculate the exact value of ΔG^0 for a given redox reaction using the value of electromotive force (E). Since $\Delta G^0 = -RT\ln K_{eq}$, one can continue and find the exact constant of equilibrium for a given redox reaction.

Taken together,

$\ln K_{eq} = (nFE)/(RT)$

Using Nernst–Peters equation one can measure so-called redox potential in a solution of an unknown content. Platinum electrode used for the measurement must be connected to another one that has stable potential (usually to the silver chloride electrode). In this way one can say whether the medium is enriched by oxidizers or by reducers. Such integral characteristic as redox potential is useful for biological systems. For example, in the medium enriched by oxidizers –SH groups of cysteine will lose their protons and form disulfide bonds. In the excess of reducers disulfide bonds will be broken, and sulfur atoms will be protonated.

Problems

1. Calculate the molar concentration of HCl solution if the specific electric conductivity of the solution is 0.277 $S \cdot m^{-1}$ and the molar electric conductivity is $1.385 \cdot 10^{-2}$ $S \cdot m^2 \cdot mole^{-1}$.

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2. Molar electric conductivity of 0.1 M CH_3COOH solution at 298K is $5.2 \cdot 10^{-2}$ $S \cdot m^2 \cdot mol^{-1}$. Calculate the dissociation constant of CH_3COOH solution and its pH.

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3. Determine the molar electric conductivity of 0.1 M $AgNO_3$ solution at 298K if its specific electric conductivity is 1.097 $S \cdot m^{-1}$.

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4. Calculate the molar electric conductivity of potassium iodide at the infinite dilution (λ_m^0) and at 298K if we know that potassium cation mobility is $73.5 \cdot 10^{-4}$ $S \cdot m^2 \cdot mol^{-1}$ and iodide anion mobility is $76.9 \cdot 10^{-4}$ $S \cdot m^2 \cdot mol^{-1}$.

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5. Determine the degree and the constant of dissociation of 0.01 M NH_4OH solution at 298K if the molar electric conductivity of this solution is $11.2 \cdot 10^{-4}$ $S \cdot m^2 \cdot mol^{-1}$·and the limiting molar electric conductivity is $271.2 \cdot 10^{-4}$ $S \cdot m^2 \cdot mol^{-1}$.

6. Specific electric conductivity of 0.02 M KCl solution at 298K is 0.277 $S \cdot m^{-1}$ and its resistance is 431.8 Ohm. Calculate the specific electric conductivity of the acetic acid solution if its resistance in the same vessel is 750 Ohm.

7. The specific electrical conductivity of 0.135 M propanoic acid solution is $4.79 \cdot 10^{-2}$ $S \cdot m^{-1}$. Calculate the equivalent electrical conductivity of the solution, the dissociation constant of the acid and pH of the solution if the limiting mobilities of the H^+ and $C_2H_5COO^-$ ions are 349.8 and 37.2 $S \cdot cm^2 \cdot mol^{-1}$, respectively.

8. The specific electrical conductivity of 0.05 M KCl solution at 298 K is 0.358 $S \cdot m^{-1}$, and its resistance is 432.8 Ohm. Calculate the electrical conductivity of the acetic acid solution if the resistance of the acetic acid solution in the same vessel is 680 Ohm.

Standard potentials of metal electrodes in aqueous solutions

K^+/K	Ca^{2+}/Ca	Na^+/Na	Mg^{2+}/Mg	Al^{3+}/Al	Mn^{2+}/Mn	Zn^{2+}/Zn	Fe^{2+}/Fe	Cd^{2+}/Cd
-2,92	*-2,87*	*-2,71*	*-2,36*	*-1,66*	*-1,18*	*-0,76*	*-0,44*	*-0,40*
Ni^{2+}/Ni	Sn^{2+}/Sn	Pb^{2+}/Pb	$2H^+/H_2$	Cu^{2+}/Cu	Hg^{2+}/Hg	Ag^+/Ag	Pt^{2+}/Pt	Au^{3+}/Au
-0,25	*-0,14*	*-0,13*	*0*	*+0,34*	*+0,79*	*+0,80*	*+1,19*	*+1,50*

9. Determine the equilibrium constant of the reaction $Cu^{2+} + Zn \leftrightarrows Zn^{2+} + Cu$, using the values of the standard electrode potentials $E^0(Cu^{2+}/Cu)$ and $E^0(Zn^{2+}/Zn)$.

10. EMF of the galvanic cell $Cd|CdCl_2||AgCl|Ag$ at 298 K is 0.675 V, and the temperature coefficient of the EMF of this element is $-6 \cdot 10^{-4}$ V/K. Write the equation of the reaction that proceeds in this galvanic element, and calculate ΔG, ΔS, ΔH for this reaction at 298 K.

11. Calculate the solubility constant $K_s(AgI)$ at 298 K, if the electrode potential of a silver electrode immersed in a saturated AgI solution is 0.325 V and $E^0(Ag/Ag^+) = 0.799$ V.

12. Determine the equilibrium constant of the reaction expressed by the equation: $KMnO_4 + 5FeCl_2 + 8HCl \leftrightarrows MnCl_2 + KCl + 5FeCl_3 + 4H_2O$, if the standard electrode potentials of the processes $Fe^{3+} + e \rightarrow Fe^{2+}$ and $MnO^{4-} + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$ are 0.77 and 1.52 V, respectively.

13. Calculate the maximal work of the reaction $Zn + CuSO_4 = ZnSO_4 + Cu$ if the EMF of the cell of $Cu \mid 1M\ CuSO_4 \| 1M\ ZnSO_4 \mid Zn$ at 298K is equal to 1.1 V.

14. Calculate the equilibrium constant of the reaction: $4FeCl_2 + O_2 + 4HCl \leftrightarrows 4FeCl_3 + 2H_2O$ if $E^0((Pt)\ FeCl_3, FeCl_2) = +0.77$ V, $E^0\ ((Pt)\ O_2, 4\ H^+ \mid 2H_2O) = +1.23$ V.

CHAPTER 4
THERMODYNAMICS OF SURFACE PHENOMENA

Main topics of the chapter:

1. *Surface tension.*
2. *Wetting.*
3. *Surface activity.*
4. *Adsorption.*
5. *ELISA.*
6. *Chromatography.*

Adsorption is the process of the accumulation of a substance on the surface of phase contact. In contrast, absorption is the process of the accumulation of a substance inside the phase. The term absorption is also used to characterize the ability of a substance to interact with radiation of a certain wavelength. There may be two types of the surface of the phase contact: mobile surface (between liquid and gas, between two liquids), and immobile surface (between solid and gas, between solid and liquid, between two solids).

In general, on the surface of phase contact particles are under the influence of different forces of attraction from particles of one phase and particles from another phase. Inside a phase each particle is under the influence of same forces of attraction from different directions. The larger the area of surface between two phases, the higher the free energy of particles on that surface. Any system tends to minimize its free energy. Because of this reason drops of each liquid are as spherical as it is possible: that is how the ratio between volume and the surface area becomes minimal. Surface tension (σ) is the partial derivative of Gibbs energy per surface area.

$\sigma = (dG/dS)_{T,p,ni}$

Surface tension shows how free energy (surface energy) changes with the growth of surface area. The higher the surface tension, the steeper the surface energy is growing with the increase of surface area. The units of surface tension are J/m^2. Since Joule is equal to Newton multiplied by meter, another unit in which surface tension can be expressed is N/m. Liquids with high surface tension (like water) form large drops, while liquids with low surface tension form small drops. Indeed, the surface area for a single drop is much smaller than the surface area for two drops of the same volume.

When drops are falling down from a capillary, we can calculate their mass using the following formula.

$m_{drop} \approx 2\pi\sigma_{liquid}r_{capillary}$

The higher the surface tension, the higher the mass (and the larger the volume) of a single drop of a given liquid. Also, the smaller the radius of a capillary, the lower the mass (and the smaller the volume) of a given liquid. If we use the same capillary, the mass (and the volume) of a drop becomes a function of surface tension only. The higher the mass of

a single drop, the lower the number of drops resulting from the same volume of a liquid. So, the easiest way to calculate the surface tension of one liquid is to compare the number of drops resulting from the same volume for it with the corresponding number for a liquid with known surface tension. A special vessel used in this comparison is called stalagmometer.

$\sigma(X) = \sigma(H_2O) \cdot (n(H_2O)/n(X))$

In this formula n is the number of drops dropping down from the same stalagmometer. That kind of formula works relatively good if the density of a tested liquid is approximately the same as the density of water. If the difference between densities cannot be ignored, one should use corrected formula with the ratio between the density of a tested liquid and the density of water.

$\sigma(X) = \sigma(H_2O) \cdot (n(H_2O)/n(X)) \cdot (\rho(X)/\rho(H_2O))$

As we know, the volume is the ratio between the mass and the density. So, the higher the density, the lower the volume of a certain mass of liquid, the higher the number of drops at the same surface tension.

Another way to estimate the surface tension is to measure the pressure that is needed to push a bubble of the air through the capillary filled with a given liquid. The formula used in this kind of calculation relies on the direct dependence between the pressure one needs to apply to push the bubble through (p) and the surface tension of a liquid (σ), the coefficient of proportionality in this equation is the half of the radius (r) of a capillary.

$\sigma = p \cdot (r/2)$

Surface tension is determined by the properties of a liquid, namely, by the strength and the nature of bonds between the particles of a liquid, as well as on such external parameters, as temperature and pressure. Logically, the higher the temperature, the weaker the bonds between molecules, the closer this liquid to its boiling point. So, surface tension decreases with the growth of temperature. The higher the external pressure, the higher the temperature of boiling. So, surface tension increases with the growth of external pressure.

From the point of view of thermodynamics, Gibbs energy per 1 meter of a surface (surface energy) is equal to the surface enthalpy minus the product of surface entropy and temperature.

$G_{surface} = H_{surface} - T \cdot S_{surface}$

Surface entropy means the increase in entropy due to the increase of a surface that is equal to 1 square meter. This value is always positive, since the disorder in a system is increasing because of such process. Surface enthalpy is the amount of energy required to form 1 square meter of a surface in isobaric and isochoric conditions. This value is positive, since some bonds between particles of a liquid must be broken to form a surface. Now we can convert the equation into the differential form.

$dG_{surface} = dH_{surface} - TdS_{surface} - S_{surface}dT$

We can divide both parts of the equation by dT and see that with the growth of temperature surface tension is really decreasing. Indeed, the temperature coefficient of

surface tension ($dH_{surface}/dT$) has a negative sign, since the process is endothermic, as well as the sign of $dS_{surface}/dT$. At certain temperature the result of the equation written below turns to zero. This temperature is known as the critical temperature, at which a liquid loses its surface tension and becomes undistinguishable from gas.

$dG_{surface}/dT = d\sigma/dT = dH_{surface}/dT - TdS_{surface}/dT - S_{surface}$

Surface energy exists both in liquids and in solids. The difference in surface energies of solid and liquid determines whether a drop of liquid will wet the surface of solid. Spreading parameter (S) is equal to the difference between the surface energy of the solid and the surface energy of the liquid, as well as the interfacial energy between the solid and the liquid.

$S = G_{s\ solid} - G_{s\ liquid} - G_{s\ solid\text{-}liquid}$

If S is lower than zero, the liquid partially wets the solid. If S is higher than zero, the liquid wets the solid surface completely.

Contact angle (θ) is the angle between the solid-gas interface and the liquid-gas interface (figure 4.1). If this angle is lower than 90°, the liquid wets the solid surface good (high wetting). Complete wetting happens when the drop is spread through the surface and θ becomes equal to 0°. If the wetting angle is higher than 90°, then the liquid does not wet the surface well (low wetting). If the contact angle is equal to 180°, the liquid does not wet the surface at all: drops are “rolling” on a surface. Surfaces with contact angles higher than 150 °C for drops of water are considered super-hydrophobic.

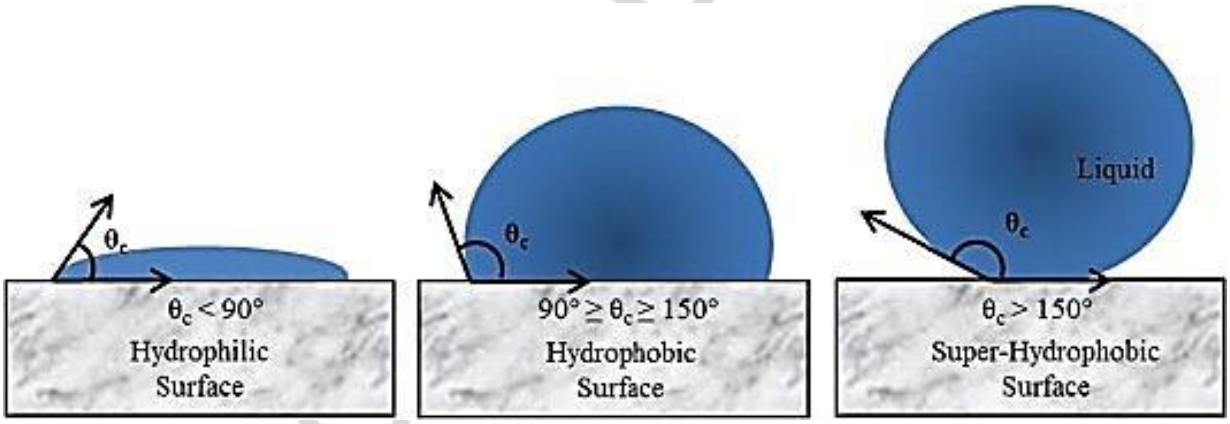


Figure 4.1. Schematic representation of contact angles for drops of water on different surfaces

Young equation shows how cosθ depends on surface tensions between solid and gas ($\sigma_{s\text{-}g}$), liquid and gas ($\sigma_{l\text{-}g}$) and solid and liquid ($\sigma_{s\text{-}l}$).

$\cos\theta = (\sigma_{s\text{-}g} - \sigma_{s\text{-}l})/\sigma_{l\text{-}g}$

As the system tends to decrease its free energy, the process of wetting is favorable if the surface tension between solid and gas is higher than the surface tension between solid and liquid: free energy is decreasing because of the wetting, cosθ is positive, the angle is lower than 90°. If the surface tension between solid and liquid is higher than that between solid and gas, the wetting is not decreasing the overall free energy, cosθ is negative, and the angle is higher than 90°. To allow the complete wetting, the surface tension between

liquid and gas must be equal to the difference in surface tensions between solid and gas and between solid and liquid.

Using the contact angle one can measure the affinity of a liquid to solid surface. If we use water as liquid, then it will wet hydrophilic surfaces, and it will not wet hydrophobic substances. Surface energy (tension) of solid substances held together by strong bonds (ionic bonds or covalent polar bonds) is usually much higher than surface energy (tension) of solid substances held together by weak bonds (or van der Waals forces). From the Young equation, one can predict that solid organic substances are wetting worse than solid ionic inorganic substances. However, the surface tension between the solid and the liquid also matters, and it depends on the affinity between them.

To measure the coefficient of hydrophilicity one may use the ratio between the enthalpies of wetting by water and by a hydrocarbon (for example, by hexane or by benzene). If the enthalpy of wetting by water is more negative than that by a hydrocarbon, a solid surface is rather hydrophilic, and the coefficient of hydrophilicity is higher than 1. If a surface is rather hydrophobic, its wetting by hydrophobic liquid will produce much more heat than its wetting by hydrophilic liquid, and the coefficient of hydrophilicity will be lower than 1.

The enthalpy of wetting usually means the enthalpy of complete immersion. The enthalpy of immersion is the difference in surface enthalpy of the surface of solid substance in contact with a gas, and surface enthalpy of the same solid surface in contact with a liquid, multiplied by the area of surface contact between solid and liquid (by the surface of a solid substance).

$\Delta H_{wetting} = (H_{s\ solid\text{-}gas} - H_{s\ solid\text{-}liquid}) \cdot S_{surface}$

The enthalpy of wetting may be related to the mass of a solid substance, and in this case it becomes the specific enthalpy of wetting. In more generalized way, the enthalpy of wetting is equal to the difference between the enthalpy of a system made from liquid and solid body completely immersed inside it, and the sum of enthalpies of the same amount of liquid and the same amount of solid taken separately from each other. Since it is hard to perform such experiment in vacuum, the air is included in the above written equation. If interactions are possible on the surface of solid only, then we can use just surface enthalpies.

The value of surface tension of a solvent depends on the nature of solute(s). We can divide substances into 3 groups depending on their effect on surface tension: surface active substances (SAS) that decrease the surface tension, surface inactive substances (SIS) that increase the surface tension, and surface nonactive substances (SNS) that have no effect on surface tension.

Molecules of surface active substances are composed of hydrophobic and hydrophilic parts. Hydrophobic part is made of hydrocarbon backbone (a nonpolar tail), while hydrophilic part contains atoms of oxygen, nitrogen, sulfur and phosphorus (a polar head).

Typical samples are alcohols, carboxylic acids, esters, amines, salts of fatty acids (soap), aldehydes. In water solutions molecules of SAS are tend to group on a surface of contact between the liquid and the air. Hydrophilic heads are immersed in water, while hydrophobic tails are outside.

Surface inactive substances are represented by hydrophilic compounds like salts of inorganic acids, inorganic acids themselves and bases. Smallest hydrophilic organic compounds (for example, glycine) also behave like SIS. Surface inactive compounds are (almost) completely hydrated, and so they tend to stay inside the layer of water, and not on its surface.

Surface nonactive substances (SNS) are distributed almost equivalently both inside the layer of water and on its surface. Such compounds are represented by polyatomic alcohols and carbohydrates (sugars).

Surface active molecules may demonstrate higher or lower surface activity. So, there is a need to compare their abilities to decrease surface tension. Surface activity (g) is the derivative of surface tension per concentration with a negative sign.

$g = -d\sigma/dC$

In figure 4.2 one can see isotherms of the dependence between surface tension of SIS, SNS and SAS on the concentration. The higher the concentration of SIS, the higher the surface tension. The higher the concentration of SAS, the lower the surface tension: the derivative of this dependence ($d\sigma/dC$) is negative. But we want to refer to the surface activity as to the positive value. That is why there is a minus before the above mentioned derivative. The isotherm of surface tension for a solution of SNS is a line that is parallel to X axis.

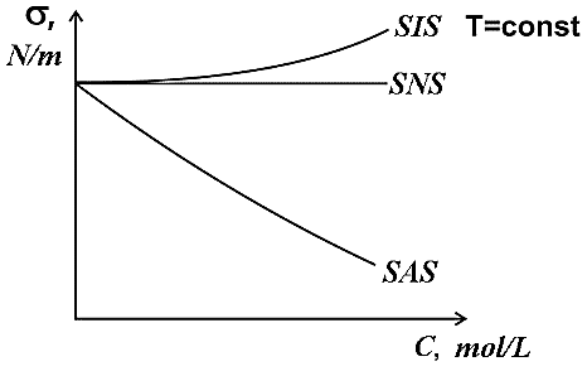


Figure 4.2. Schematic isotherms of surface tension for surface inactive (SIS), surface nonactive (SNS), and surface active substances (SAS)

To calculate the adsorption (surface excess concentration) from the concentration of a substance inside a solution one should use Gibbs equation (Gibbs isotherm of adsorption). To derive this equation one may start from the statement that the spontaneous adsorption of a substance on the surface of a liquid decreases the Gibbs energy until the establishment of equilibrium. At this moment $dG = 0$. To calculate dG one may consider the sum of dG of each of the phases (that is eliminated) and dG of the surface between them. To calculate dG

of the surface one should make a sum between the product of the area of contact between phases and the differential of surface tension "Sdσ", and the product of the amount of substance adsorbed on a surface and the differential of its chemical potential "ndμ". Since the sum is equal to zero, we can rearrange the equation.

$nd\mu = -Sd\sigma$

This equation works for a solution with just a single solute in case if a system does not produce any mechanical work. If we divide both parts of the equation by the area of surface, in the left part there will be a new variable that is called "adsorption" or "surface excess concentration" (Γ) that is equal to the number of moles of adsorbed substance over the area of surface contact.

$nd\mu/S = -d\sigma \qquad \Gamma d\mu = -d\sigma$

Since in the state of equilibrium chemical potential of a substance inside the liquid is equal to the chemical potential of a substance in the surface, we can substitute dμ by the differential of chemical potential of the same substance but inside the solution.

$\mu = \mu^0 + RT\ln C$ and $d\mu = RTd\ln C$

So, the substitution gives a new equation.

$\Gamma RTd\ln C = -d\sigma$ and $\Gamma = (-1/RT)\cdot(d\sigma/d\ln C)$

This equation can be further modified to bring the concentration itself back. Since $d\ln C = C/dC$, and "$-d\sigma/dC = g$", we can continue.

$\Gamma = (-C/RT)\cdot(d\sigma/dC)$ and $\Gamma = g\cdot(C/RT)$

These two last forms of the Gibbs isotherm equation bring some sense into the relationships between concentration and adsorption. The higher the concentration of a substance with positive surface activity (g) in the solution, the higher its adsorption on the surface of a liquid. The higher the temperature, the lower the adsorption of SAS. If we deal with SIS ($g < 0$), the situation is opposite: the higher the concentration and the lower the temperature, the lower the adsorption of such substance on a surface.

For organic surfactants an empiric rule has once been found: with the increase of the length of an aliphatic chain by one $-CH_2-$ group, the value of surface activity (g) becomes 3 times higher. This rule should be corrected for different types of organic substances. The equation of Shyshkowsky uses a specific constant for a given set of homologs (B) and nonspecific constant (A) that becomes 3 times higher for each additional $-CH_2-$ group (for the first one it is equal to 1).

$\sigma = \sigma^0 - B\cdot\ln(1+A\cdot C)$

In this equation σ^0 is the surface tension of a solvent, and C is the concentration of a solute. The constant for a given set of homologs depends on the value of a maximal possible adsorption Γ_∞.

$B = RT\Gamma_\infty$

The isotherm of adsorption may have different shapes depending on the nature of a solute, the nature of a solvent, and the nature of a solid phase, if we consider

the adsorption of a solute from a solution on the solid phase. If we consider the adsorption of a nonvolatile solute on the surface of a liquid, then it should follow the model of a monomolecular layer formation. Such model, known as Langmuir model, is also working good for some solutes and gases adsorbed on a solid phase.

There are several statements in the Langmuir theory. First of all, adsorption ends up with the formation of a monomolecular layer. Adsorption is possible only on active sites of a surface: each molecule occupies its own active center and they cannot interact with each other. Adsorption is reversible: in the equilibrium state the rate of adsorption is equal to the rate of desorption.

Langmuir equation connects the actual adsorption (Γ) with the concentration of a solute in the liquid phase through the value of maximal adsorption (Γ_∞) and the specific constant for a given system (K).

$\Gamma = (\Gamma_\infty \cdot K \cdot C)/(1 + K \cdot C)$

This equation can be derived kinetically. So, the rate of adsorption is equal to the multiple of a specific constant (K_{ad}), the concentration of a solute (C) and the concentration of available active sites (S) per square meter.

$r_{ad} = K_{ad} \cdot C \cdot S$

The rate of desorption is equal to the multiple of the specific constant of desorption (K_{des}) and the concentration of occupied active sites ($S_{occupied}$).

$r_{des} = K_{des} \cdot S_{occupied}$

In the equilibrium state these rates are equal to each other.

$K_{ad} \cdot C \cdot S = K_{des} \cdot S_{occupied}$ and $K_{ad}/K_{des} = S_{occupied}/C \cdot S$

Since the sum of S and $S_{occupied}$ is equal to the maximal surface concentration of occupied sites, and the ratio between two constants is also a constant (K) we can continue.

$\Gamma_\infty = S + S_{occupied} = S_{occupied}/(KC) + S_{occupied} = S_{occupied} \cdot (1/KC + 1)$

$\Gamma_\infty = S_{occupied}\ ([1 + KC]/KC)$

Now the fraction of sites occupied by a solute (α) can be calculated from this equation.

$\alpha = S_{occupied}/\Gamma_\infty = KC/(1 + KC)$

If we multiply the fraction of occupied sites by the maximal adsorption, then we will get the desired actual adsorption value.

$\Gamma = \Gamma_\infty \cdot \alpha = (\Gamma_\infty \cdot K \cdot C)/(1 + K \cdot C)$

Graphically (figure 4.3) adsorption shows almost linear dependence on concentration at low concentrations of a solute, since “1 + KC” is almost equal to “1”. At very high concentrations of a solute adsorption shows no dependence on the concentration, since “1 + KC” is almost equal to “KC”. That is how Langmuir showed that at very high concentration all the active sites are completely saturated. At average concentrations the plot is quite curvy. If one half of active sites is occupied, then KC is equal to 1. One can find the value of C when the adsorption is two times lower than the maximal one, and calculate the constant as “$1/C_{0.5\Gamma\infty}$”.

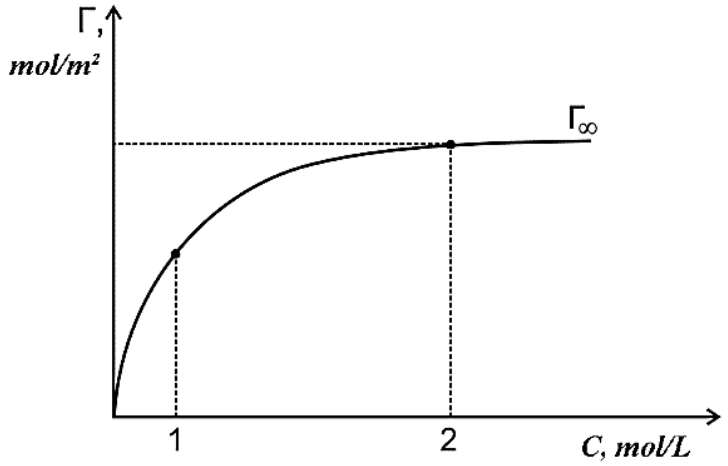


Figure 4.3. The isotherm of monomolecular adsorption according to the Langmuir theory

Langmuir equation may be simplified. To make it, one needs to leave K behind the brackets in both numerator and denominator. Then we can say that "1/K" is also a constant (L).

$\Gamma = \Gamma_\infty \cdot (K/K) \cdot [C/(1/K) + C] = (\Gamma_\infty \cdot C)/(L + C)$

If we know the value of maximal adsorption, we can calculate some parameters of adsorbed molecules. To calculate the mass of SAS per surface area one needs just to multiply Γ_∞ by the molar mass of SAS. If we divide the mass by the density, we obtain the volume. If we divide the mass per the unit of surface area (kg/m^2) by the density (kg/m^3), we will obtain the length of a molecule in the adsorption layer (in meters). To get the area occupied by a single molecule one needs to divide 1 by the multiple of Γ_∞ and Avogadro's constant.

$S_{molecule} = 1/(N_A \cdot \Gamma_\infty)$

$S_{molecule} = 1/(N_{of\ molecules}/S) = S/N_{of\ molecules}$

Actually, in this way one will find the area of surface in which just a single molecule is adsorbed. If active sites are situated far from each other, that area will be much larger than the area of a single molecule itself.

Freundlich adsorption isotherm (figure 4.4) is different from the Langmuir one. The most important difference is in the fact that adsorption does not end up with the formation of a monomolecular layer. There are two constants (K and n) that Freundlich used to describe the dependence between the equilibrium concentration and the adsorption according to the equation written below.

$\Gamma = K \cdot C^{1/n}$

How to get the values of K and n? Of course, one should use logarithmic scales to get them graphically.

$\log\Gamma = (1/n) \cdot \log C + \log K$

The value of "1/n" is the slope of the dependence between logΓ and logC, while logK is the length of the part of Y axis that is cut off by the extended line of the dependence.

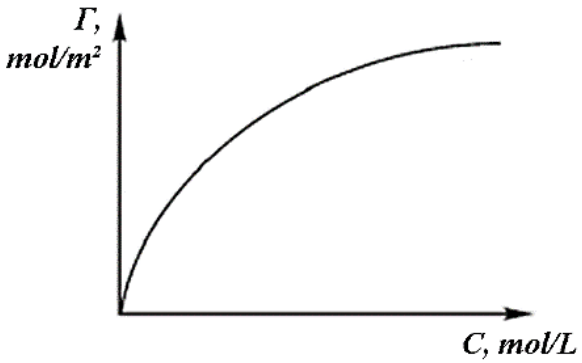


Figure 4.4. The isotherm of adsorption according to the Freundlich theory

It is thought that the dependence given by the Freundlich equation is more appropriate in average concentrations of a solute than the dependence given by the Langmuir equation. Why adsorption is not ending with the formation of a monomolecular layer in many cases? Because molecules can be adsorbed on the surface of the same molecules that have already been adsorbed.

Brunauer, Emmett and Teller (BET) created the theory of polymolecular adsorption. According to that theory, there are columns of molecules (those columns may have different lengths) attached to active sites of an adsorbate. However, this theory does not allow interactions between molecules from different columns. The isotherm of adsorption in this case has a shape of stairs (figure 4.5). After the formation of a monomolecular layer, molecules are starting to form the second layer. Adsorption of each new layer follows Langmuir equation.

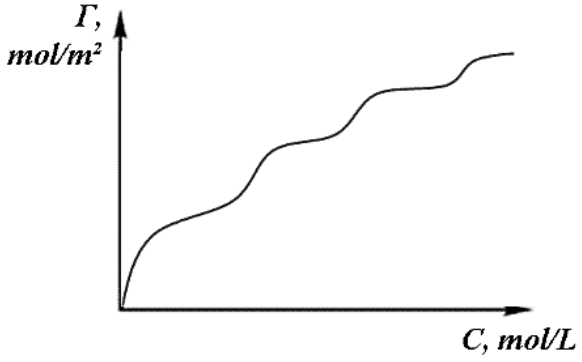


Figure 4.5. The isotherm of polymolecular adsorption according to the Brunauer, Emmett and Teller (BET) theory

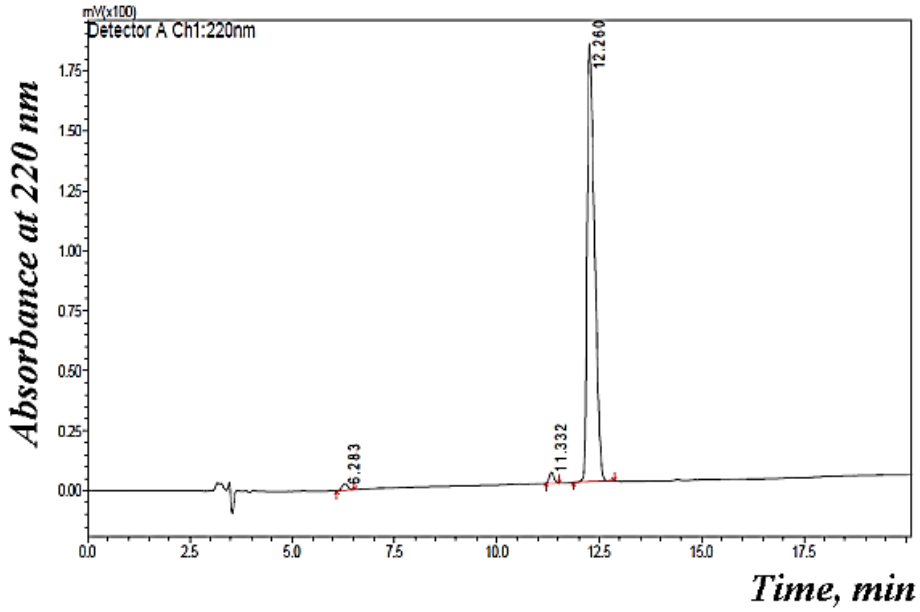
In each concrete case the isotherm of adsorption has its unique shape. To find the existence of "stairs" on the isotherm one needs to perform experiments with a very short "step" (one may say with a very high resolution). In each next experiment the concentration of a solute should be increased by a very small value. In this case "the stairs" will become visible. Otherwise, the isotherm of polymolecular adsorption will follow the Freundlich equation: we will never observe "the stairs" if we have a few number of points to build the graph.

Such immunological technique as ELISA (enzyme-linked immunosorbent assay) is based on the adsorption. One of the variants of ELISA includes the adsorption of an antigen on a surface of a plate. The plates were originally made from pure polystyrene. That material is completely hydrophobic. Lately, modified plates with both hydrophobic and hydrophilic active sites have become more popular. Indeed, some proteins that have rather hydrophilic surface demonstrate low adsorption on unmodified polystyrene plates. Moreover, proteins may undergo some structural changes during the adsorption on a hydrophobic surface. These changes may be as drastic as the "wearing the inside out", when hydrophobic core of a protein becomes exposed to hydrophobic surface.

Adsorbed antigenic proteins are covered by a tested serum. If there are specific antibodies against an antigen, they will be adsorbed on the layer of antigen as strong, that they will not be washed away by new portions of a solvent. Then the immune complex is covered by a solution with specific anti-human antibodies linked with an enzyme called horseradish peroxidase (or other enzyme). In case if some antibodies have been adsorbed on a layer of an antigen, secondary antibodies will form the third layer. The last step of the analysis is the addition of a specific substrate for an enzyme linked to secondary antibodies. Enzymatic reaction leads to the color change in a given well of a plate. The intense of color is checked by spectrophotometer. Other variants of ELISA are also based on nonspecific (the first layer) and specific adsorption (all other layers). From this point of view, one can understand the IUPAC definition of adsorption that includes the following notice: "adsorbed molecules are those that are resistant to washing with the same solvent in the case of adsorption from solutions". Sometimes chemisorption (adsorption with the formation of chemical bonds between active sites and adsorbed molecules) is used instead of physical adsorption described in this chapter. Physical adsorption is due to the formation of hydrophobic and polar interactions, as well as hydrogen bonds, between active sites of a surface and adsorbed molecules. During the chemical adsorption covalent and ionic bonds are formed.

Adsorption is the phenomenon that is the basis of chromatography. Nowadays chromatography is the group of methods for qualitative and quantitative analysis. It is used for both the identification of chemical substances and for the estimation of their amounts (concentrations) in a sample. The principle of chromatography is in the difference in the affinity to immobile and mobile phases for chemical substances. Traditionally, adsorption chromatography is based on the passing of a sample through the column. A sample should be dissolved in a mobile phase (a solvent or a mixture of solvents). Immobile phase is inside the column. Solution is passed through the column. Then the column is washed by the same solvent. One should monitor the solvent passing out from the column with the aim to detect substances. If a substance shows higher affinity to the mobile phase than that to the immobile phase, it will pass through the column very soon (it will have a short retention time). If a substance shows higher affinity to the immobile

phase than that to the mobile phase, it will pass through the column after the long period of time (it will have a long retention time). That is how one can separate several substances from each other. Since each substance has its own retention time for a given pair of column and solvent, one can identify the presence of a given substance in a sample with the help of chromatography. With the help of a detector (photometer, fluorometer, mass spectrometer) one can check the outflowing solution for the presence of specific substances, and then build a graph of their appearance and calculate the area under the curve for each peak in the chromatogram (figure 4.6). That is how one can estimate the amount of each substance in a sample. If some substances from a sample have very strong affinities to the column, they may not be washed away by a solvent at all. In this case another solvent (eluent) is used. To overcome this problem one can use a chromatograph that changes the content of a solvent with the course of time. For example, one can use a mixture of water and acetonitrile (CH_3–C≡N). The last one is completely soluble in water, but it interacts with hydrophobic molecules much better than water. So, one can even estimate relative hydrophilicity of substances using chromatography. The number of types of columns used for chromatography now is uncountable. So, one is able to choose the best one for a certain purpose.



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Area %	Height
1	6.283	27135	1.141	2746
2	11.332	34396	1.447	4557
3	12.260	2316023	97.412	182379
Total		2377555	100.000	

Figure 4.6. An output of HPLC chromatograph with the information on peaks: retention time, absolute area, percent of the area, the height

Thin-layer chromatography uses thin plates instead of columns. These plates may be made of glass or plastic covered by a layer of silica gel, cellulose or aluminum oxide. Mobile phase should demonstrate quite different properties from the immobile phase to

allow good separation. Samples are applied on a starting line of a plate. Then plate is omitted into the solvent, and the solvent starts to ascend on a plate. If a substance shows high affinity to solvent, it runs to the top of the plate together with the solvent. If substance shows low affinity to solvent, it does not migrate good. Molecular mass also plays significant role in the thin-layer chromatography, together with hydrophilicity and polarity. Indeed, the heavier the molecule, the shorter its migration path.

Ion-exchange chromatography is based on reversible stoichiometric substitutions between cations from the solution and cations from the ionite (cationite), as well as between anions from the solution and anions from the ionite (anionite). Ionite is a polymeric substance that has active groups able to participate in ion exchange. Demineralization of water can be described by the following reactions.

Cationite:

$2R - An^{-}H^{+} + CaCl_2 \leftrightarrow (R - An^{-})_2Ca^{2+} + 2HCl$

Anionite:

$R - Cat^{+}OH^{-} + HCl \leftrightarrow R - Cat^{+}Cl^{-} + H_2O$

First, water is passed through the cationite: cations of metals are exchanged by H^{+} cations. Then resulting solution is passed through the anionite: inorganic anions are exchanged by OH^{-} anions. Finally, H^{+} and OH^{-} ions react with each other and form water molecules.

Each cationite (or anionite) can be characterized by its ion-exchange capacity. This value shows the number of moles of equivalents of active groups per 1 gram of the dry ionite. In other words, it is the amount of charge that can be exchanged by 1 gram of the dry ionite. So, the same cationite will exchange two times less number of a divalent cation than that of a monovalent cation.

Size-exclusion chromatography is based on the separation of molecules by their sizes. Depending on the nature of a solvent this kind of chromatography is classified into gel-permeation (when solvent is organic) and gel-filtration (when solvent is water). In both cases water solution passes through the gel. There are pores in a gel that are filled by the solvent. Small molecules retain in these pores, while big molecules just cannot get inside those pores, and so they pass through the column fast. We can say that a solvent in pores of a gel acts as an immobile phase, while a solvent that does not fill pores acts as a mobile phase. Gels may have different pore size. So, one can choose the needed gel to separate molecules according to the threshold size.

Affine chromatography is based on specific interactions between proteins, or between proteins and their ligands. Usually this technique is used in immunology. For example, one may covalently link a viral protein to the gel from a column (an immobile phase). Then one may incubate a serum inside that column and wash the column with the same buffer in which the serum has been dissolved. Finally, all the nonspecifically bound molecules will be washed away, while specific antibodies to the covalently linked protein will stay inside the column. To break highly specific bonds between antigen and antibody, one needs to

change the solvent. Usually, acidic solutions with pH around 3 are used for this purpose. At this pH, immunoglobulins change their conformation and lose the affinity to antigens. That is how antibodies can be purified. In this way one can check the presence of antibodies, the amount of antibodies, and also the affinity of antibodies (the higher the volume of eluent used to wash them away, the higher the affinity). Instead of an antigen, one can immobilize an antibody on such column to check serum for the presence of specific proteins.

Problems

1. What will be the surface tension of the aqueous solution of amyl alcohol if the number of the drops of this solution outflowing from the stalagmometer is 72 and the number of water drops is 60? The surface tension of water at the temperature of the experiment 293 K is $72.8 \cdot 10^{-3}$ J/m^2 (the density of the solution is equal to 1 g/ml).

2. At 20 °C the surface tension of 0.2 M SAS aqueous solution is $55 \cdot 10^{-3}$ J/m^2. Calculate SAS adsorption value (surface tension of water at 20 °C is $72.75 \cdot 10^{-3}$ J/m^2).

3. It is determined experimentally that the maximum adsorption value of propionic acid on coal is $3.0 \cdot 10^{-3}$ mol/g; K coefficient is $6.0 \cdot 10^{-2}$ mol/L. What mass of propionic acid has been adsorbed from the solution if the equilibrium acid concentration is 0.1 mol/L? The adsorbent mass is 1 g.

4. Show how the surface activity and adsorption of butyric acid in aqueous solution change with the increase in concentration (T = 298K):

C, mol/L	0.0625	0.125	0.25
σ·103, N/m	60.4	55.1	47.9

5. The surface activity of pentanol in aqueous solution with 0.015 mol/L concentration is 0.555 N·L/(mol·m) at 298 K. Calculate the adsorption value of butanol from the solution of the same concentration at the same temperature.

6. Determine the Gibb's energy Gs of the surface for 4 g of water fog droplets at 293 K if water surface tension at this temperature is $72.7 \cdot 10^{-3}$ J/m^2, water density is 0.998 g/cm^3, particle dispersion is 50 μm^{-1}.

7. For aqueous solution of butyric acid at 273 K, the Shishkovsky equation constants are as follows: B = $12.6 \cdot 10^{-3}$ N/m, A = 21.5 L/mol. The surface tension of pure water (at the given temperature) is $75.45 \cdot 10^{-3}$ N/m.
   a) Estimate the surface tension (σ) of the solution at two concentrations of butyric acid: c_1 = 0.007 mol/L and c_2 = 0.104 mol/L.

   b) Estimate the approximate values of the parameters of the Shishkovsky equation (B and A) for acetic, propionic and valeric acids.

8. Calculate the length and area of the molecule of isoamyl alcohol if the limiting adsorption is $\Gamma_\infty = 7.0 \cdot 10^{-6}$ mol/m^2 (density of isoamyl alcohol is 0.81 g/ml).

9. 3 g of solid adsorbent was placed in 60 ml of a solution of some substance with the concentration of 0.440 mol/L. After reaching the adsorption equilibrium,

the concentration of the substance decreased to 0.350 mol/L. Calculate the amount of adsorption.

10. The maximum value of the adsorption Γ_∞ of stearic acid $C_{17}H_{35}COOH$ on the surface of the aqueous solution is $7.465 \cdot 10^{-10}$ mol/cm^2. The density of the acid is 850 kg/m^3. Find the cross-sectional area of the molecule (S) and the length of the molecule (l).

11. The maximum adsorption on carbon is $3.0 \cdot 10^{-3}$ mol/g. The constant K in the Langmuir equation is $6.0 \cdot 10^{-2}$ mol/L. What mass of propionic acid was adsorbed from the solution in which an equilibrium concentration of 0.1 mol/L was established, if the mass of the adsorbent was 1 g?

12. The adsorption of the surfactant dissolved in water on the mercury-water surface obeys the Langmuir equation. The degree of filling of the surface is 0.5 at a surfactant concentration of 0.2 mol/L. Calculate the surface tension of mercury at the interface with the solution at 298 K and the concentration of surfactant in the solution 0.1 mol/L. The area of the surfactant molecule on the surface is 0.2 nm^2, the surface tension of mercury at the boundary with water is 0.373 J/m^2.

13. During the chromatography of the pigment of green leaves on the polar adsorbent Al_2O_3, the colored layers are arranged top-down in the following way:
    a) yellow-green — β–chlorophyll; c) yellow — xanthophylls;
    b) blue-green — β-chlorophyll; d) red — carotene.
    Make conclusions about the degree of polarity of the pigments of separate leaves.

14. In the column filled with a strong-acid cation exchanger (cationite) we introduced a solution containing Fe^{3+}, Ca^{2+}, Li^{+} and K^{+} cations. What is the sequence of the appearance of these cations from the column if they are washed out by the solution of 0.5 M of HCl?

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15. 1.00 g of dry cation exchanger (cationite) in the form of H^{+} was filled up with 100 mL 0.10 M of NaOH solution. To titrate 10 mL of equilibrium solution containing the excess of the alkali which hasn't reacted with the ionite we used 4.8 mL 0.10 M of HCl solution. Calculate the exchange capacity of cationite.

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16. At the separation of lipid mixture on the plate with silica-gel we obtained four stains, the distances from the start line are the following: a) 1.2 cm; b) 2.5 cm; c) 6.4 cm; d) 7.2 cm. The distance passed by the solvent is 11.6 cm. Identify the stains of cholesterol and stearic acid on the chromatogram if the retention index R of cholesterol and stearic acid in the mixture "water-mixed organic solvent" are the following: 0.103 and 0.560. Which of the components of the lipid mixture is more polar? Explain the answer.

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17. Arrange the cations of $CaCl_2$, Na_2SO_4, KCl, $FeCl_3$, $LiNO_3$ salts into a row according to the increase in their ability to be absorbed by the H^{+} cationite from aqueous solutions. How will this row change if the solvents are slightly polar?

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18. To titrate 0.50 g of air-dried strong-acid cationite with sulfate groups — SO_3H we used 25.5 mL of 0.100 M sodium hydroxide solution. Calculate the exchange capacity of cationite if the mass fraction of water in the cationite was 8 %.

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CHAPTER 5
COLLOID SOLUTIONS AND COARSELY DISPERSED SYSTEMS

The main topics of the chapter:

1. *Classification of dispersed systems.*
2. *Sedimentation and Brownian movement.*
3. *Tyndall's effect and opalescence of colloid solutions.*
4. *Double electric layer.*
5. *Coagulation of colloid solutions.*
6. *Coarsely dispersed systems.*
7. *Colloid surface active substances.*

In colloid solutions the size of particles may vary from 10^{-9} to 10^{-7} m (from 1 to 100 nm). Solutions with smaller particles are classified as real solutions, and they are considered to be homogeneous. Colloid solutions are heterogeneous, and each particle has its own surface area that is the area of the contact between two phases. Solutions with bigger particles are known as coarsely dispersed systems. Interestingly, exactly because of specific size, colloid solutions demonstrate some distinctive physical properties. However, first we should define what is meant behind the term "size of a particle".

For spherical particles under the term "size" we mean diameter (or radius), for cubic particles under the term "size" we mean the length of the edge (rib) of a cube. Dispersity is a value that is opposite to the size of particles: one should divide one by the size of a particle to get it. So, solutions are dispersed systems. When dispersity is high, they are real, when dispersity has average level, they are colloid, and when dispersity is low, solutions are coarsely dispersed.

Another characteristic of dispersed system is its specific area of surface. This value is either the ratio between the surface of a particle and its mass, or between the surface and the volume. For spherical particle we can use the equation written below.

$S_{specific} = S/V = 4\pi r^2/[(4/3)\cdot\pi r^3] = 3/r = 6/d$

From geometric definitions of the surface of a sphere and of its volume we can obtain an easy expression: specific area is equal to 3 over radius, or to 6 over diameter. So, the smaller the size of a particle, the larger the area of surface contact between solid and liquid phases.

For particles of cubic shape we can get the same expression in which "l" is the length of an edge.

$S_{specific} = S/V = 6l^2/l^3 = 6/l$

In general, for particles of a certain shape the area of the surface contact is proportional to the dispersity. The coefficient of proportionality for perfect spheres and cubes is equal to 6, while for other particles it may be different than 6.

So, *coarsely dispersed systems* are characterized by: kinetic and thermodynamic instability; they are not transparent; one can see the particles with the naked eye or with the help of optic microscope; the particles cannot pass through paper filter and through ultrafilters.

Colloid solutions are characterized by: kinetic stability but thermodynamic instability; they are transparent but opalescent; particles cannot be seen in optic microscope but can be seen in electron microscope; particles can pass through the paper filter but cannot pass through ultrafilters.

Finally, *real solutions* are characterized by: kinetic and thermodynamic stability; transparency; particles cannot be seen in both optic and electron microscopes; particles can pass through both paper filter and ultrafilters.

According to the aggregate state of dispersed phase and dispersed medium we can classify colloid and coarsely dispersed systems.

Dispersed systems based on a gas as a medium can contain either liquid drops (fog, clouds), or solid particles (smoke, dust, powders). Coarsely dispersed systems based on a liquid as a medium can contain bubbles of gas (foam), drops of liquid (emulsions); solid particles (suspensions). Solid substance can also play the role of a dispersed medium for bubbles of gas (holystone, bread); for drops of liquid (soil); or for particles of another solid substance (minerals and alloys).

Dispersed systems can be classified according to the strength of interactions between the medium and the phase into: lyophobic (with weak interactions) and lyophilic ones (with strong interactions). Lyophobic systems are represented by: colloid solutions, suspensions, emulsions, aerosols and foams. Lyophobic systems cannot be formed spontaneously, and so they are thermodynamically instable. Such systems require a specific stabilizer. In contrast, lyophilic systems (solutions of colloid surface active substances and biopolymers) are formed spontaneously, since they are thermodynamically stable in the absence of any stabilizers.

Another classification takes into account the possibility of interactions between different particles of the dispersed phase. In free dispersed systems particles of the dispersed phase are free to move, they are not connected with each other. Such systems are: sols, suspensions, emulsions and aerosols. In coherent dispersion systems the particles of dispersed phase are forming a solid framework for dispersed medium, just like in protein gels.

Lyophobic colloid solutions are known as sols. Initially such systems were known as “pseudosolutions”. Sol can be formed only if dispersed phase has very low solubility in the dispersed medium. Moreover, there must be a stabilizer: the excess of one of the initial reactants, surface active substance or biopolymer. Colloid solution can be produced by the dispersion of bigger particles or by the condensation of smaller particles.

Dispersion can be achieved by: mechanical fragmentation, splitting by ultrasound, by electricity, or by the peptization. Condensation may be achieved by the physical method of the change of solvent or by the condensation of vapor. Chemical methods are based on

double displacement, redox, or complexation reactions in which insoluble substance is formed in the excess of a stabilizer.

Colloid solutions must be purified from big particles by filtration, and from the excess of small particles by dialysis, electric dialysis or ultrafiltration.

Molecular kinetic properties of colloid solutions are: Brownian movement, diffusion and osmosis. Brownian movement is a chaotic constant movement of particles of dispersed phase that happens because of collisions with particles of the dispersed medium. It is known that colloid particle changes the direction of its Brownian movement about 10^{14} times in one second. However, we can estimate an average shift (Δ) of that particle according to the Einstein–Smoluchovsky equation.

$$\Delta = \sqrt{2D\tau}$$

In this equation D is the coefficient of diffusion, and τ is the time.

The higher the temperature, the more intensive the Brownian movement. The decrease in viscosity of the medium and the decrease in the size of particles of dispersed phase also result in the increase of the Brownian movement.

Diffusion is a spontaneous process that leads to the equivalent distribution of each type of particles throughout the whole volume of a solution. This process is spontaneous since the entropy of mixing is always positive. Because of the same reason diffusion is irreversible (in kinetic sense). The mechanism of diffusion is nothing but the Brownian movement. Diffusion stops (a system reaches the equilibrium) when the sum of chemical potentials for all the components becomes as low as it is possible.

The first law of Fiche describes the process of diffusion mathematically. The mass of a substance (m) diffused from one layer to another layer during the certain time (τ) through the certain surface of contact (S) is directly proportional to the gradient of concentration of a given substance between two layers (ΔC) and indirectly proportional to the distance between two layers (Δx). The coefficient of proportionality in this equation (D) is called the coefficient of diffusion.

$$m = D \cdot S \cdot \tau \cdot (\Delta C/\Delta x) \quad \text{or} \quad dm/d\tau = DS(-dC/dx)$$

The coefficient of diffusion can be calculated with the help of Einstein's equation written below.

$$D = (R \cdot T)/(6 \cdot \pi \cdot \eta \cdot r \cdot N_A)$$

In this equation η is a viscosity of a medium, while r is the size of a particle. The value of D is determined by such internal parameters, as the viscosity of a medium and the dispersity of a phase. Indeed, the lower the viscosity of a medium, and the smaller the mass of particles, the faster they diffuse.

Molar mass of a particle can be calculated from the value of its radius using the density of a dispersed phase (ρ). Actually, the mass of a single particle is calculated and multiplied by Avogadro's number.

$$M = (4/3) \cdot \pi \cdot r^3 \cdot \rho \cdot N_A$$

Osmotic pressure in a colloid solution should be calculated from the value of partial concentration ($C_{colloid}$) that is equal to the number of colloid particles in 1 Liter.

$P_{osmotic} = (C_{colloid}/N_A)\cdot R\cdot T$

To calculate the partial concentration one should not count all the colloid particles in a certain volume. It is enough to estimate an average mass of a colloid particle ($m_{particle}$). Then one can divide the whole mass of a dispersed phase (m_{phase}) by the mass of a single particle, and divide this number by the volume.

$C_{colloid} = m_{phase}/(m_{particle}\cdot V_{solution})$

In general, colloid solutions have much lower osmotic pressure than real solutions with the same mass percentage of a solute. Since the mass of a particle (that is spherical) is proportional to the radius in the power of 3, two times increase of a size of a particle results in 8 times decrease of osmotic pressure. Since colloid particles have variable sizes, and the size is growing in time because of aggregation, osmotic pressure in such solutions is not something stable: it tends to decrease.

Sedimentation is the process of precipitation of colloid particles under the influence of the gravity. The force of tension confronts the force of gravity. Both forces can be calculated from some basic characteristics of dispersed phase and dispersed medium. So, the force of gravity depends on the size of a particle (directly) and the difference in densities ($\rho - \rho^0$) between the phase and the medium (also directly).

$F_{gravity} = (4/3)\cdot\pi\cdot r^3\cdot(\rho - \rho^0)\cdot g$

In this equation g is the acceleration of gravity. So, the lower the density of a particle, the weaker the force of gravity.

The force of tension also depends on the size of a particle, as well as on the viscosity of a medium.

$F_{tension} = 6\cdot\pi\cdot r\cdot\eta\cdot v$

In this equation v is the movement rate of a particle.

If we consider that the force of gravity is equal to the force of tension, then we can calculate the rate of sedimentation (the rate of the movement of particles towards the bottom).

$v = (2/9)\cdot(r^2/\eta)\cdot(\rho - \rho^0)\cdot g$

Taken together, the bigger the size of particles, the lower the viscosity of medium, and the higher the difference in densities of phase and medium, the faster the rate of sedimentation.

Sedimentation can be prevented by diffusion. So, if the rate of sedimentation is equal to the rate of diffusion, solutions is said to be resistant to sedimentation. This situation is known as sedimentation-diffusion equilibrium. Colloid solutions are relatively resistant to sedimentation. To accelerate the rate of sedimentation one may increase the value of g by the way of centrifugation.

Optical properties of colloid solutions require special attention. Colloid solutions are opalescent because of the light scattering. The wavelength of visible light varies from 400 to

750 nm. When light passes through colloid solution with a size of particles between 1 and 100 nm, Willis–Tyndall scattering appears. Scattering is the process in which radiation (in our case the light) is forced to deviate from a straight trajectory because of non-unifromities of a medium through which it passes (colloid particles in our case). The light is not just scattered on colloid particles, it also becomes polarized. The shorter the wavelength of light, the better it scatters. The intensity of scattered light depends on the intensity of initial light (I_0), partial concentration of colloid solution ($C_{colloid}$), the volume of colloid particle (V) and the wavelength (λ) of light (in the power of 4).

$$I = (K \cdot I_0 \cdot C_{colloid} \cdot V^2)/\lambda^4$$

In this equation K is the constant that depends on the index of refraction for dispersed phase (n_1) and the index of refraction for dispersed medium (n_0). The exact equation is given below.

$$K = 24 \cdot \pi^3 \cdot [(n_1^2 - n_0^2)/(n_1^2 + 2n_0^2)]$$

Conclusions from these equations that work well if a sol is dilute and if the particles are spherical and they are not absorbing visible light, are as follows. The intense of scattered light becomes higher with the growth of partial concentration, with the growth of the volume of particles, with the increase of the difference between indices of refraction for dispersed phase and dispersed medium, as well as with the increase in intense of the initial light. White light (day light) is the combination of light of different wavelength. Visible light of a shortest wavelength is violet. Visible light of a longest wavelength is red. The shorter the wavelength, the more intensive the scattering. That is why we can see the Tyndall's effect when the beam of light is passing through the colloid solution (figure 5.1), and that is why the color of the scattered light is blue. If we just observe a tube with colloid solution on a black background, we will see white opalescence around it (figure 5.1). To see the Tyndall's effect, it is better to pass the light through the lens, while the passing of light through the hole in the wall also works well. It is better to put a tube in the closed box to see just the light that is passing through the hole. Similar effect can be observed when a spotlight is used in the area with a smoke or fog (both of them are also colloid systems) and we can see the pass of light.

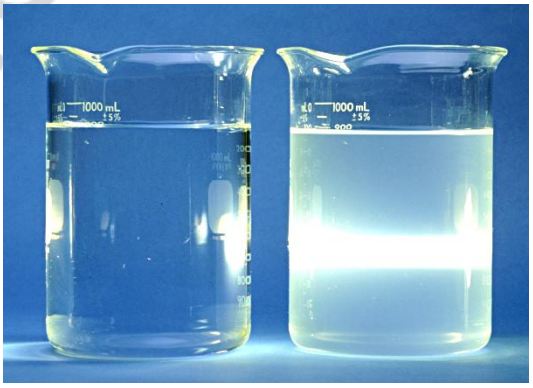

Figure 5.1. Tyndall's effect and opalescence of a colloid solution (right glass) in comparison with a real solution (left glass); a beam of light is passing through both of them

To estimate the size of a colloid particle one may use an ultramicroscope. In the indirect manner one may calculate the size of colloid particles from the coefficient of diffusion. Another indirect way to estimate the size of a particle is to use a nephelometry. This method is based on the measurement of the intense of light passing through a sample. Comparison with a standard colloid solution is required. Centrifugation can also be used as a method to calculate the mass (and so the size) of colloid particles: the lighter the particles, the faster the speed of centrifuge should be to separate them from the solution. Of course, one can use a set of micro filters to separate colloid particles of a given size from the real solution.

Colloid particles possess double electric layer on their surfaces. That layer can be formed by two mechanisms: by selective adsorption and by ionization. Selective adsorption may be associated with the building up of the crystal lattice of a dispersed phase: the same or similar ions from water solution continue the crystal lattice of an ionic or atomic substance from the dispersed phase. Selective adsorption may not be associated with the building up of the crystal lattice. This scenario works when the dispersed phase is molecular. For example, if dispersed paraffin particles are dissolved in KOH water solution, OH^- ions will be adsorbed on the solid surface, and not K^+ cations. Ionization of the surface of colloid particles produces certain ions from the solid phase, and then some of those ions build up the lattice. For example, the surface of SiO_2 particles is hydrated, and partially turns to H_2SiO_3. The last one is partially ionized. So, $HSiO_3^-$ ions are adsorbed on a surface, while the solution is enriched by H^+ ions.

Double electric layer is made from potential determining ions that are tightly bound by the solid surface, and the equivalent amount of oppositely charged ions (counter ions). The layer of counter ions is divided into two parts: the first layer is called adsorption layer and it is made from oppositely charged ions interacting with ions from potential determining layer; the second layer is called diffusion layer since those ions are not directly adsorbed on a surface. Electrothermodynamical potential (φ) exists between the layer of potential determining ions and the layer of counter ions. Electrokinetical potential (ζ) exists between the adsorption layer of counter ions and the diffusion layer of counter ions. To memorize this order of potentials one may notice that thermodynamics goes first, and then goes kinetics. The border between the adsorption layer and the diffusion layer of counter ions is sometimes called a sliding boarder.

As an example we can take a sol formed after the reaction between water solutions of two salts: the excess of potassium iodide (KI) and relatively low amount of silver nitrate ($AgNO_3$). As a result of this reaction insoluble silver iodide is formed (AgI).

$KI + AgNO_3 \rightarrow KNO_3 + AgI\downarrow$

Insoluble silver iodide forms an aggregate that consists of numerous units of AgI. In the presence of an excess of stabilizing ions (I^- and K^+ in this case) precipitate does not form. Iodide anions are adsorbed on a surface of an aggregate, since they are able to build up its crystal lattice. That is how the layer of potential determining ions (PDI) is formed.

The charge of this layer is negative (in this case). Potential determining ions are responsible of electrothermodynamical potential formation. Aggregate and the layer of potential determining ions form a nucleus of colloid particle. The next layer is formed by counter ions (K^+) adsorbed on negatively charged surface of a nucleus. Nucleus together with adsorption layer forms a granule of colloid particle. Actually, granule is a real particle that exists in colloid solution (figure 5.2). Its charge is equal to the sum of the overall charge of potential determining ions and the overall charge of adsorption layer of counter ions. The module of a charge for all counter ions is always lower than the module of a charge for all potential determining ions. That is why the charge of a granule has the same sign as the charge of potential determining ions (in our case it is negative). We say that colloid particle has an overall charge equal to zero. To make this rule obey we should say that all the counter ions that are necessary to compensate the charge of a granule are situated in the diffusion layer. Schematically we should show the structure of colloid particle in the following way.

$\{mAgI \cdot nI^- \cdot (n - x)K^+\}^{-x} \cdot xK^+$

{aggregate·PDI·counter ions from adsorption layer}·diffuse layer

{nucleus· counter ions from adsorption layer}·diffuse layer

{granule}·diffuse layer

In this scheme “m” shows the number of units of AgI in the aggregate; “n” shows the number of potential determining ions; “x” shows the number of counter ions in the diffusion layer. The charge of a granule in this scheme is equal to “–x”. The boarders of a granule are shown by braces. The numbers of “m”, “n” and “x” are variables. They are different even for different colloid particles of the same sol.

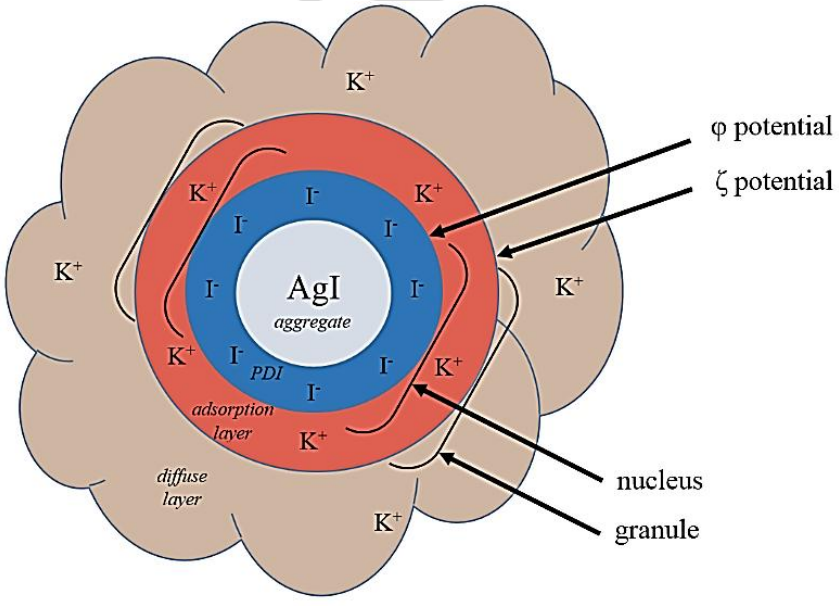

Figure 5.2. The scheme of micelle in a sol

If the magnitude of charge for potential determining ions is different from the magnitude of charge of counter ions, one needs to use some coefficients in the scheme

to make the overall charge of a micelle (colloid particle) equal to zero. If we mix an excess of $(NH_4)_2S$ with $CuSO_4$, then the scheme is as follows.

$\{mCuS \cdot nS^{2-} \cdot (2n - x)NH_4^+\}^{-x} \cdot xNH_4^+$

If the magnitude of charge of counter ions is higher than 1, we also need to modify a scheme of a micelle: notice the charge of a granule in a scheme below.

$\{mCuS \cdot nCu^{2+} \cdot (n - x)SO_4^{2-}\}^{-2x} \cdot xSO_4^{2-}$

The last sol could have been made from potassium sulfide and the excess of copper (II) sulfate.

Colloid particles can be acquired by the way of peptization: when already formed precipitate is turned to colloid particles by the ions of peptizator. For example, one can prepare a precipitate of $Fe(OH)_3$ by the way of an exchange reaction between $FeCl_3$ and NH_4OH. After the formation of precipitate one should add an excess of $FeCl_3$, and the precipitate will be dissolved in the form of colloid particles. This kind of peptization is called adsorption-based peptization.

Dissolution peptization happens when we add a reactant to the precipitate that produces peptizator ions by the way of chemical reaction. For example, one may add a limited amount of HCl to the precipitate of $Fe(OH)_3$. As a result, FeO^+ cations will be formed on a surface of precipitate. Those cations will be the potential determining ions. Chloride anions will then be adsorbed on such surface, and colloid particles will be formed according to the following scheme.

$\{mFe(OH)_3 \cdot nFeO^+ \cdot (n - x)Cl^-\}^{+x} \cdot xCl^-$

Colloid solutions may be more or less stable. Stability of colloid solution is the ability of such system to keep the dispersion degree of dispersed phase constant and maintain the random distribution of colloid particles throughout the whole volume of a solution.

There are two types of stability for colloid solution: sedimentation stability and aggregation stability. Sedimentation stability is the ability to overwhelm the gravity with the help of Brownian movement. Sedimentation stability is determined by: the size of particles (the smaller the better), and the viscosity of the medium (the higher the better). Aggregation stability is the ability to overwhelm the tendency of colloid particles to aggregate (to form bigger particles). Aggregation stability is determined by: electrostatic factor and adsorption-solvatation factor. Electrostatic factor is determined by the electrokinetic potential (ζ). The higher the value of ζ, the stronger the repulsion between granules (because they have the same charge). Adsorption-solvatation factor is determined by the existence of hydrated coats (water molecules) around counter ions from the diffuse layer. Because of this fact the density and the viscosity of water in diffuse layer is higher than in the rest of the solution, and that is why so-called disjoining pressure works against the aggregation of colloid particles. Disjoining pressure directly depends on the charge of the potential determining ions (φ potential), and on the thickness of the diffuse layer (ζ potential). Indeed, the higher the charge of the nucleus, the thicker the diffuse layer, and

the stronger the disjoining pressure, as well as the value of ζ potential responsible of electrostatic repulsions between particles. In colloid particles made from molecular or atomic substances Van der Waals forces are playing significant role in aggregation (and aggregation stability) along with electrostatic attraction.

When two micelles get close to each other, electrostatic repulsion exists between the layers of counter ions, enhanced by the disjoining pressure. However, if micelles are getting to the shorter distance, the force of electrostatic attraction between the nucleus of one particle and the adsorption layer of another particle becomes strong, and particles aggregate. The thicker the diffuse layer the lower the chance that nuclei of two particles will get close enough to each other to form an aggregate.

An average threshold of ζ potential is equal to 30 mV. If that potential is lower than 30 mV, sol is prone to aggregation; when it is higher than 30 mV but less than 50 mV, sol is relatively stable. Colloid solutions with the value of ζ higher than 50 mV are thought to be stable.

One can cause coagulation of a colloid solution: by the increase in concentration of a solution, by the increase or the decrease in temperature, by different types of radiation, by the addition of an electrolyte.

Coagulation threshold is the minimal concentration of a given electrolyte that causes visible coagulation of a certain sol. To calculate this concentration one should take care about the dilution of the sol. So, the coagulation threshold ($C_{coagulation}$) is calculated from the molarity of electrolyte solution (C) and its volume (V), and from the volume of sol (V_{sol}).

$C_{coagulation} = (CV)/(V_{sol} + V)$

The coagulative ability (ϒ) is a value that is opposite to the coagulation threshold.

$\Upsilon = 1/C_{coagulation}$

The higher the coagulation threshold, the weaker the coagulative ability; and the lower the coagulative threshold, the stronger the coagulative ability of a given electrolyte.

Coagulation includes three phases: hidden coagulation, visible slow coagulation and visible fast coagulation. As it is shown in figure 5.3, during the hidden coagulation the rate of coagulation is slowly increasing with the growth of concentration of added electrolyte. One cannot see that coagulation is already started during the hidden phase by the naked eye. However, in the ultramicroscope one can see that the size of particles is growing. During the slow visible coagulation one can observe coarsely dispersed particles in the solution by the naked eye. The rate of coagulation demonstrates almost linear dependence on the concentration of added electrolyte. Fast visible coagulation is characterized by the lack of the dependence between the concentration of added electrolyte and the rate of coagulation: sol is coagulated as fast as it is possible.

When we use a term “coagulation threshold” we mean the minimal concentration of added electrolyte in a sol at which coagulation becomes visible. The value of

electrokinetical potential (ζ) at the point of the start of visible coagulation is called critical electrokinetical potential ($\zeta_{critical}$).

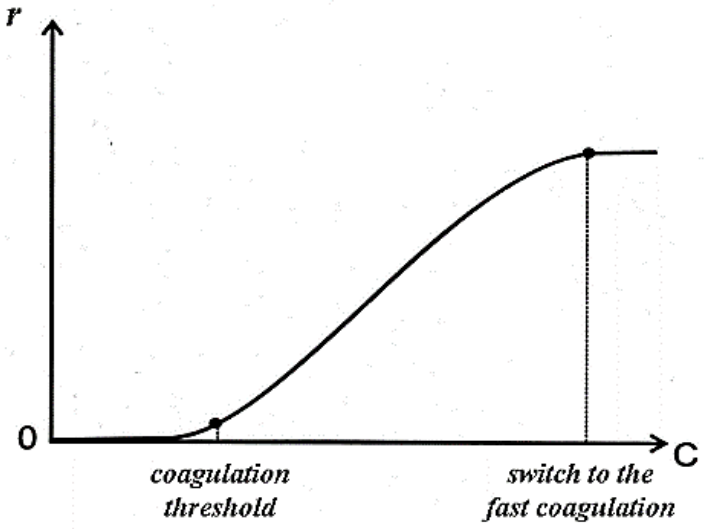

Figure 5.3. The dependence between the rate of coagulation and the concentration of added electrolyte

The rule of Shultze–Hardi tells that only one of the ions from an added electrolyte really coagulates particles of sol. That coagulating ion has a charge that is opposite to the charge of granules. It means that negatively charged granules are coagulated by cations, while positively charged granules are coagulated by anions. The higher the charge of an ion, the better it coagulates granules of an opposite charge. Typically, coagulation constants for ions of different charges are related to each other in the following way.

$C^+:C^{2+}:C^{3+}$ or $C^-:C^{2-}:C^{3-} = 1:(1/2^6):(1/3^6) = 1:(1/64):(1/729)$

Using this rule one can find out the charge of granules. Typically, three probes of the same colloid solution are titrated by KCl, K_2SO_4 and K_3PO_4. If the coagulation threshold is decreasing in this sequence according to the ratios provided above, then granules have positive charge. The second experiment is performed with KCl, $CaCl_2$ and $AlCl_3$. If the coagulation threshold is decreasing in this line largely, according to the Shultze–Hardi rule, then granules have negative charge.

The rule of Shultze–Hardi works good if the coagulation happens under the influence of indifferent ions: those ions that cannot be adsorbed on a surface of colloid particles. This kind of coagulation is called concentrational coagulation. Electrothermodynamical potential in this case stays the same, while elctrokinetical potential decreases because of the contraction of diffuse layer. The size of an ion that causes coagulation determines its coagulation threshold. The bigger the hydration radius of an ion, the higher its coagulation threshold. That is why alkali metals are arranged in the following lyotropic line in the order of the increase of their ability to cause coagulation and the decrease of their coagulation thresholds: **Li^+ / Na^+ / K^+ / Rb^+ / Cs^+**. Cations of cesium are entering the diffuse layer better than lithium cations. They do it because they are attracted by the negative charge of

granules and because they have small hydration radii. That is how diffuse layer becomes smaller (thinner). The smaller the diffuse layer, the weaker the repulsion force between colloid particles.

In case if coagulating ions are not indifferent, they are adsorbed on the surface of colloid particles. This adsorption leads to the decrease of the electrothermodynamical potential, and so, electrokinetical potential decreases as well. In case of this "neutralizing" coagulation Shultze–Hardi rule does not work. Coagulation thresholds are proportional to the one divided by the charge in the power of 2, and not six, as in the case with concentrational coagulation.

If one uses a mixture of electrolytes for coagulation, then electrolytes may show additive effect (when the resulting coagulation ability is equal to the sum of such abilities for individual electrolytes), antagonism (when the resulting coagulation ability is lower than the sum of such abilities for individual electrolytes), or synergism (when the resulting coagulation ability is higher than just the sum of such abilities for individual electrolytes). Interestingly, the coagulation threshold becomes higher if one adds a coagulating electrolyte slowly and in small portions. We may say that sols can develop resistance against the addition of electrolyte if it is added slowly.

If one mixes two sols with opposite charges of granules, they will usually coagulate because of the rearrangements of ions in both diffuse and potential determining layers happening because of electrostatic forces of attraction between them. However, in the excess of one of the sols, particles of the first sol may be completely recharged, and coagulation will not happen. Something similar happens after the addition of a big excess of coagulating electrolyte to the sol.

Colloid protection leads to the increase of coagulation threshold for a given electrolyte in the presence of certain substances. Usually surface active substances or biopolymers are used for this purpose. Protective number is the mass of a substance (mg) that protects 10 ml of a given sol from coagulation by 1 ml of 10 % NaCl solution.

Good protective properties are demonstrated by substances that show high solubility in dispersed medium, high ability to be adsorbed on the surface of colloid particles, and so by those that can be presented in high concentration in colloid solutions. Surface active substances or biopolymers should cover colloid particles by one of their sides, and interact with the medium (water) by another side. That is how colloid particles acquire new protective layers that do not allow them to aggregate with each other.

Electrophoresis is the movement of dispersed phase (colloid particles) in the electric field. Granules and not the whole micelles are moving in this case, since granules possess electric charges. The rate of electrophoresis directly depends on the value of electrokinetic potential (ζ) according to the following equation.

$$r = (\varepsilon \cdot \varepsilon^0 \cdot E \cdot \zeta)/(K \cdot \pi \cdot \eta \cdot l)$$

In this equation ε and ε^0 are the relative dielectric constant of the medium and the electric constant that is equal to $8.9 \cdot 10^{-12}$ F/m; E is electromotive force (V); η is the viscosity of

a medium ($N \cdot sec/m^2$); l is the distance between electrodes; K is the specific parameter describing the shape of particles (K = 6 for spherical particles, K = 4 for cubic particles).

So, from the rate of movement in the electric field during the electrophoresis experiment one can estimate the value of electrokinetic potential for colloid particles. Indeed, the higher the value of ζ, the higher the charge of those particles, the stronger their attraction to the oppositely charged electrode.

Electrophoretic mobility is the value that is equal to the ratio between the rate of electrophoresis and the gradient of the potential (E/l).

One may also calculate the value of electrokinetic potential from the rate of electroosmosis. Electroosmosis is the movement of dispersed medium in the electric field. The rate (r_V) is calculated as the volume of liquid (together with counterions) passed through the porous membrane in a given amount of time.

$$r_V = (K \cdot \pi \cdot \eta \cdot \kappa \cdot \zeta)/(\varepsilon \cdot \varepsilon^0 \cdot I)$$

In this equation there are two new parameters compared to the previous one, like specific electric conductivity (κ) and the amperage (I). Electroosmosis becomes significant only in rather small channels: in a porous material, in capillary tubes, in membranes.

Emulsion is a coarsely dispersed system made from two immiscible liquids. Emulsions are classified into two types. Direct emulsions or emulsions of the 1st type are known as "oil in water": hydrophobic substance is a dispersed phase, while hydrophilic substance is a dispersed medium. Indirect emulsions or emulsions of the 2nd type are known as "water in oil": hydrophilic substance is a dispersed phase, while hydrophobic substance is a dispersed medium.

Emulsions are also classified into dilute (less than 0.1 % of dispersed phase by mass), concentrated (from 0.1 to 74 % of dispersed phase by mass), and highly concentrated (more than 74 % of dispersed phase by mass). Since the size of drops of the dispersed phase is large, they are instable. Those drops are prone to settle down (if their density is higher than the density of the dispersed medium) or to bob up (if their density is lower than that for dispersed medium). This kind of instability is known as sedimentation instability. Moreover, smaller drops are prone to fuse with each other into bigger ones. This process is known as coalescence. This kind of instability is known as aggregative instability.

To estimate the stability of an emulsion one can use the rate of separation: the ratio between the height of the column of a given emulsion and the time required for its complete separation into two phases. Under the microscope one can also find out the average time of life for a single drop of emulsion.

Emulsifier is a substance that stabilizes emulsion. Emulsifiers are usually surface active substances, biopolymers or insoluble powders. Surface active substances decrease surface tension on a border between dispersed phase and dispersed medium. That is why the size of drops stays relatively small in emulsions stabilized by a surface active substance. Biopolymers usually act as substances that sterically prevent coagulation of drops. Stable

emulsions are formed when emulsifier is soluble in the dispersed medium or when it is at least wetted by it.

It is known that sodium oleate stabilizes drops of hydrophobic liquid in the hydrophilic one. In contrast, calcium oleate stabilizes drops of hydrophilic liquid in the hydrophobic medium. Indeed, emulsifiers that are soluble in water better than in oil generally form oil-in-water emulsions (they stabilize drops of oil), while emulsifiers that are more soluble in oil form water-in-oil emulsions (they stabilize drops of water). Calcium oleate is really insoluble in water, unlike sodium oleate. In general, calcium salts are known to stabilize water in oil emulsions, since calcium ions form calcium oleate with oleic acid. In contrast, sodium and potassium salts stabilize oil in water emulsions because of formation of sodium or potassium oleate.

To predict whether each surface active substance is more hydrophilic or hydrophobic (lipophilic), one may use a special index that is called hydrophilic-lipophilic balance. The higher the value of this index, the more hydrophilic is the molecule. The formula for calculation of that index includes the sum of indexes for all the hydrophobic groups (each of them is negative) and the sum of indexes of all the hydrophilic groups (each of them has a positive sign), as well as seven (from table 5.1).

HLB = 7 + Σhydrophobic groups + Σhydrophilic groups

Table 5.1

Indices of hydrophilicity and lipophilicity for certain functional groups of organic substances

Hydrophilic groups	Indices	Lipophilic groups	Indices
$–SO_3Na$	38.7	$–CH_2–$	–0.475
–COOK	21.1	$–CH_3$	–0.475
–COONa	19.1	–CH=	–0.475
=N	9.4	$–(CH_2–CH_2)–O–$	–0.150
–COOH	2.1		
–OH	1.9		
–O–	1.3		

This method is quite empiric, but it helps to choose an appropriate emulsifier. The table with indices for certain groups is provided below.

For example, for sodium oleate the HLB index is equal to 18, while for oleic acid it is just 1.

Direct emulsion can be converted to indirect one and vice versa, in case of the change of emulsifier. For example, one can add calcium chloride to the direct emulsion stabilized by potassium oleate and turn it to indirect one because of the formation of calcium oleate.

Foam is a highly concentrated coarsely dispersed system with gaseous dispersed phase and liquid or solid dispersed medium. Foams may be open-cell or closed-cell ones. In the last type each bubble of the gas is isolated from others. To characterize the stability of a foam one can use such parameter as the time during which the volume of foam reduces two times (a half-life of foam), as well as the ratio between the volume of foam and

the volume of liquid from which it has been formed (the multiplicity of the foam). In the last case one should divide the volume of foam by the difference in volumes of the initial and the remaining liquid.

Substances that increase the stability of a foam are known as foam makers. Among them there are surface active substances and biopolymers. Ionogenic surface active substances create double electric layers in films of a foam (in thin liquid walls of bubbles). Noninogenic surface active substances and polymers (namely, proteins) form adsorption layers in those films.

Aerosols are colloid or coarsely dispersed systems with the air as a dispersed medium and liquid (fog) or solid (smoke, dust) substance as a dispersed phase. Aerosols are characterized by high level of sedimentation and aggregation instability. Aerosols demonstrate optical properties of colloid solutions when their particles or bubbles have appropriate sizes. Aerosols demonstrate such property as thermophoresis: their particles move towards the area with lower temperature because they are pushed by hot molecules of the medium away from the source of heat. Particles of aerosol precipitate on cold surfaces. Photophoresis is the movement of aerosols under the influence of direct light. In case of direct photophoresis the particles are rejected by photon impulses and move in the same direction as the beam of light. Indirect photophoresis may be positive or negative. If the particles absorb light well, positive photophoresis occurs. The "light" sides of particles are becoming hotter than "dark" sides and they increase the energy of surrounding molecules of the medium to higher levels. Because of this the molecules of the medium are pushing the "light" side more frequently and more intensive than they push the "dark" side. As a result, aerosol migrates together with the beam of light. In case if the particles adsorb light weakly, they will move towards the source of light: their "dark" sides will be pushed by molecules of the medium.

Particles of aerosols lack double electric layer. However, they possess a charge due to the tension and adsorption of ions of gases. So, the charge may be different (by both sign and magnitude) for different particles in the same aerosol.

One can destroy emulsion, foam or aerosol in several different ways. Emulsions and foams can be destroyed by the addition of inorganic acids or salts of monovalent metals, by the addition of another emulsifier with a higher surface activity, by the addition (and change) of solvent. Anyway, all these actions have the same aim that is to disturb relationships between emulsifier, dispersed phase and dispersed medium.

Physical methods of emulsion destruction are: heating, centrifugation and filtration. To destroy an aerosol one may use the method of condensation of water vapor in the medium of aerosol. Aerosols can be destroyed by other aerosols if they are mixed together. They can also be destroyed by ultrasound.

Powders are coarsely dispersed systems made from solid dispersed phase and the air as the dispersed medium. The size of particles in powders is rather large (10^{-7}–10^{-4} m, that is

between 100 nm and 0.1 mm). Powders demonstrate a property that is called flowability: particles of powders are free (they are not connected with each other), they can move under the influence of external force. Powders are quite hygroscopic. Their hygroscopic properties may be modulated by surface active substances. Powders can be granulated: particles can form conglomerates of approximately same size with the shape of a ball or cylinder.

Suspensions are coarsely dispersed systems with solid particles and liquid dispersion medium. These systems are unstable and prone to sedimentation and flotation. Unlike sols, suspensions do not demonstrate opalescence and Tyndall effect, they are cloudy and opaque.

Sedimentational analysis is used for the determination of size of particles in suspensions. One needs to measure the mass of particles that settle down from suspension during the certain period of time. To make it one needs to immerse a scalepan into the suspension and calculate the difference in weight between two points in time. The resulting value is the rate of sedimentation that is determined by the size of particles (r) according to the formula given below.

$U = (2r^2(\rho - \rho_0) \cdot g)/(9 \cdot \eta)$

In this formula ρ is the density of dispersed phase, ρ_0 is the density of dispersed medium, g is the gravity acceleration, η is the viscosity of dispersed medium. Highly concentrated suspensions are known as Pastes.

Surface active substances may be completely miscible with water. Such molecules usually have relatively short hydrophobic parts (ethanol, acetic acid, ethylamine, sodium acetate). Surfactants with longer hydrophobic parts (with a length of 10–20 carbon atoms) are known as colloid surfactants, since they can form colloid particles at certain concentration. Such colloid surfactants may be ionogenic (cationic, anionic, or ampholytic) or noninogenic. Since colloid noninogenic surfactants usually demonstrate lower solubility in water than ionogenic ones (if their hydrophobic parts are identical), noninogenic surfactants are starting to form micelles at lower concentration than ionogenic ones.

The concentration of surfactant at which it starts to form micelles is called the critical micelle concentration. As one can see in figure 5.4, colloid surfactant decreases the surface tension of a solution until a certain limit. After that moment surface tension stays the same after the increase of concentration of surfactant, and real solution turns to sol. Micellization is a spontaneous process, it is associated with the decrease of Gibbs energy in a system. This process is reversible. The value of Gibbs energy of micellization is approximately equal to the $RTln(C_{micellization})$. One can estimate the critical micelle concentration by the way of the monitoring of electric conductivity, osmotic pressure and surface tension. Electric conductivity (as well as osmotic pressure) starts to decrease faster after the start of micellization because of the formation of diffuse layer on the surface of micelles: adsorbed ions are losing their mobility.

Critical micelle concentration (CMC) depends on the length of hydrophobic part of surfactant (the longer that part, the lower the CMC), on the nature of the polar group of

surfactant, on the presence of electrolytes in a solution, on temperature (the lower the temperature, the lower the CMC).

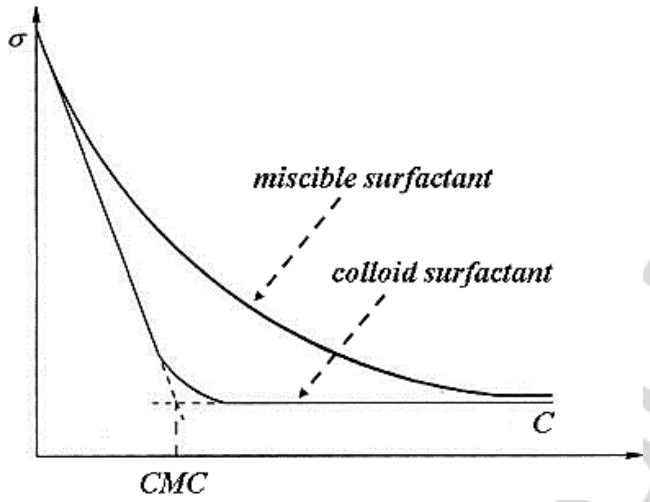

Figure 5.4. Schematic plots of the dependence between surface tension and concentration for completely miscible and colloid surfactants

Schematically the structure of the micelle can be represented in the way that is similar to inorganic micelles. Let us analyze the scheme of sodium oleate micelles.

$\{[m(C_{17}H_{33}COO^{-}) \cdot (m–x)Na^{+}] \cdot xNa^{+}\}$

These micelles are surrounded by sodium cations from the side of water. Some of them form adsorption layer, while others are in the diffuse layer. That is how diffuse layer of sodium cations stabilizes those micelles from coagulation.

Solutions of colloid surfactants (with micelles) are able to solubilize insoluble substances. Surfactant is called a solubilizator, while the dissolved substance is called a solubilizate. The solubilization ability depends on the length of hydrophobic part of a surfactant and on its concentration, on molecular mass of a solubilizate and its polarity. Solubilization capacity (S) is the ratio between the number of moles of solubilized substance and the number of moles of surfactant in micelles.

Micellar solubilization is the process that takes place during laundry washing with detergents. Those detergents are adsorbed on a surface of water. Hydrophobic tails of those molecules are looking outside the water. Water gets in contacts with the solid surface covered by a hydrophobic dirt. Of course, hydrophobic tails interact with the dirt (they get deeper inside it), and it becomes surrounded by a micelle. That is how hydrophobic dirt acquires a hydrophilic coat made from polar heads of a surfactant (figure 5.5). Then such micelle gets inside the water to be washed away together with the captured dirt.

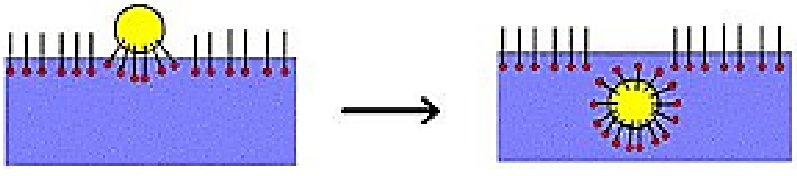

Figure 5.5. The scheme of solubilization by a colloid surfactant with the formation of a micelle

Micelles of colloid surfactants may solubilize both absolutely hydrophobic and amphiphilic substances. Absolutely hydrophobic ones get inside the micelle (figure 5.5) and interact with hydrophobic tails of surfactant molecules only. If noninogenic surfactant is forming a micelle, hydrophobic substances may not even get inside them, but they can be adsorbed on the surface. Amphiphilic substances join the layer of surfactant molecules: hydrophilic heads are interacting with water, while tails are interacting with similar parts of surfactant molecules.

Coarsely dispersed systems are widely used in pharmacology. For example, direct emulsions are used for oral administration, while indirect emulsions are used for external applications (on a skin). Suspensions are administered via injections. Aerosols can be simply inhaled. Foams are used for external applications for the healing of wounds and burns. Ointments, gels and powders are also used for external applications on skin and mucosa. Hemostatic sponges are used to stop bleeding. They are nothing but solid foams with adsorbed coagulants that induce a platelet adhesion and clot formation.

Problems

1. The diffusion coefficient of colloidal gold is $2.7 \cdot 10^{-5}$ m^2/day at 285 K and the viscosity of the medium is $1.21 \cdot 10^{-3}$ $N \cdot s/m^2$. Calculate the radius of colloidal gold particles.

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2. Determine the sedimentation rate of particles formed after grinding coffee with a radius of $1 \cdot 10^{-6}$ m in water ($\eta = 1 \cdot 10^{-3}$ $N \cdot s/m^2$) and in air ($\eta = 1.8 \cdot 10^{-5}$ $N \cdot s/m^2$). The density of coffee is $1.1 \cdot 10^3$ kg/m^3, the density of water is equal to $1 \cdot 10^3$ kg / m^3, the density of air is 1.025 kg/m^3. How many times the rate of settling down of coffee particles in the air is higher than the rate of their settling down in water?

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3. The coefficient of diffusion of milk sugar in water at 291 K is $3.94 \cdot 10^{-5}$ m^2/day. The water viscosity is $1.06 \cdot 10^{-3}$ $N \cdot s/m^2$. Calculate the radius of the molecule (m) and the molar mass of this organic substance. The density of cane sugar is $1.542 \cdot 10^3$ kg/m^3. Compare the obtained value of the molar mass to the theoretical value (M = 324 g/mol).

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4. The diffusion coefficient of maltose in water at 291 K is $3.92 \cdot 10^{-5}$ m^2/day. The water viscosity is $1.06 \cdot 10^{-3}$ $N \cdot s/m^2$. Calculate the radius of the molecule (m) and the molar mass of that organic substance. The density of maltose is $1.540 \cdot 10^3$ kg/m^3. Compare the obtained value of the molar mass with the theoretical value (M = 342 g/mol).

5. Determine the specific surface area of the barium sulfate powder (m^2/kg) if its particles settle down in an aqueous solution from a height of 0.226 m in 1350 s. The particles have a spherical shape. Barium sulfate density is $4.5 \cdot 10^3$ kg/m^3, water density is $1 \cdot 10^3$ kg/m^3, water viscosity is $1 \cdot 10^{-3}$ $N \cdot s/m^2$.

6. Determine the osmotic pressure of the colloidal copper solution at 19 °C if the mass concentration of the copper sol particles is 0.084 kg/m^3, the length of the rib of the cubic particle is equal to $1.35 \cdot 10^{-9}$ m, the density of copper is $8.93 \cdot 10^3$ kg/m^3.

7. Calculate the size of silicon dioxide particles if it is known that the time of their settling down at a distance of 10^{-2} m is equal to 60 minutes. The density of the dispersed phase is $2.7 \cdot 10^3$ kg/m^3, the density of dispersion medium is $1 \cdot 10^3$ kg/m^3, and the viscosity of the medium is $1.5 \cdot 10^3$ Pa·s.

8. Calculate the radius of the particle of the gold sol, if it moved by $1.065 \cdot 10^{-5}$ m in 60 s at a temperature of 20 °C and viscosity of the medium is $1 \cdot 10^{-3}$ $N \cdot s/m^2$.

9. The average displacement of colloid particles of platinum was $6.2 \cdot 10^{-6}$ m in acetone at 17 °C in 16 s. The viscosity of acetone at a given temperature is $3.2 \cdot 10^{-4}$ N·s/m^2. Calculate the radius (m) of particles of platinum sol and their diffusion coefficient (m^2/s).

10. Electrophoresis of the $Fe(OH)_3$ sol was carried out under the following conditions: potential difference between electrodes is 150 V; distance between electrodes is 30 cm; the particles migrated to the distance of 24 mm in 20 minutes. Calculate the ξ-potential of the sol particles if the dielectric constant for water is 81 and the viscosity is 0.001 N·s/m^2. The shape of sol particles is cylindrical.

11. Calculate the gradient of potential if the ξ-potential of the sol $Fe(OH)_3$ = 52.5 mV, the rate of movement of particles during electrophoresis is $3.74 \cdot 10^{-4}$ cm/s, the viscosity of the medium is 0.001 N·s/m^2, the dielectric constant is 81. The shape of particles is cylindrical.

12. Calculate the rate of movement and electrophoretic mobility of colloid platinum particles if the ξ-potential of the particles is 60 mV, the difference of potential between electrodes is 240 V, the distance between electrodes is 20 cm, the viscosity is $1 \cdot 10^{-3}$ N·s/m^2, the dielectric constant is 81. The shape of the particles of sol is cylindrical.

13. Electrophoresis of the $Fe(OH)_3$ sol was carried out under the following conditions: potential difference between electrodes is 150 V; distance between electrodes is 30 cm; the particles migrated to the distance of 24 mm in 20 minutes. Calculate the ξ-potential

of the sol particles if the dielectric constant for water is 81 and the viscosity is 0.001 $N \cdot s/m^2$. The shape of sol particles is cylindrical.

14. Calculate the gradient of potential if the ξ-potential of the sol $Fe(OH)_3$ = 52.5 mV, the rate of movement of particles during electrophoresis is $3.74 \cdot 10^{-4}$ cm/s, the viscosity of the medium is 0.001 $N \cdot s/m^2$, the dielectric constant is 81. The shape of particles is cylindrical.

15. Calculate the rate of movement and electrophoretic mobility of colloid platinum particles if the ξ-potential of the particles is 60 mV, the difference of potential between electrodes is 240 V, the distance between electrodes is 20 cm, the viscosity is $1 \cdot 10^{-3}$ $N \cdot s/m^2$, the dielectric constant is 81. The shape of the particles of sol is cylindrical.

16. The emulsion is obtained by the way of the mixing of equal volumes of oil and water with the addition of K_2CO_3 solution. Determine the type of this emulsion and indicate what type of emulsion we would obtain in the presence of $CaCl_2$ solution.

17. The emulsion is obtained by the way of the mixing of equal volumes of sunflower-seed oil and water in the presence of calcium chloride. Indicate, if the drop of this emulsion will combine with water drop. Explain your answer.

18. Determine the relative stability of the emulsion, if the following results were obtained: the height of the emulsion column (h) was 75 cm; after 10 seconds the height of the column of the exfoliated phase was 5 cm. Determine the lifetime of the emulsion (τ).

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19. A foam was formed from 200 ml of a liquid soap solution which, together with the remaining liquid of 50 ml volume (V_{rem} = 50 ml), occupied a volume of 500 ml (V_{total} = 500 ml). Determine the multiplicity of the foam and its stability ($\tau_{1/2}$) if the phase separation rate (U) is 1.5 ml/s.

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20. Indicate which of the following compounds are colloid surfactants:

a) $CH_3CH_2CH_2CH_2OH$; b) $C_{15}H_{31}COONa$; c) $CH_3CH_2CH_2NH_2$;
d) $C_{12}H_{25}OSO_3Na$; f) CH_3COOH; g) $n–C_8H_{17}C_6H_4SO_3Na$;
h) $[C_{18}H_{37}NH_3]^+Cl^-$; i) C_6H_5OH; j) $C_{17}H_{33}COOH$

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21. Draw a diagram of the inclusion of: a) benzene in the micelle made from ionogenic colloid surfactant; b) polar organic substances insoluble in water (long-chain fatty acids, amines, alcohols) into the micelle made from ionogenic colloid surfactant.

22. For two colloid surfactants the numbers of CMC were established experimentally: $2 \cdot 10^{-6}$ mol/L and $3 \cdot 10^{-4}$ mol/L. What conclusions can be drawn on the basis of this: a) the nature of the surfactant (ionogenic or non-ionogenic); b) the length of the hydrophobic part of surfactant molecules?

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CHAPTER 6
BIOPOLYMERS AND THEIR SOLUTIONS

Main topics of the chapter:

1. Classification of biopolymers.

2. Crystal and amorphous states of biopolymers.

3. Thermodynamics of the dissolving of proteins.

4. Isoelectric point.

4. Viscosity of biopolymers solutions.

5. Osmotic pressure of biopolymers solutions.

Solutions of biopolymers are unique systems that somehow evolved into systems that can reproduce themselves and maintain the life. Those solutions have some similar features with real solutions of inorganic substances and some features that makes them similar to colloid solutions. Real solutions of biopolymers are monomolecular (or oligomolecular), lyophilic, thermodynamically stable and reversible systems.

Historically, solutions of biopolymers have been classified as colloid solutions. Indeed, they demonstrate several common properties:

1) molecules of biopolymers are in the permanent movement (Brownian movement), just like micelles of inorganic sols;

2) solutions of biopolymers demonstrate low diffusion rate and low osmotic pressure compared to real inorganic solutions of the same mass even at high mass percentage of a solute;

3) solutions of biopolymers coagulate at high concentration of electrolytes and with the change in temperature;

4) molecules of biopolymers cannot passively pass through cell (semipermeable) membrane;

5) sizes of particles for sols (1–100 nm) and solutions of biopolymers (10–100) are almost the same.

However, solutions of biopolymers have several distinctive properties compared to sols:

1) solutions of biopolymers are much more stable;

2) solutions of biopolymers are formed spontaneously in the absence of stabilizers;

3) the portion of an electrolyte necessary to salt out a biopolymer is usually several hundred times higher than the portion required to salt out a sol with the same mass percentage of dispersed phase;

4) after the salting out process, biopolymers can be dissolved again in a pure solvent.

These distinctive properties have previously been explained by the high affinity of the dispersed phase (biopolymers) to the solvent (water). That is why those solutions were called “lyophilic sols”. Nowadays, that name is inappropriate, since solutions of biopolymers are not making micelles, and so they are definitely not sols. In other words, there is no separate phase in solutions of biopolymers and there is no real surface of contact

between two phases. It means that solutions of biopolymers are homogenous — they are real, and not colloid solutions. However, frequently biopolymers exist as oligomers (dimers, tetramers, octamers) in water solutions. Just like micelles in solutions of colloid surfactants, the most of the proteins have relatively hydrophobic cores.

Biopolymer can be defined as the molecule made from identical or different subunits connected with each other by chemical bonds into linear or branched structure of a high molar mass 10^4–10^6 g/mol.

Each subunit in a biopolymer corresponds to the monomer. Monomers are individual substances that can react with each other and form a polymer. The number of subunits in a given molecule of a biopolymer is known as the degree of polymerization (n). That value is not something constant for artificial biopolymers. That is why an average molar mass of a biopolymer is used for mixtures of chains of a different length and content.

There are two processes resulting in the formation of a biopolymer: polymerization and polycondensation.

The process of polymerization is characterized by the absence of any subproducts. This process is possible if monomers with double or triple bonds react with each other. Double (or triple) bonds in monomers turn to single (double, or aromatic) bonds between subunits. For example, 1,3-butadiene polymerizes into polybutadiene (an artificial rubber); vinylchloride polymerizes into polyvinylchloride.

$n CH_2=CH–CH=CH_2 \rightarrow (–CH_2–CH=CH–CH_2–)_n$

$n CH_2Cl=CH \rightarrow (–CH_2Cl–CH–)_n$

Polymerization is an addition reaction.

Polycondensation is a process in which subproducts are formed along with a biopolymer. Functional groups of monomers react with each other, join each other and release small molecules like H_2O, NH_3, HCl, etc. For example, polyethylenetherphtalate is a heteropolymer joined by ester bonds between therephtalic acid carboxyl groups and ethyleneglycol hydroxyl groups. Formation of each ester bond is associated with the release of one water molecule.

Usually, biochemists use the term “polymerization” for both polymerization and polycondensation processes. For example, we say “DNA polymerase” and “polymerize chain reaction (PCR)”, while the process of DNA synthesis is obviously a polycondensation process: subproducts are water molecules and pyrophosphate anion.

There are several classifications of biopolymers that are complementary to each other. According to their origin, biopolymers are classified into natural, artificial and synthetic.

Natural biopolymers are the products of metabolism of different species of life (prokaryotes, eukaryotes, viruses). Among these biopolymers we must mention nucleic acids (DNA and RNA), proteins, polysaccharides, natural rubber, and silk.

Artificial biopolymers are the products of chemical modification of natural biopolymers. The modification should not influence significantly the nature of bonds between subunits. The modification affects just some functional groups of subunits. For example, cellulose

(natural biopolymer) can react with acetic acid anhydride and form triacetate of cellulose (artificial biopolymer) in which the remains of acetic acid make ester bonds with hydroxyl groups of β-glucose (a monomer of cellulose). Cellulose can also be modified in the reaction with nitric acid. The artificial biopolymer formed in this reaction is trinitrocellulose.

Synthetic polymers have no analogues in nature. That is why it is better to refer to them as to just "polymers" and not "biopolymers". They are produced industrially from different chemical substances (mostly from components of natural oil and gas). Among them we can mention polyethylene, polypropylene, nylon, capron, teflone, lavsan.

Biopolymers can be classified according to the chemical content of their backbone:

a) carbocentric polymers contain just carbon atoms in their backbone. The samples are polypropylene and natural rubber, also known as polyisoprene or poly-2-methyl-1,3-butadiene.

b) heterochain polymers contain in their backbone atoms other than carbon (usually oxygen or nitrogen), just like proteins, polysaccharides and some synthetic polymers like capron. The last one contains amide bonds in the backbone, just like proteins do.

From another point of view, polymers can be classified according to the number of types of their monomers:

a) homopolymers are made from the same type of a monomer. For example, amylose is made from α-glucose only.

b) co-polymers are made from two or more types of monomers. Among synthetic polymers we can mention rubber made from 1,3-butadiene and styrene, and rubber made from 1,3-butadiene and akrylonitrile. Among natural polymers we can mention nucleic acids (they are made from four types of monomers) and proteins (they are made from 20 monomers).

Co-polymers are classified according to the sequence of subunits in their chains:

a) random co-polymers do not have permanent repeating sequence of subunits;

b) alternating polymers have a permanent repeating sequence of subunits;

c) blocked co-polymers have linear molecules made from long sequences (blocks) that differ from each other by the content and structure;

d) grafted co-polymers are branched molecules with branches that are different from the backbone (table 6.1).

Table 6.1

Schemes of the structure of different types of polymers

Polymer type	**The scheme of the structure of macromolecule**
1. Homopolymer	–A–A–A–A–A–A–A–A–A–A–A– or $(–A–)_n$
2. Co-polymer (binary)	
a) random	–A–B–B–A–B–A–A–B–A–B–B–
b) alternating	–A–B–A–B–A–B–A–B–A–B–A–B–
c) blocked	–A–A–A–A–A–A–A–A–B–B–B–B–B– or $–(A)_n–(B)_m$
d) grafted	–A–A–A–A–A–A–A–A–A–A– | | $(B)_n$ $(B)_m$

4. According to the topology polymers are classified into the following types:

linear — there is just one non-branched backbone of such polymers (the samples are cellulose and amylose);

branched — there are branches connected with the backbone of such polymer (the sample is amylopectine);

cross-linked polymers are made from numerous backbones connected together by linkers (the sample is ebonite).

Specific properties of biopolymers are determined by two main causes.

1. There are two types of bonds in polymers: covalent bonds exist between subunits in every chain, as well as inside each subunit (their energy is in the range of hundreds of kJ/mol), and weak bonds exist between different chains, or between subunits of the same chain (their energy is in the range of dozens of kJ/mol or even less).

2. The chains of polymers are flexible, since rotations of their subunits are allowed. Because of this, polymers may adopt different conformations. It is important to highlight that the term “conformation” is different from the term “configuration”. The last one is used to describe different forms of the same molecule if the transition between them is possible due to the destruction of some old covalent bonds and the formation of new covalent bonds. Transition between different conformations doesn’t require destruction of covalent bonds: only weak bonds are rearranged (Van der Waals bonds and hydrogen bonds).

Exactly for proteins the change in conformation may be associated with the change in secondary structure. There are two main types of secondary structure in proteins: alpha helices and beta strands. Both of them are characterized by a specific pattern of hydrogen bonding between –NH and C=O groups from peptide bonds.

In alpha helices hydrogen bonds exist between –C=O group of i-th residue and –NH group of “i+4”th residue. At least two bonds like this must exist to make a shortest alpha helix made from four amino acid residues. However, usually alpha helices have a length of 10–16 residues. Amino acids in alpha helices are packed compactly. In beta strands the packing is not so tight. That is why beta strands are sometimes called extended strands. At least two beta strands are necessary to make a beta structure. In such structure –NH groups from one strand make hydrogen bonds with –C=O groups from another strand, and vice versa (figure 6.1). Beta structure may be parallel or antiparallel. Several beta strands can form together a beta sheet (a planar beta structure), or a kind of tube that is called beta bundle. According to the 3-type classification of secondary structure, the parts of polypeptide chain that are not forming alpha helices or beta strands are called “random coil”. Hydrogen bonds between main chain atoms exist in random coil, while they are not arranged in a specific pattern (they are random).

Some proteins change their conformation in certain conditions. That kind of change may affect just a short fragment of a protein, or the most of the protein. For example, human prion protein is well known for its ability to change its mostly alpha helical conformation

into the mostly beta structural conformation. Beta structural prion proteins are infectious: they can cause the same kind of alpha–beta transition in normal prion proteins and make beta structure between different molecules of the same prion protein.

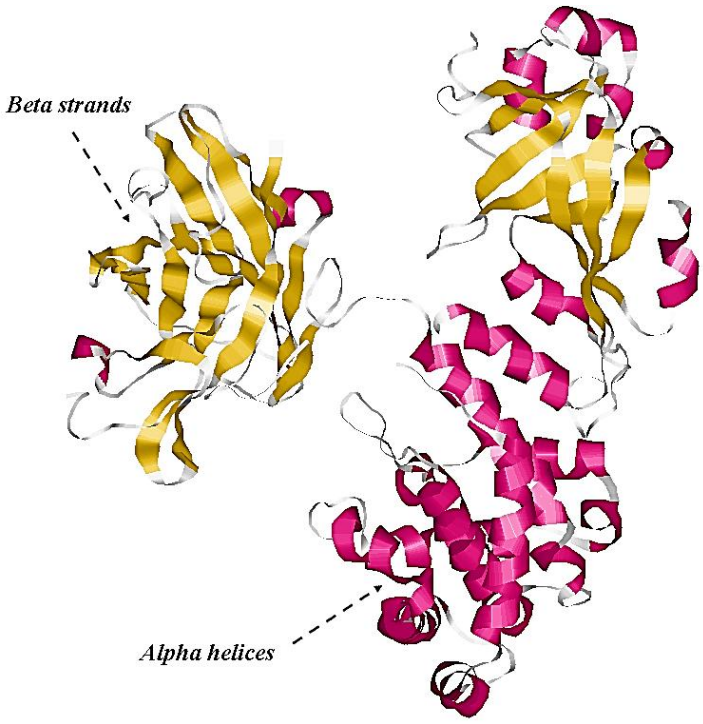

Figure 6.1. 3D-structure of diphtheria toxin that has beta-structural domain, alpha-helical domain and mixed domain

The possibility of the change of conformation depends on the thermodynamic potentials: usually ΔG is used for this purpose in calculations. Gibbs energy of the transition depends on the enthalpy and entropy of the process. One should also take into consideration a kinetic threshold for such transition: the energy of activation may be too high to make a conformational change possible.

Usually biopolymers adopt the shape of the globule: hydrophobic parts are hidden in the core of such globule, while hydrophilic ones are exposed on the surface and hydrated. An approximate radius of a globule of a polymer can be calculated with the formula written below.

$$r^0 = l\sqrt{n}$$

In this formula "*l*" is the length of a bond between two subunits, while "n" is the number of subunits in a chain (the degree of polymerization).

Since the molar mass of the whole polymer is directly proportional to the polymerization degree, we can use another formula for the calculation of approximate radius of a given polymer.

$$r^0 = K\sqrt{M}$$

In this formula M is the molar mass of a polymer, while K is the coefficient of proportionality that is specific for a given type of polymer.

The ratio between the real (experimentally determined) radius of a polymer and the calculated approximate radius shows the rigidity of polymer's chain. For polymers with flexible backbone this ratio is lower than that for polymers with rigid backbone. For example, for natural rubber this ratio is equal to 1.7, while for rigid nitrocellulose it is equal to 5.0.

The flexibility of the backbone of polymer depends on numerous variables. Among them we can mention the number of polar groups. If a solvent is polar, the higher the number of polar groups, the higher the rigidity of polymer's backbone: the most of the fragments of its chain are exposed to solvent. If a solvent is nonpolar, the dependence is opposite. Also, the higher the density of the matrix of a polymer, the lower the flexibility of its backbone. The growth of temperature leads to the decrease in flexibility.

Flexibility should not be confused with elasticity. The last one is the ability to be extended under the influence of a mechanical force, and to restore the previous shape when the force is no longer applied. Elasticity of polymers can be explained by their flexibility. So, there is a clear dependence between the structure of polymers and their physical properties.

Physical states of polymers are different from the regular set (solid, liquid and gas). Usually analogous states for polymers are called: crystalline, amorphous and gaseous. The last one is almost impossible for polymers at room temperature.

Crystalline polymers form regular supermolecular structures with all the chains existing in the same conformation.

In amorphous state polymers form numerous different supermolecular structures formed from chains existing in different conformations.

About 70–80 % synthetic polymers are produced in the crystalline state.

Amorphous state of a linear polymer has three different substates (figure 6.2). With the growth of temperature they are changing in the following order: glassy state, viscoelastic (rubbery) state and plastic (melt) state.

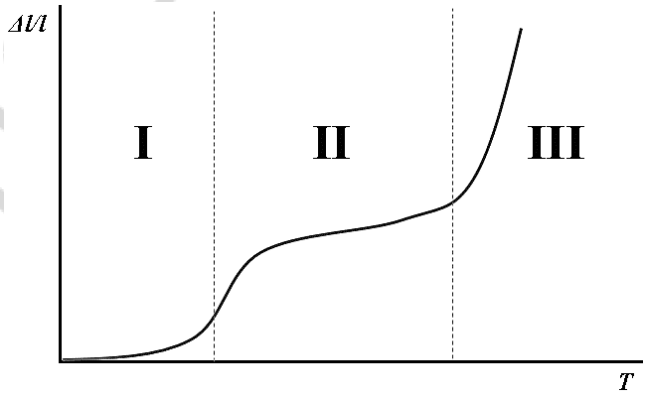

Figure 6.2. Thermomechanic curve for an amorphous polymer

In figure 6.2 one can see the dependence between relative deformation ($\Delta l/l$) on the temperature for a linear polymer. Relative deformation means the ratio between

the increase in length of a polymer over its initial length due to the application of a certain force. There are two phase transitions in the graph from figure 6.2: in the first part of the graph (I) polymer shows high resistance to deformation: it exists in the glassy state. At certain temperature (at the glass transition temperature) a polymer changes its glassy state to the viscoelastic state. In the viscoelastic state (II) polymer shows higher elasticity: it can restore its shape after the elongation. However, at higher temperature (at the temperature of melting) a polymer exists in the plastic state (III) when it acquires the ability to flow. Plasticity means the ability to be elongated irreversibly. Plastic polymer is no longer elastic.

In the glassy state the kinetic energy (E) of subunits is much less then the inner energy of the change in conformation (ΔU). Kinetic energy of a subunit is calculated according to the following equation.

$E = (3kT)/2$

In this formula k is the Boltzmann's constant ($1.38 \cdot 10^{-23}$ J/K), and T is the temperature in K.

In other words, in the glassy state the energetic threshold of the rotation (and the change in conformation) of subunits is rather high. So, chains cannot change their conformation $\Delta U >> (3kT)/2$.

At higher temperature the value of E is increasing, and it is becoming some higher than the value of ΔU for some fragments of chains. In this state some fragments of chains are able to change their local conformations. Polymer becomes viscoelastic: some fragments of its chains are able to change a conformation, while others are not.

In the plastic state the value of E is much higher than the value of ΔU through the whole length of polymer's chains. Because of this reason polymer can flow: chains are easily moving relative to each other. Moreover, deformations are irreversible in the plastic state. Polymers in plastic state are prone to slow plastic flow.

Thermomechanical curves for polymers of a different length are different (figure 6.3). The longer the length of a chain (the higher the molecular mass), the wider the range of temperature for the viscoelastic state. Indeed, relatively short polymers almost completely skip the elastic state: they may be either glassy, or plastic.

The temperature of glassy state formation shows a weak dependence on the length of chain. All four polymers from figure 6.3 have approximately the same temperature of the first phase transition. After this phase transition some chains are acquiring the ability to rotate, but not to move along. The longer the chain, the higher the number of bonds between different chains, the higher should be the kinetic energy to jump over the energetic threshold. Using the phase diagram of a polymer one can even approximately estimate the average length of its chains.

Polymers can form both real and colloid solutions. If a polymer is dissolved in the sufficient amount of a solvent of the same polarity as the one of that polymer, a real solution will finally be formed. If a polymer is dissolved in a solvent of a different polarity, then only colloid solution (sol) can be formed.

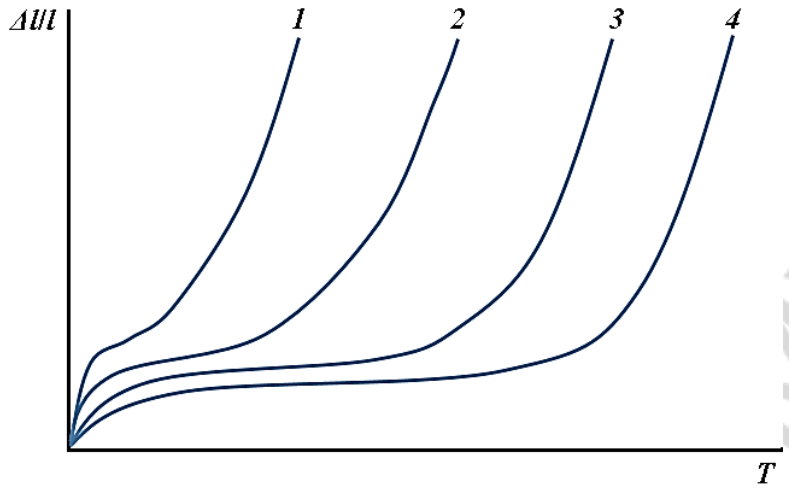

Figure 6.3. The dependence between relative deformation and temperature for polymers of a different length: n = 100 for the curve #1; n ≈ 1000 for the curve #2; n ≈ 10 000 for the curve #3; n = 60 000 for the curve #4

Because of the difference in the diffusion rates between small molecules of a solvent and large molecules of a polymer, the process of dissolving requires an additional intermediate step that is called swelling. The process of swelling is caused by the entrance of molecules of a solvent in the space between the chains of a polymer. Because of this the visible volume of a polymer is increasing, as well as the mass of solvated polymer. One can describe this process with the help of the swelling degree (the ratio between the difference in mass or volume and the initial mass or volume).

$a = \Delta m/m_0$ or $a = \Delta V/V_0$

During the swelling molecules of a solvent solvate (in case of water – hydrate) the fragments of chains of a polymer. This process is associated with the formation of bonds between polymer and molecules of a solvent. So, this process is exothermic. Moreover, the volume contraction takes place: the final volume of a swelled polymer is less than the sum of its initial volume and the volume of solvent that solvated it.

Polar solvents are good for the swelling of polar polymers, nonpolar solvents are good for the swelling of nonpolar polymers. Swelling may be limited or unlimited. If the swelling is limited, the volume of a polymer stops its growth after some period of time. If the swelling is unlimited, finally the real solution is formed. From the point of view of thermodynamics, the enthalpy of solvatation and the enthalpy of the formation of bonds between different chains of a polymer determine the heat effect of the whole process. That heat effect together with the entropy of the solvatation determines the Gibbs energy of this process at a given temperature.

The transition from the state 1 to the state 2 (figure 6.4) is associated with the release of heat ($\Delta H_{solvatation} < 0$) due to the solvatation of polymer chains. The entropy stays almost the same, since solvatation is associated with its decrease, but the disappearance of bonds between long chains of a polymer is associated with its increase ($\Delta S_{1,2} \approx 0$). The Gibbs

energy is determined mostly by the enthalpy at this step of the swelling. If the swelling proceeds, it means that the enthalpy of swelling is negative.

$\Delta G_{1,2} \approx \Delta H_{solvatation} < 0$

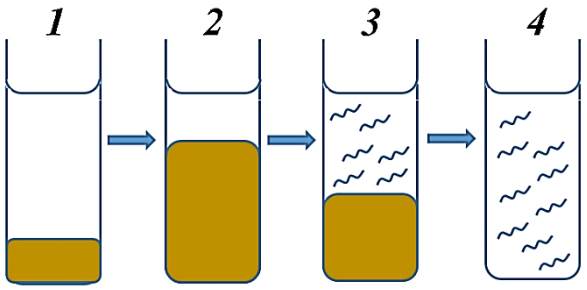

Figure 6.4. The dissolving of a polymer: swelling (1 and 2) and formation of a real solution (3 and 4)

The transition between the state 2 and the state 3 (figure 6.4) is characterized by the substantial increase in entropy, since molecules of a polymer are starting to spread through the whole volume of a solvent ($\Delta S_{2,3} > 0$). The enthalpy of this process is almost equal to zero ($\Delta H_{2,3} \approx 0$), since the chains are already hydrated. So, the value of Gibbs energy mostly depends on the difference in entropy and the current temperature.

$\Delta G_{2,3} \approx -T\Delta S_{2,3} < 0$

In general, the process of the dissolving of a polymer should be spontaneous, if the enthalpy of solvatation is negative, and the entropy of the formation of a real solution is positive.

It should be clear that polymers will dissolve only in those solvents that form numerous bonds with their subunits (to make overall ΔH of the swelling negative). So, "like dissolves like".

The process of the dissolving depends on the nature of a polymer. Some polymers are completely hydrophobic, while others possess some hydrophilic functional groups. Certain hydrophilic groups may become charged ones in water solutions. It happens because of protonation or deprotonation. So, a polymer that have such groups, is called polyelectrolyte, since one molecule of a polymer like that behaves as several units of electrolytes.

There are polymers that contain just acidic groups (–COOH, $–SO_3H$, –SH) that can act as donors of a proton. For example, oxidized starch contains carboxylic groups, while agar-agar contains sulfo groups. There are also polymers that contain just $–NH_2$ groups that can act as acceptors of a proton. All such polymers are synthetic. They are important for ion exchangers. The most of the polymers known as polyelectrolytes are polyampolytes: they contain both acidic and basic groups.

Polyampholytes include such important biopolymers as nucleic acids and proteins, as well as mucopolysaccharides of connective tissues. Nucleic acids are made from nucleotides. Each nucleotide is built from amine base, pentose and phosphate. There are four major amine bases in deoxyribonucleic acid (DNA) known as adenine, thymine, guanine and cytosine. Deoxyribose is used as a pentose in DNA. Deoxyribose units are

connected with each other by phosphodiester bonds: phosphate makes an ester both with 5’ OH group of one deoxyribose and 3’ OH group of another deoxyribose group. Because of this DNA is linear polymer. Moreover, two chains of DNA are connected together by hydrogen bonds between amine bases. Ribonucleic acid contains ribose instead of deoxyribose, uracil is used instead of thymine. RNA molecules form secondary structures because of the hydrogen bonds between amine bases from the same strand. Some viruses use doublestranded RNA as a replicative intermediate, others have doublestranded RNA in their virions.

Among mucopolysaccharides from connective tissues we can mention chondroithine-4-sulfate (with carboxylic and sulfo groups), hyaluronic acid, heparin. These polysaccharides are connected with proteins, they bind metal cations. Together, they are responsible of elasticity of tissues and organs.

Each protein is made of amino acids. Those amino acids are connected in a single chain (backbone) with the help of amide (peptide) bonds. There are 20 proteinogenic amino acids. They are all alpha amino acids. Side chains of those amino acids are quite different from each other. Some of them are just saturated hydrocarbons, others contain aromatic rings, hydroxyl group, sulfhydryl group, carboxylic group, amino group, guanidine group, amide group. So, they are different in terms of hydrophobicity, polarity, size and charge. That is why they can make many types of bonds with each other: hydrogen bonds, disulfide bonds, hydrophobic contacts, polar contacts, ionic bonds, aromatic — aromatic contacts, cation — pi contacts, sulfur — aromatic contacts.

Each protein has its unique definite structure. That structure is classified into the primary structure (the sequence of amino acid residues in a chain), secondary structure (the pattern of hydrogen bonds between –N–H and C=O groups of peptide bonds), tertiary structure (all other contacts between amino acid residues of the same chain), and even quaternary structure (it forms when two or more chains are connected together). Formation of such a complicated structure is thermodynamically favorable in a dry state. The overall enthalpy of the formation of hydrogen bonds and all other contacts is quite negative, so it compensates the decrease of entropy because of the formation of secondary, tertiary and quaternary structure. However, the most of the proteins in nature exist in water solutions. The structure of proteins changes significantly during the process of the dissolving. The bonds between different chains should be broken, while bonds between hydrophilic parts of each chain and water molecules should be formed during the process of the dissolving. The difference between the values of ΔH for these two processes, as well as the heat effect of the rearrangement of the structure of a protein, determines whether it is soluble or not.

It is known that the presence of electrolytes influences the process of swelling (and so the dissolving) of polymers.

The swelling degree of a protein decreases with the increase of hardness of Lewis acids and bases added to the solution.

According to the Lewis theory of acids and bases, hard acids contain electronegative atoms of a small radius and low polarizability that prone to gain lone electron pairs, while hard bases are also made of electronegative atoms with low polarizability that prone to donate lone pairs of electrons. Overall, acids are acceptors of lone electron pairs (they must have empty orbitals), while bases are donors of lone electron pairs. Instead of terms "strong" and "weak" acids and bases, Lewis decided to use terms "hard" and "soft". It was done to highlight that "strong" Arrhenius acid doesn't always mean "hard" Lewis acids.

If we arrange cations and anions in the order of the increase of their "hardness" as Lewis acids and bases, respectively, then we will create lyotropic series (figure 6.5).

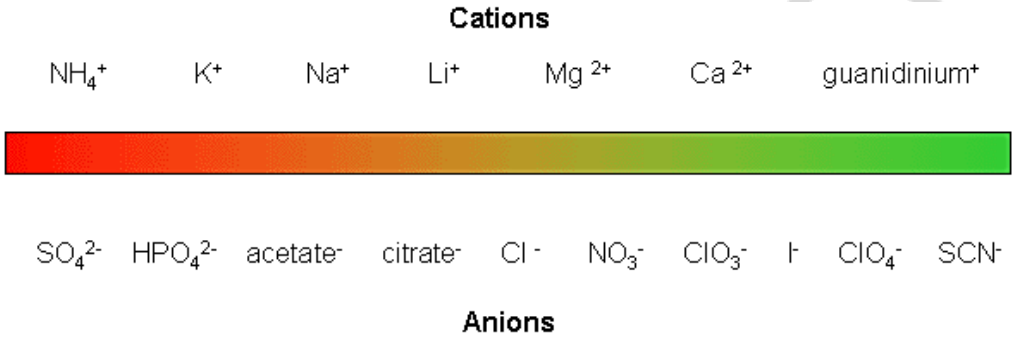

Figure 6.5. Lyotropic series of ions: the intense of the concurrence with proteins for water molecules is decreasing from left to right

Ions participate in the concurrence for water molecules with proteins. Hard Lewis bases (like F^-) and hard Lewis acids (like Li^+) are hydrated much better than soft Lewis bases (like I^-) and soft Lewis bases (like Cs^+). So, the smaller concentration of hard ones is enough to prevent the swelling of a protein. Interestingly, some ions promote the swelling of proteins. Such ions are bound by numerous sites on the surface of a protein. If such an ion makes a contact with certain part of a polypeptide, its hydrate coat becomes a common hydrate coat for the complex of that ion and protein. The most well known anion that promotes the swelling of proteins is thiocyanate (NCS^-).

One should understand that ions that are able to prevent swelling should be supplied at a high concentration to win the competition with proteins. In low concentrations even sulfate ions can help some proteins that have several appropriate binding sites to be dissolved in water.

The same series of ions can be used to estimate their ability to salt out proteins from their water solutions. The strongest salting out agents, according to the Figure 5.6, are NH_4^+ and SO_4^{2-} ions. That is why ammonium sulfate is usually used to salt out a protein. Those ions are also the best agents to prevent the swelling of a protein in water.

The influence of pH in water solution on the swelling degree is represented in figure 6.6. The swelling degree has the lowest value at the certain pH. At this pH a given protein has no overall charge: the total positive charge existing in some regions of a protein is equal to the total negative charge existing in other regions of the same protein. Because of

this, that kind of state is called isoelectric point. The value of pH at which a given protein exists in the isoelectric point is called pI.

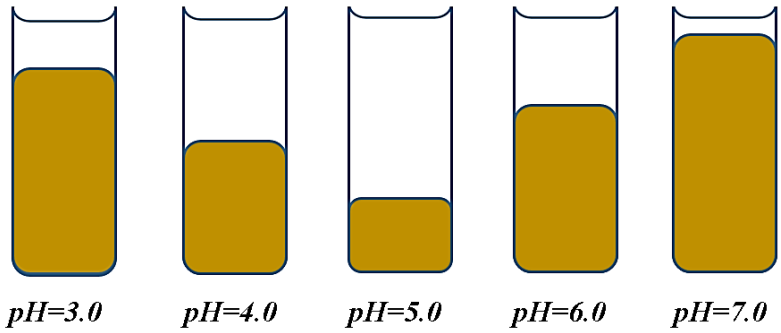

Figure 6.6. The influence of pH on the swelling of a protein with pI = 4.8

There are three amino acid residues that can acquire positive charge in the protonated state: lysine (with amino group in its side chain), arginine (with guanidine group in its side chain) and histidine (with imidazole nitrogen in its side chain). In addition to them, amino group from the N-terminus of a protein can also be positively charged. Nitrogen atoms from the abovementioned groups can be protonated in the relatively acidic medium (when the concentration of H^+ ions is high enough).

There are two amino acid residues that can acquire negative charge in deprotonated state: aspartic acid and glutamic acid. Both of them contain carboxyl group in the side chain. Additionally, each protein has one carboxylic group on the C-terminus. In relatively basic medium (at low concentration of H^+ ions) carboxylic groups are deprotonated. That is how protein acquires negative charge.

Ones again, at very low pH all proteins are positively charged, at very high pH they are all negatively charged. However, the pI is quite variable among different proteins. Its concrete value depends on the content of a protein. Proteins enriched by lysine and arginine have pI at basic pH. Proteins enriched by aspartic acid and glutamic acid have pI at acidic pH. Exact value of pI can be calculated from the set of pK values for all functional groups of amino acids able to be protonated or deprotonated. However, this theoretical pI may not be equal to the experimentally determined one. Some side chains of charged amino acids may not be exposed on a surface of a protein, even though they are hydrophilic. It happens when such hydrophilic amino acid is surrounded by strongly hydrophobic ones. Only those functional groups that are in contact with water really contribute into the charge of a protein and its pI.

In water solution with pH higher than pI a protein will gain negative charge. The higher the difference between pH and pI, the more negative will be the charge of a protein.

In water solution with pH lower than pI a protein will gain positive charge. the higher the difference between pI and pH, the more positive will be the charge of a protein.

Charged groups are hydrated better than uncharged (but polar) ones. This is one of the reasons why charged proteins are more soluble in water than those that have no charge.

The higher the magnitude of an overall charge, the better the solubility. In these conditions all the chains have the same charge through the most of their lengths. Electrostatic repulsions between different chains help a protein to be dissolved in water. In contrast, in the isoelectric point different parts of the same chain have different charges. Because of the electrostatic attraction between oppositely charged parts of different chains they stay together, even though they are partially hydrated. In general, at pI the enthalpy of formation of all the bonds between different chains of a protein is very high (by the module), so it overwhelms both the overall enthalpy of hydration and the entropic factor. Protonation and deprotonation of functional groups may lead to rearrangements in secondary and tertiary structure of each chain. These rearrangements also contribute into the swelling degree (and solubility) of proteins at different pH levels.

So, if we try to dissolve protein in buffers with different values of pH, we can say that the lowest degree of swelling will show us a solution with pH equal to pI. Vice versa, if we try to salt out a protein from its real solution, then it will precipitate from the solution with pH = pI at the lowest concentration of a salt.

The value of pI can also be determined by the electrophoresis. In this method uncharged molecules will not migrate in the polyacrylamide gel neither to anode, nor to cathode. Positively charged proteins will migrate to negatively charged electrode (cathode), while negatively charged proteins will migrate to positively charged electrode (anode). However, electrophoresis is mostly used with the aim to determine the molecular mass of a protein, and not its charge. In the SDS PAGE (sodium dodecyl sulfate polyacrylamide gel electrophoresis) proteins are treated by SDS and mercaptoethanol first. SDS binds proteins and brings them a negative charge, so all the proteins will have the same charge during the electrophoresis. Moreover, SDS acts as denaturant. Mercaptoethanol reduces all the disulfide bonds and breaks possible oligomers stabilized by these bonds. Finally, the proteins (actually, polypeptide chains) are separated according to their molar masses only: the heaviest shows the shortest migration path, the lightest shows the longest migration path. Only so-called native gel electrophoresis is based on a separation of proteins by both electric charge (pI) and molecular mass, since SDS and other denaturants and reducing agents are not used in this technique. With the help of native gel electrophoresis one can estimate molecular masses (actually, shapes and sizes) of protein complexes or oligomers of proteins with the same values of pI. To overcome the problem with different pI values, one can use a charged dye like Coomassie blue that will make the charges of all proteins identical, but will not cause their denaturation (this technique is called Blue native polyacrylamide gel electrophoresis).

The process that is opposite to swelling is called gelatinization. At low temperature real solutions of proteins make a gel. This phenomenon can be explained by the slowdown of the Brownian movement at low temperature that favors formation of interactions between different molecules of proteins. Because of these interactions protein and water molecules

form homogenous elastic system that is called gel. Once again, proteins are not completely dehydrated in gels. gelatinization of protein solutions is a reversible process: the increase in temperature and the addition of water shift the equilibrium towards real solution. Moreover, protein gels are relatively stable in time. They are not losing their elasticity even when they are dried.

However, gels are getting older. After some period of time the excess of water is released from the gel, and the system loses its homogeneity. This phenomenon is called syneresysis. First, water molecules that are not directly bound by protein are separated from the gel. Next, chains are getting closer to each other and in some parts they are losing water of hydration and starting to form direct contacts. As a result, the volume of gel is decreasing, but its shape stays the same. The process of syneresysis proceeds better at low temperatures.

Gels and real solutions of proteins and many other polymers demonstrate a property that is called thixotropy. After the shaking of gel it starts to flow: the viscosity of a system decreases in time and it turns to real solution. However, if a system is not agitated, viscosity starts to decrease in time again, and real solution turns back to gel. This phenomenon is explained by the existence of weak bonds between different chains of a polymer. Even in hydrated form they interact with each other, and some parts of those chains are making van der Waals bonds being not hydrated. These bonds keep the gel structured and elastic. Because of the agitation, interchain contacts become broken, and gel turns to real solution losing its elasticity. Then new similar interchain contacts are formed again.

On the way from gel to real solution, as well as on the way back, polymers can form coacervates. These structures are relatively large spherical particles (1–100 micrometers) that are similar to colloid droplets held together by hydrophobic forces. These structures behave like living cells under the microscope. That is why A. Oparin suggested that coacervation played an important role in early steps of the history of spontaneous life creation.

Solutions of polymers demonstrate high viscosity. Viscosity is expressed with the help of the coefficient of viscosity (η). It is known that different layers of liquid are moving at different speed in a capillary. The closer this layer to the center of a capillary, the faster it moves. The layer situated at the surface of capillary is not moving at all. This situation is known as laminar flow. At higher overall speed laminar flow is disturbed and it turns to turbulent flow (when different layers are mixed with each other).

Laminar flow is described by two main laws. The first one is the Newton's postulate that determines the force of viscous resistance of a liquid (F) with the following equation.

$F = \eta S(dV/dx)$

In this equation η is viscosity; dV/dx is the gradient of the flow; dV is the difference in speed of movement for two neighboring layers; d*x* is the distance between two layers; S is the area of a contact between two layers.

The second law is the law of Puazeil. It determines the amount of liquid (Q) passing through the tube (capillary).

$Q = (\pi r^4 P\tau)/(8\eta l)$

In this equation r is the radius of a capillary; *l* is the length of a tube; P is the difference in external pressure between two ends of a tube; τ is the time.

From this equation one can calculate viscosity. Viscometers, however, have constant values of the radius of capillary and the length of a tube. If we ignore the difference in pressures of columns of two liquids (water as a standard and water solution of a biopolymer), then the only thing we need to find the viscosity is the time of the outflow of water and the time of the outflow of tested solution. So, relative viscosity is equal to the ratio between the time of outflow for biopolymer solution and the time of outflow for water.

$\eta_{relative} = t_{biopolymer}/t_{water}$

To calculate the viscosity one needs to multiply the relative viscosity by the viscosity of pure water ($8.9 \cdot 10^{-4}$ Pa·sec).

These laws are not working if the flow is turbulent. They obey for real solutions and some colloid solutions, as well as for pure liquids if their flow is laminar.

Solutions of polymers demonstrate anomalous viscosity. Initial viscosity of solutions of polymers is higher than that for normal (Newtonian) liquids. With the growth of pressure viscosity of solutions of polymers decreases and reaches its lowest point. After that point it starts to increase because of the turbulence, just like the one for Newtonian liquids (figure 6.7). This phenomenon is explained by the high number of weak interactions between solvated chains of polymers. Because of them the solution is rather viscous. After the application of a pressure, chains are changing their chaotic orientation to the same regular orientation, the number of contacts between chains decreases, and the viscosity goes down.

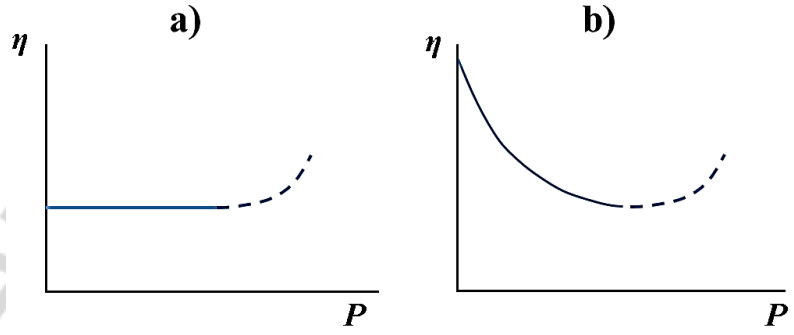

Figure 6.7. The dependence of the viscosity on pressure for pure liquids (a) and for solutions of polymers (b). Dotted lines correspond to turbulent flow

The higher the concentration of the solution of polymer, the higher its viscosity: chains are getting closer to each other and make more contacts. Interestingly, at high pressure solutions of polymers may behave like Newtonian liquids. It is possible when the chains are not connected with each other at all, but the flow is still laminar.

The increase in viscosity caused by the increase in concentration is called specific viscosity (η_y) that is calculated with the formula written below.

$\eta_y = (\eta_p - \eta_o)/\eta_o$

In this formula η_p is the viscosity of a solution, η_o is the viscosity of a pure solvent. For sols the dependence between viscosity and concentration is linear, while for solutions of polymers it is quite nonlinear (figure 6.8).

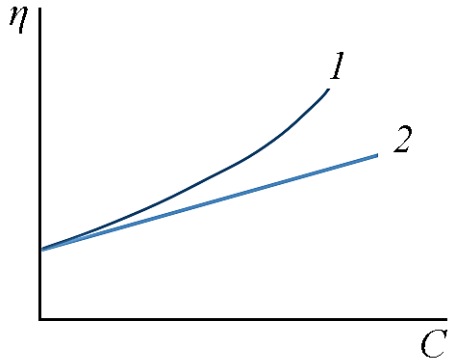

Figure 6.8. The dependence between viscosity and the concentration of polymer (1) and sol (2)

The same formula for specific viscosity calculation can be modified: we can change the values of viscosity by the times of outflow from the viscometer. Indeed, the time of outflow is directly proportional to the viscosity.

$\eta_y = (\tau_p - \tau_o)/\tau_o$

In this equation τ_p is the time of the outflow for polymer solution, τ_o is the time of outflow for a pure solvent (water) from the same viscometer.

There is a dependence between the specific viscosity (η_y) and molecular mass of a polymer found by Straudinger.

$\eta_y = KMc$

In this equation K is the constant for a given set of homologous polymers; c is the mass concentration of a polymer in a solution (g/ml); M is the molecular mass of a polymer.

Straudinger's equation can be re-written in the following manner.

$\eta_y/c = KM$

The value of "η_y/c" is known as reduced viscosity that is measured in ml/g (cm^3/g), since specific viscosity is dimensionless.

The highest possible value of reduced viscosity when the concentration is getting close to zero ($c \rightarrow 0$) shows the hydrodynamic resistance to the movement of molecules of polymer, and it is called characteristic viscosity [η].

$[\eta] = KM$

For long and flexible polymers the formula of Straudinger is modified in the following way.

$[\eta] = KM^{\alpha}$

In this equation, known as Mark–Hauwink–Kun equation, [η] is the characteristic viscosity; α is the value that depends on flexibility of chains. This variable is determined in experiments, and it can take values from 0.5 (if the shape of macromolecule is close to spherical) to 1 (for rigid molecules).

To get the values of K and α one need to arrange the set of viscosimetric experiments with several homologous biopolymers. After that Mark–Hauwink–Kun equation should turned into the logarithmic form.

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

The value of ln*M* should be plotted on X-axis, while the value of ln[η] should be plotted on Y-axis. In this case α is the slope of the linear dependence, while lnK is the value of ln[η] when ln*M* is equal to zero.

Some information on the flexibility of chains of a given polymer, and even on its shape, can be obtained in experiments on the measurement of the viscosity of its solution. However, at higher concentration polymers usually form associates that disturb the flow of the solution and make the formula of Straudinger inapplicable.

Solutions of the high viscosity flow very slow at extremely low gradients of pressure. This kind of movement is called “crawling”. At high pressure that kind of system decreases its viscosity and becomes pseudoplastic.

Systems with extremely high viscosity obey the Bingham’s law.

The equation of Bingham relates the viscosity of plastic and pseudoplastic systems and pressure.

$p = p_B + \eta(dV/dx)$

In this equation p is the applied pressure; p_B is the maximal applied pressure; η is the viscosity; dV/dx is then gradient of flow.

Viscosimetry helps to calculate the molar mass of a polymer. First, one should estimate the viscosity of a pure solvent. Then the viscosity of a solution should be determined. After that specific and relative viscosities are calculated. These operations are repeated for solutions of different concentration. Then relative viscosity is plotted against the concentration (figure 6.9). The direct line of the dependence is extrapolated to the Y-axis. Characteristic viscosity is the value of relative viscosity at c=0. So, one can estimate [η] graphically and use it for the calculation of molar mass ($M = [\eta]/K$) if the value of K is known.

The part of the osmotic pressure that occurs due to the presence of proteins is called oncotic pressure. The distribution of water between capillary and intercellular liquid is controlled by the oncotic pressure. The concentration of proteins is higher inside the vessels than outside them. That is why water returns back to the blood when the hydrostatic pressure (created by the heart muscle) decreases along the length of capillaries. Concentrations of other substances (except proteins) are almost same in the blood plasma and in the intercellular liquid.

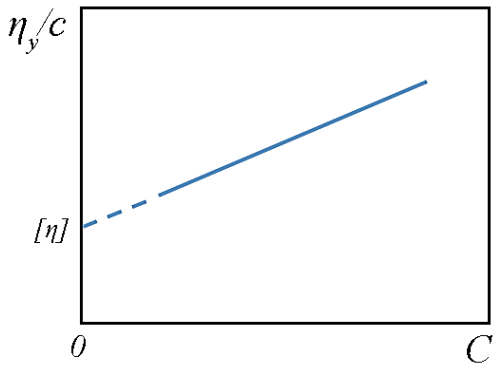

Figure 6.9. The dependence between η_y/c and c for a solution of polymer

Overall osmotic pressure of human blood plasma is about 7.7–8.1 atmospheres (780–821 kPa), while oncotic pressure is just about 0.04 atmospheres (4 kPa).

Osmotic pressure in solutions of proteins highly depends on pH and on temperature. The increase in temperature leads to the growth of osmotic pressure that is higher than theoretically calculated one. The explanation of this deviation is in the increase in dissociation degree for ionogenic groups of proteins and in the dissociation of aggregates and oligomers of proteins. Additional hydration of monomers (or smaller oligomers) increases the concentration of a solution because of the decrease of the amount of free solvent.

In the isoelectric point the degree of dissociation for ionogenic groups of a protein reaches its lowest value. Moreover, proteins tend to form aggregates at pI. So, the number of particles becomes much lower at pI, and so the osmotic pressure. If we move from pI in both directions, the osmotic pressure of a protein solution will grow.

It is known that the osmotic pressure in water solutions of proteins is higher than expected according to the formula $P_{osm} = CRT$. As one can see in figure 6.10, experimental curve of the dependence between osmotic pressure and concentration is getting higher and higher than the theoretical curve with the growth of molarity. Indeed, each chain of a protein behaves like many electrolytes. With the increase in concentration the number of free water molecules is decreasing drastically. These effects are considered in the Galler's equation for the osmotic pressure of polyelectrolytes (P_{osm}).

$P_{osm} = (RTc)/M + \beta c^2$

In the above written equation c is the mass concentration of a solution in g/L; M is the molar mass of a polymer (g/mol); β is the coefficient that considers flexibility and shape of a molecule in water solution.

The difference between Vant'Hoff's equation and Galler's equation is equal to βc^2. The value of β and the molar mass of a protein may be calculated from the plot built in the following coordinates: "P_{osm}/c" on the Y-axis and "c" on the X-axis. In this case the slope of the linear dependence is equal to β, while the value of osmotic pressure at the lowest possible concentration is calculated with the help of approximation. Then standard Van't Hoff's equation is used to get the molar mass.

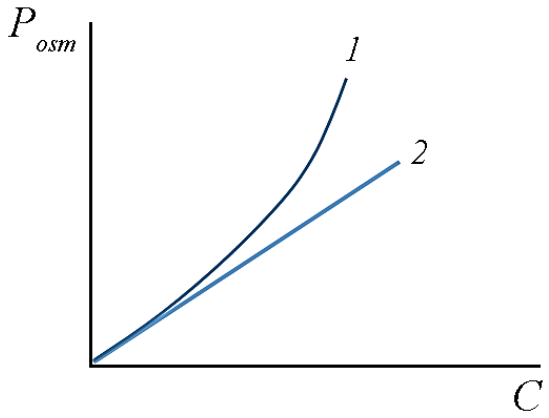

Figure 6.10. The dependence of osmotic pressure on the molarity: experimental curve for a solution of a protein (1), theoretical plot (2)

The method of osmometry shows better results for the calculation of molar mass of a polymer than methods of ebullioscopy and cryoscopy, while it is much worse than mass spectrometry.

Proteins significantly influence the distribution of ions between two sides of a semipermeable membrane. If we assume that water and small ions can pass through the membrane passively, while proteins cannot, then negatively charged proteins will attract positively charged ions. Donnan's equilibrium equation states that the multiple of concentrations of permeable ions must be the same in both sides of a membrane.

inside $[Na^+]\cdot[Cl^-]$ = outside $[Na^+]\cdot[Cl^-]$

Imagine that there are 9 mol of Na^+ cations inside the cell bound by anionic groups from proteins. Outside the cell there are 9 mol of Na^+ and 9 mol of Cl^-. Since just permeable ions are considered in the equation, initially there is no balance between two sides of the membrane.

inside $9[Na^+]$ < outside $9[Na^+]\cdot 9[Cl^-]$

The balance can be achieved if 3 mol of Na^+ and 3 mol of Cl^- will get inside the cell.

inside $12[Na^+]\cdot 3[Cl^-]$ = outside $6[Na^+]\cdot 6[Cl^-]$

So, the osmolarity inside the cell will become much higher, especially, if we consider that proteins also contribute into the osmotic pressure.

Donnan's equation is based on the simplified model of cell membrane functioning. The balance of cations and anions is controlled by a cell with the help of ionic channels. However, negatively charged proteins do attract positively charged ions, and positively charged proteins do attract negatively charged ions. This effect can be observed even in the absence of semipermeable membrane. For example, in a system made from gel and solution around it the concentration of ions inside the gel is higher than that outside the gel. In the same manner, pH inside the gel is usually different from the pH outside the gel.

Donnan's effect may be considered as a spontaneous cause of the membrane potential occurrence, as well as a factor that enhances the influence of oncotic pressure on the water balance between tissues and capillaries.

Problems

1. The isoelectric point of pepsin of gastric juice is 2.0. What will be the sign of the charge of the macromolecule of the enzyme when it is placed in a buffer solution with pH of 8.5. Explain your answer.

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2. Gelatin is placed in a buffer solution with pH = 3. Determine the sign of the charge of gelatin particles if the isoelectric point of gelatin is 4.7. Explain your answer.

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3. The isoelectric point of the albumin is 4.9. The protein is placed in a buffer solution with a concentration of hydrogen ions equal to 10^{-6} mol/L. Indicate the charge of the electrode to which the protein will migrate during the electrophoresis. Explain your answer.

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4. Myosin from the muscles with pI = 5.0 is placed into the solution with the concentration of H^+ ions 100 times higher than that in pure water. What charge will the protein have in this solution? Explain your answer.

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5. Which electrode (cathode or anode) will the protein migrate to during the electrophoresis, if its pI is 4.0 and the pH of the solution is 5.0?

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6. In which of the solutions of the following salts — NaI, Na_2SO_4, NaCNS, NaCl — at their equal molar concentration the swelling degree of biopolymers has the highest and the smallest values? Explain your answer.

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7. Arrange solutions of the following salts — CH_3COOK, KCNS, K_2SO_4, KCl — at their equal molar concentration according to the increase of the swelling degree of biopolymers. Explain your answer. Will the same pattern be observed for the processes of salting out, coagulation, gelling?

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8. Five portions of a protein with pI = 5.1 were poured over with the solutions of the following pH values:1.0; 4.0; 5.0; 6.5; 8.0. In which of these solutions the swelling degree will have the highest and the lowest values?

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9. Calculate the degree of swelling (by mass) of starch if 1 g of starch after 2 hours absorbs 0.3 ml of a solution with a density of 1.05 g/ml.

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10. Calculate how many water molecules are bound by albumin in the water solution. Find an average number of water molecules per one amino acid residue of albumin. It is known that 1 g of albumin binds 0.3 g of H_2O, *M*(albumin) = 68 000 g/mol, the number of amino acid residues in albumin is 515.

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11. The time of water outflow in Ostwald's viscometer is equal to 50 s and for the polyglucin solution with the mass fraction of 2 % it is equal to 72 sec. Calculate the reduced viscosity of the solution.

12. The time of outflow of polymer solution with the mass percentage of 1 % in the viscometer is twice higher than that of a pure solvent. Calculate the relative molecular mass of the polymer if the constant K in Straudinger's equation is $2 \cdot 10^{-3}$ cm^3/g (macromolecules in the solution form rigid sticks).

13. Calculate the relative molecular mass of myoglobin if its characteristic viscosity in a n aqueous solution is 3.1 cm^3/g. Constants K and α in the equation of Mark–Hauwink–Kun are equal to $2.32 \cdot 10^{-2} \cdot cm^3/g$ and 0.5.

14. The osmotic pressure of the solution containing 26 g/L of hemoglobin in the isoelectric state is equal to the osmotic pressure of the solution containing 0.0117 g/L NaCl. Calculate the molar mass of hemoglobin if the density of both solutions is 1 g/ml, the temperature is 25 °C and the deviation from the vant Hoff's law can be neglected.

15. An aqueous solution of protein with a concentration of 10 g/L at standard temperature has an osmotic pressure of 18.57 mm Hg. Calculate the molar mass of the protein. The deviation from the Van't Hoff law can be neglected.

16. Calculate the reduced viscosity (cm^3/g) of the polymer solution using the experimental data of the viscosimetric method: the solution flow time is 89 s, the solvent flow time is 85 s, the polymer content is 2.5 g/L.

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17. The osmotic pressure of the aqueous solution of hemoglobin at 15 °C is 483.9 N/m^2. The concentration of the solution is 3.43 kg/m^3. Calculate the molar mass of hemoglobin. The deviation from the Van't Hoff law can be neglected.

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Laboratory work 1. CRYOSCOPIC DETERMINATION OF THE MOLECULAR WEIGHT OF SUCROSE

Objective: to determine the molecular weight of sucrose and compare it with the true molecular mass.

Reactants:

− test solution of sucrose (with a known mass fraction of sucrose), distilled water;

− a cooling mixture (crystalline sodium chloride, water and ice).

Labware:

− a thick-walled glass (crystallizer), a glass stick, a laboratory thermometer for measuring the temperature of the mixture;

− the apparatus for measuring the crystallization temperature (figure 1).

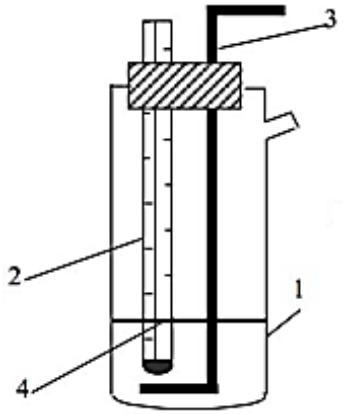

Figure 1. Apparatus for measuring crystallization temperature
1 — tube with side opening, tightly closed with stopper; *2* — thermometer (scale from –5 to +30 °C, value of division 0.1); *3* — mixer; *4* — label indicating the level of the liquid

Instruction:

1. Preparation of the cooling mixture. Put finely fragmented ice into a thick-walled glass (crystallizer), add small volume of water and table salt to it, fill approximately $^2/_3$ of the glass. The mixture is blended with a glass stick and stake off that the temperature of the cooling mixture during the experiment is kept at about –5 °C.

2. Determination of the freezing temperature of the solvent. 10–15 ml of distilled water is poured into the tube (1) to the mark (4) and the tube is closed with a stopper (figure 1). The thermometer (2) is immersed in water so that the water level is above the ball of the thermometer by about 1 cm. The lower end of the thermometer should be about 1 cm above the bottom of the tube. The tube with water and the thermometer fixed in it are immersed in the cooling mixture. Stake off the change in water temperature, periodically stirring the water in a test tube with a mixer (3). After the water temperature goes down by about 1–1.5 °C below zero (supercooled water), the water is intensively mixed with the mixer (3). The process of water freezing begins with the release of heat, and the mercury column in the thermometer rises sharply upward. Note the maximum temperature (accurate

to 0.05–0.10), which is the freezing point of water. Then the tube is placed in the glass with tap water (room temperature) and, mixing, dissolve the formed ice crystals. Repeat the determination of the freezing point of water. The results of a two experiments are recorded in the Table.

3. Determination of the freezing temperature of the sucrose solution. The solution of sucrose with a known mass fraction of sucrose in solution is poured into a dry test tube to the same label. The tube is placed in the cooling mixture and, periodically mixing the test solution, supercooled to about 3–3.5 °C below zero. The freezing point of the solution is determined twice according to the scheme described above. All the results should be written down in the table.

Substance	**Freezing temperature (T), °C**		
	Experiment 1	**Experiment 2**	**Average value**
Solvent (water), t_0			
Solution of sucrose, $t_{p\text{-}pa}$			

4. Calculations. According to the Second Law of Raoult

$$\Delta t_{\text{freezing}} = K \cdot C_m,$$

where

$$C_m = \frac{n_{\text{sub}}}{m_{\text{solvent}}} = \frac{m_{\text{sub}}}{M_{\text{sub}} \cdot m_{\text{solvent}}} \text{ mol/kg}$$

$$\Delta t_{\text{freezing}} = \frac{K \cdot m_{\text{sub}}}{M_{\text{sub}} \cdot m_{\text{solvent}}}$$

The mass of substance m_{sub} and the mass of solvent m_{solvent} are calculated from the mass fraction of sucrose in the test solution:

$$\boldsymbol{W = \frac{m_в}{m_в + m_{р\text{-}ля}} \cdot 100\ \%}$$

m_{sub} = _____ g;

m_{solvent} = _____ g = _____ kg.

Hence, the molar mass (g/mol) of sucrose found experimentally:

$$M_{\text{exper}} = \frac{K \cdot m_{\text{sub}}}{\Delta t_{\text{freezing}} \cdot m_{\text{solvent}}} = \text{————} = \quad \text{g/mol,}$$

where $\Delta t_{\text{freezing}} = t_0 - t_{\text{solvent}}$ (°C), m_{sub} (g), m_{solvent} (kg), $K_{(\text{H2O})}$ =1.86 kg·°C·mol^{-1}.

The true molar mass of sucrose $C_{12}H_{22}O_{11}$ is 342 g/mol.

Relative error is

$$\Delta X = \left| \frac{M_{\text{true}} - M_{\text{exper}}}{M_{\text{true}}} \right| \cdot 100\ \% = \left| \text{————————} \right| \cdot 100\ \% = \text{\_\_\_\_\_}\ \%.$$

Conclusion: The molecular weight of sucrose M =_____ g/mol was determined and it differs by _____ % from its true molecular mass.

Laboratory work 2. PREPARATION OF BUFFER SOLUTIONS WITH NEEDED pH AND INVESTIGATION OF THE EFFECT OF DILUTION ON THE pH VALUE

Objective: to learn how to prepare buffer solutions with a given pH, and also to study the effect of dilution on the pH.

Reactants: 0.1 M solutions: CH_3COOH, CH_3COONa, NH_4OH, NH_4Cl, $NaHCO_3$, Na_2CO_3, distilled water.

Labware: educational-laboratory complex "Chemistry" in the following configuration: central controller, module "Electrochemistry" with two glasses (50 cm^3), two electrodes for potentiometric measurements (glass electrode and chlorine silver); volumetric flasks, pipettes.

Instruction:

1. Calculate the quantities of initial solutions necessary for the preparation of buffer solutions with a volume of 100 ml (the composition and approximate pH of which are given in the table 1) according to formulas 1–4. The obtained data should be entered in table 1.

Proceeding from the formula:

$$pH = pK + \log(C_{acid}/C_{salt}),$$

where pK is the index of the constant of dissociation of a weak acid; C_{acid} is the equilibrium concentration of a weak acid; C_{salt} is the equilibrium salt concentration.

For buffer systems made from weak base and its salt the formula is modified.

$$pH = 14 - pK - \log(C_{base}/C_{salt}),$$

where pK is the index of the constant of dissociation of a weak base; C_{base} is the equilibrium concentration of a weak base; C_{salt} is the equilibrium salt concentration.

We obtain formulas for calculating the composition of buffer solutions:

Acetate $\log(C_{acid}/C_{salt)} = pK_{acid} - pH =$ _____

Ammonium $\log(C_{base}/C_{salt)} = pH + pK_{base} - 14 =$ _____

Carbonate $\log(C_{NaHCO3}/C_{Na2CO3)} = pK_{NaHCO3} - pH =$ _____

$C_{acid}/C_{salt} = V_{acid}/V_{salt}$ since the concentrations of solutions are equal.

Table 1

Buffer	**The composition of the buffer solution**	**Approximate pH**	**$\log(C/C_{salt})$**	**V/V_{salt}**
Acetate	0.1 M CH_3COOH + 0.1 M CH_3COONa	4.74		
Ammonium	0.1 M NH_4OH + 0.1 M NH_4Cl	9.2		
Carbonate	0.1 M $NaHCO_3$ + 0.1 M Na_2CO_3	10.0		

2. Prepare these buffer solutions with a volume of 100 ml each.

3. Measure the EMF value for the initial buffer solutions prepared, and record the results in table 2.

4. Carry out a successive dilution of the solutions in 2, 10 and 100 times, measure the EMF value of the diluted solutions, record the results in table 2.

5. From the obtained EMF values, calculate the pH values of the resulting buffer solutions.

Since the dependence of the electrode potential of the hydrogen electrode on the pH of the medium is described by the equation:

$$\varphi = -0.058 \cdot pH,$$

then knowing the EMF of the element (E), you can calculate the pH of the solution by the formula:

$$pH = -\frac{E - \varphi_{chlor}}{0.058}$$

The values of chlorine-silver potential should be taken as reference data. All the obtained data should be written down in table 2:

Table 2

Buffer	**E, V**				**pH**			
	Initial solution	**Diluted solution**			**Initial solution**	**Diluted solution**		
		2 times	**10 times**	**100 times**		**2 times**	**10 times**	**100 times**
Acetate								
Ammonium								
Carbonate								

Conclusion: the dilution of buffer solutions _____ the value of pH.

Reference data

Table 3

Dissociation constants of acids and bases

Ammonia solution	$NH_3 + H_2O$	$K_b = 1.76 \cdot 10^{-5}$	$pK_b = 4.755$
Carbonic acid	H_2CO_3	$K_{a1} = 4.5 \cdot 10^{-7}$ $K_{a2} = 4.8 \cdot 10^{-11}$	$pK_{a1} = 6.35$ $pK_{a2} = 10.32$
Acetic acid	CH_3COOH	$K_a = 1.74 \cdot 10^{-5}$	$pK_a = 4.76$

Table 4

Dependence of the potential of a silver chloride electrode (φ_{chlor}) on temperature (T)

T, °C	φ^0, V
0.0	0.23655
5.0	0.23413
10.0	0.23142
15.0	0.22857
15.5	0.22827
16.0	0.22797
16.5	0.22767
17.0	0.22737
17.5	0.22707
18.0	0.22677
18.5	0.22647
19.0	0.22617
19.5	0.22587
20.0	0.22557
20.5	0.22525
21.0	0.22492

T, °C	φ^0, V
21.5	0.22460
22.0	0.22428
22.5	0.22396
23.0	0.22363
23.5	0.22331
24.0	0.22299
24.5	0.22266
25.0	0.22234
25.5	0.22201
26.0	0.22168
26.5	0.22135
27.0	0.22102
27.5	0.22069
28.0	0.22036
28.5	0.22003
29.0	0.21970

T, °C	φ^0, V
29.5	0.21937
30.0	0.31904
30.5	0.21788
31.0	0.21763
31.5	0.21739
32.0	0.21714
32.5	0.21689
33.0	0.21664
33.5	0.21639
34.0	0.21615
34.5	0.21590
35.0	0.21565
40.0	0.21208
50.0	0.20449
60.0	0.19640
70.0	0.18782

Laboratory work 3. CONDUCTOMETRIC DETERMINATION OF THE DISSOCIATION DEGREE AND DISSOCIATION CONSTANT OF ACETIC ACID

Objective: to learn how to determine the resistance of conductors of the second type and use the conductometric measurements to calculate the constant and the degree of dissociation of weak electrolytes.

Instruction:

Task 1. Determine the constant of the vessel K_c with 0.001 M KCl solution.

The electrode vessel is washed twice with a small amount of a solution of 0.001 M KCl. After that it is filled to the mark with a solution and covered with a cover. The electrodes are connected to the terminals of the measuring device. Measure and record the value of the electrical conductivity (L) of the KCl solution and the temperature working with the device strictly according to the instructions. The specific electrical conductivity $æ_{KCl}$ of the KCl solution at the given temperature found from table 1 and the vessel constant K_c is calculated from the formula:

$\mathbf{K_c = æ_{KCl}/L =}$ **_____.**

Task 2. Determine the degree and the dissociation constant of acetic acid.

The electrode vessel and electrodes are washed with distilled water. Then they are washed with a solution of 0.1 M acetic acid. After that the vessel is filled with this solution to the mark. The electrodes must be completely covered by a solution. Measurement of the electrical conductivity (L) of the acetic acid solution and temperature is carried out in the same way as the electrical conductivity of the potassium chloride solution (task 1).

The specific electric conductivity (æ) of the acetic acid solution is found using the results of measurements and the obtained data in task 1. Use the formula:

$\mathbf{æ(CH_3COOH) = K_cL =}$ **_____.**

Then the molar electrical conductivity λ_m, the dissociation degree α and the dissociation constant K_d of the acid are calculated by the equations:

$\mathbf{\lambda_m = æ(CH_3COOH)/(1000 \cdot C(CH_3COOH)) =}$ **_____/(1000·_____) = _____;**

$\mathbf{\alpha = \lambda_m/\lambda_m =}$ **_____/_____=_____.**

According to Kohlrausch's law (from table 2):

$\mathbf{\lambda_m(CH_3COOH) = \lambda_m(H^+) + \lambda_m(CH_3COO^-)}$

$\mathbf{\lambda_m(CH_3COOH) = U_{H+} + U_{CH3COO-} =}$ **_____=_____;**

$$K_d = \frac{\alpha^2 \cdot C}{1-\alpha} = \text{\_\_\_\_\_} = \text{\_\_\_\_\_}.$$

The values of mobility (U) for H^+ and CH_3COO^- ions at a given temperature are taken from table 2.

The experimental value of the dissociation constant K_d is compared with the theoretical value and the relative error of the experiment in % is calculated (K_d $(CH_3COOH)_{theory} = 1.75 \cdot 10^{-5}$ mol/L):

$$\Delta X = \left| \frac{K_{d(theory)} - K_d}{K_{d(theory)}} \right| \cdot 100\ \% = \left| \_\_\_\_\_ \right| \cdot 100\ \% = \_\_\_\_\_ \%.$$

Conclusion: dissociation constant K_d =_____ was determined and the relative error of the experiment is _____ %.

Reference data

Table 1

Specific electrical conductivity of 0.001 M KCl as a function of temperature

Temperature, °C	**Specific electrical conductivity æ, $S \cdot m^{-1}$**
18	0.0127
19	0.0130
20	0.0133
21	0.0136
22	0.0139
23	0.0142
24	0.0145
25	0.0148

Table 2

Mobility of ions as a function of temperature

Temperature, °C	**Mobility of ions U ($S \cdot m^2\ mol^{-1}$)**	
	H^+	**CH_3COO^-**
18	$315 \cdot 10^{-4}$	$35 \cdot 10^{-4}$
19	$320 \cdot 10^{-4}$	$35.9 \cdot 10^{-4}$
20	$324.8 \cdot 10^{-4}$	$36.6 \cdot 10^{-4}$
21	$329.8 \cdot 10^{-4}$	$37.4 \cdot 10^{-4}$
22	$334.7 \cdot 10^{-4}$	$38.2 \cdot 10^{-4}$
23	$339.7 \cdot 10^{-4}$	$39.1 \cdot 10^{-4}$
24	$345 \cdot 10^{-4}$	$40.1 \cdot 10^{-4}$
25	$349.8 \cdot 10^{-4}$	$40.9 \cdot 10^{-4}$

Laboratory work 4. DETERMINATION OF THE CONCENTRATION OF Zn^{2+} IONS IN EYE DROPS "ZINC SULFATE 0.25 % AND BORIC ACID 2 %" BY CONDUCTOMETRY

Objective: to determine the concentration of Zn^{2+} ions in the eye drops "Zinc sulfate 0.25 % and boric acid 2 %" by conductometric titration.

Reactants: medicinal preparation eye drops "Zinc sulfate 0.25 % and boric acid 2 %" in 1 ml ampoules, distilled water, 0.01 N NaOH solution.

Labware: educational-laboratory complex "Chemistry" in the following configuration: central controller; module "Electrochemistry" complete with conductometric and temperature sensors, magnetic mixer, glass 100 cm^3.

Instruction:

1. Preparation of working solution: 4 ampoules of eye drops "Zinc sulfate 0.25 % and boric acid 2 %" transferred quantitatively to the titration glass. Add 16 ml of distilled water.

2. Switch on the educational-laboratory complex "Chemistry" and run the control program elsms2.exe on the PC.

3. The glass with the working solution is installed in the module "Electrochemistry" and conductometric and temperature sensors are connected.

4. Mixing of the solution is provided by means of a magnetic stirrer (stirring speed 2).

5. Titration of working solution is carried out by a 0.01 N NaOH solution. Add portions of 0.5 ml using a measuring pipette with a periodicity of 30 s. Fix the changes in conductivity with the program elsms2.exe. Titration is carried out until two titration jumps appear in the elsms.exe program window: the first for Zn^{2+}, the second for boric acid.

6. The graph of the dependence of the electrical conductivity (L) on the volume of the added alkali solution (V(NaOH)) is constructed from the obtained data. V (NaOH) needed for the titration of $ZnSO_4$ is determined from the position of the first titration jump.

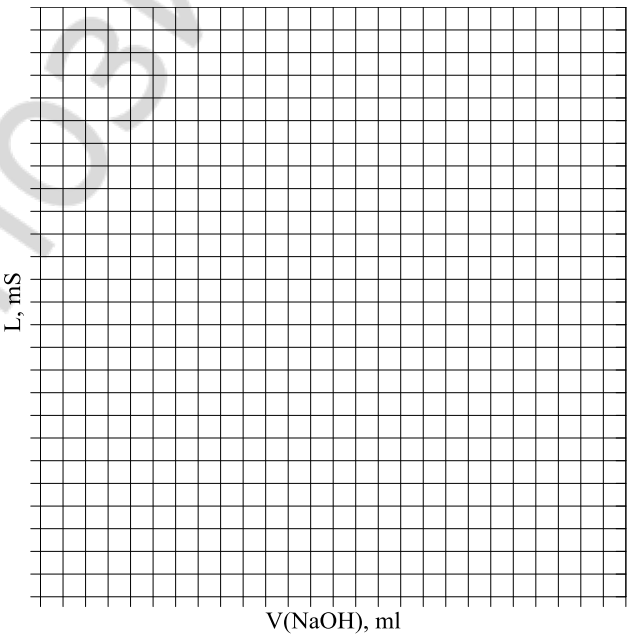

Figure 1. The curve of conductometric titration of eye drops "Zinc sulfate 0.25 % and boric acid 2 %"

The content of $ZnSO_4$ (g) in 1 ml of the drug is calculated by the formula:

$$m(ZnSO_4) = \frac{C_N(NaOH) \cdot V(NaOH) \cdot 161 \cdot 0.5}{4} = \frac{\qquad\qquad \cdot 161 \cdot 0.5}{4} = \_\_\_\_\_ \text{ g},$$

Concentration of Zn^{2+} ions is calculated by the formula:

$$C(Zn^{2+}) = \frac{C_N(NaOH) \cdot V(NaOH) \cdot 5 \cdot 0.5}{V_{solution}} = \frac{\qquad\qquad \cdot 5 \cdot 0.5}{\qquad\qquad} = \_\_\_\_\_ \text{ mol/l.}$$

where V(NaOH) is the volume of the solution which was used for the titration of the analyzed sample l; C_N(NaOH) is the normality of NaOH solution, mol/L; $V_{solution}$ is the volume of working solution l; 161 is the molar mass of zinc sulfate, g/mol; 0.5 is the equivalence factor of zinc sulfate; 4 is the volume of the sample, ml; 5 is the frequency of dilution of the sample of the drug.

Conclusion: the concentration of Zn^{2+} ions $C(Zn^{2+})$ = _____ mol/L in the eye drops “Zinc sulfate 0.25 % and boric acid 2 %” was determined.

Laboratory work 5. DETERMINATION OF THE AVERAGE COEFFICIENT OF ELECTROLYTE ACTIVITY BY THE POTENTIOMETRY METHOD

Objective: to determine the coefficient of electrolyte activities for hydrochloric acid solutions of various concentrations by potentiometry.

Reactants: 0.1 M HCl solution, distilled water.

Labware: educational-laboratory complex "Chemistry" in the following configuration: central controller; module "Electrochemistry" complete with two electrodes (silver chloride and glass electrodes) and temperature sensors; glass 50 cm^3, two 10 cm^3 pipettes.

Instruction. The actual ion concentration (activity, *a*) differs from the analytical concentration (C) in solutions of strong electrolytes. This is due to electrostatic interionic interactions in the electrolyte solution. The higher the concentration of electrolyte, the lower the activity. This is because the activity coefficient (f_a) decreases with increase in concentration. The activity and analytical concentration are related by the formula:

$$a = f_a \cdot C.$$

To determine the average coefficient of activity, we need to make up a galvanic cell consisting of electrodes that are reversible relative to the cation and anion of the electrolyte under study. In this work we use a GE without transfer consisting of silver chloride and glass electrodes (figure 1):

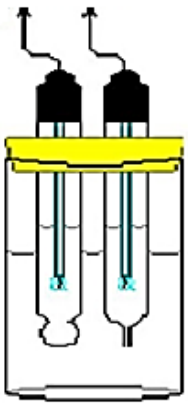

Figure 1. The scheme of pH-meter

(−)Ag|AgCl|HCl (solution)|glass|HCl (0.1M)|KCl_{sat}|AgCl|Ag(+)

The EMF of such GE (E) is calculated as follows: $E = E_{gl} - E_{s-cl}$.

Because the

$E_{gl.} = E^0_{gl} + 0.059\lg a(H^+)$, and $E_{s-cl} = E^0_{s-cl} - 0.059\log a(Cl^-)$,

then $E = E^0_{gl} + 0.059\log a(H^+) - E^0_{s-cl} + 0.059\log a(Cl^-) = (E^0_{gl} - E^0_{s-cl}) + (0.059\log a(H^+) + 0.059\log a(Cl^-))$.

Given that $a(H^+) = a(Cl^-)$ and $(E^0_{gl.} - E^0_{s-cl}) = E^{0*}$, we have:

$$E = E^{0*} + 0.118\log a(H^+) = E^{0*} + 0.118\log(C \cdot f_a) = E^{0*} + 0.118 \cdot (\log C + \log f_a).$$

From here $E = E^{0*} + 0.118\log C + 0.118\log f_a$,

$$E^{0*} = E - 0.118\log C - 0.118\log f_a.$$

We replace E with $0.118\log C = y$. The straight-line dependence of y on C should be observed for very dilute solutions according to the Debye–Hückel theory.

1. 40 cm^3 of 0.1 M HCl solution is placed by pipette into a 50 cm^3 glass.

2. The glass with the solution is installed in the tripod of the module and the electrodes are connected. After the equilibrium is established (3–5 min), the EMF measurements of the GE are made and the values obtained are tabulated.

3. HCl solution is diluted 2 times. To do this, 20 cm^3 of HCl solution is pipetted and 20 cm^3 of distilled water is placed in place of it. The electrodes are placed in the glass, after the equilibrium is established, one should measure the EMF write the data to the table.

4. Paragraph 3 is repeated.

5. The value of y is calculated by the formula: $y = E - 0.118\log C$.

6. The graph of the dependence of y on $C^{0.5}$ is constructed from the results of the measurements (table 1). The value of the standard EMF of the GE (E^{0*}) is determined by extrapolating the dependence line to zero concentration.

Table 1

C (HCl), mol /L	**$C^{0.5}$**	**E, V**	**y**	**E^{0*}**	**log f_a**	**f_a**
0.1						
0.05						
0.025						

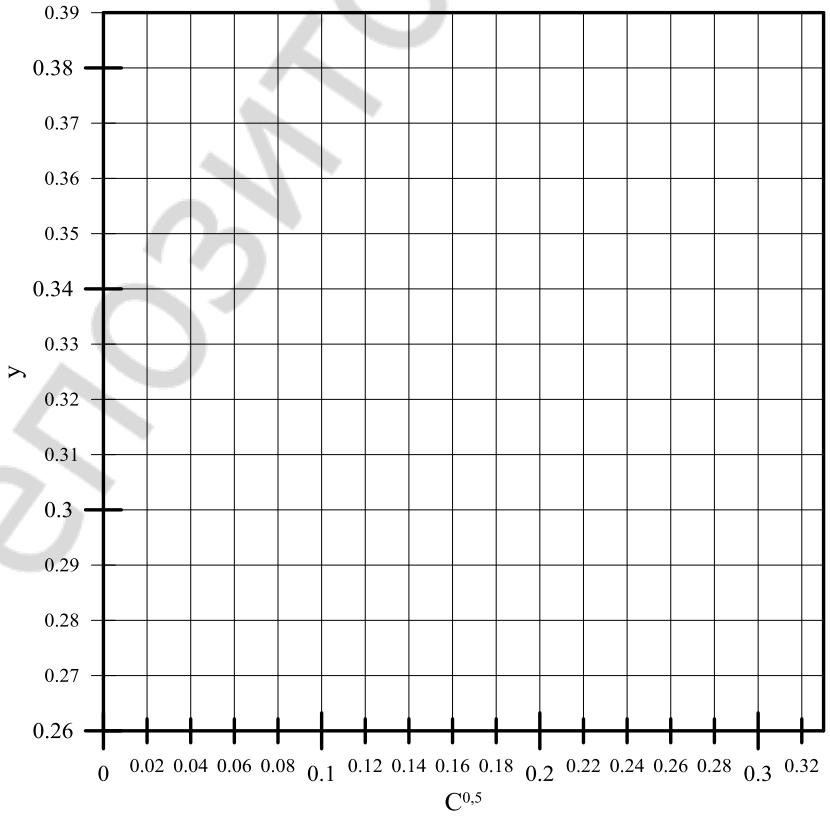

Figure 2. The dependence of y on $C^{0.5}$

7. The value of the activity coefficient f_a for different concentrations of HCl solution is calculated by the formula:

$$\lg f_a = \frac{E - E^{0*} - 0.118 \log C}{0.118}$$

$\lg f_a(0.1\,\text{M})$ = ——————————————— = _____;

$f_a(0.1\,\text{M})$ = _____;

$\lg f_a(0.05\,\text{M})$ = ——————————————— = _____;

$f_a(0.05\,\text{M})$ = _____;

$\lg f_a(0.025\,\text{M})$ = ——————————————— = _____;

$f_a(0.025\,\text{M})$ = _____;

$$f_a(\text{average}) = \frac{f_a(0.1\,\text{M}) + f_a(0.05\,\text{M}) + f_a(0.025\,\text{M})}{3} = \text{————————} =$$

= _____.

Conclusion: the average activity coefficient f_a(average) = _____ was determined from hydrochloric acid solutions of various concentrations by potentiometry.

Laboratory work 6. DETERMINATION OF THE DEPENDENCE OF THE SOLUTION SURFACE TENSION ON THE LENGTH OF THE HYDROCARBON CHAIN OF THE SURFACTANT MOLECULE

Objective: to study the influence of the length of the hydrocarbon chain of the surfactant molecule on the value of the surface tension of its solution.

Instruction: The essence of the work is to calculate the number of drops of investigated SAS solutions and water which outflow from the same volume. To determine surface tension we use Traube's stalagmometer (figure). That's why the method bears the name stalagmometric.

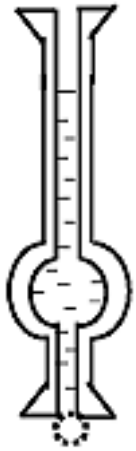

Figure 1. Scheme of stalagmometry

The main idea of the method is as follows: the liquid is pumped in above the highest mark and as soon as its level lowers to this mark we should begin to calculate the number of drops outflowing from the tube until its level reaches the lowest mark. The drop flows out of the capillary and falls down under the influence of gravity of its own mass. But the surface tension tries to prevent the falling of the drop as its formation is connected with the increase of liquid surface. The higher the surface tension, the heavier must be the falling drop in order to overcome the surface tension and to fall down. So, surface tension is inversely proportional to the number of drops outflowing from the same volume.

Surface tension is determined using the following formula:

$$\frac{\sigma}{\sigma_{H_2O}} = \frac{\rho \cdot n_{H_2O}}{\rho_{H_2O} \cdot n} \quad \Rightarrow \quad \sigma = \sigma_{H_2O} \cdot \frac{\rho \cdot n_{H_2O}}{\rho_{H_2O} \cdot n}, \tag{1}$$

where σ and σ_{H_2O} are the surface tensions of the studied liquid and water respectively, ρ and ρ_{H_2O} are the densities of the studied liquid and water; n and n_{H_2O} are the numbers of drops of the studied liquid and water.

For diluted aqueous solutions with the density nearly 1 the formula can be simplified:

$$\sigma = \sigma_{H_2O} \cdot \frac{n_{H_2O}}{n}, \tag{2}$$

where σ_{H_2O} = 72.8 mJ/m^2 at 20 °C.

As we can see from the formula (2) it's enough to calculate the number of drops of the studied liquid and water in order to determine the surface tension.

Task 1. Determine the dependence of solution surface tension on the length of the hydrocarbon chain of SAS.

At first we should determine the number of water drops and calculate the number of drops of 0.1 M of aqueous solutions of the following alcohols in the indicated order:

C_2H_5OH, C_3H_7OH, C_4H_9OH, $C_5H_{11}OH$. Then we calculate the surface tension of these alcohols using the formula (2).

The results of measurements and calculations are added to the table.

	n_1	**n_2**	**n_3**	**$N_{average}$**	**σ, mJ/m^2**
water					–
C_2H_5OH					
C_3H_7OH					
C_4H_9OH					
$C_5H_{11}OH$					

We build the plot of the dependence of surface tension on the number of carbon atoms in alcohol molecules (N atoms of carbon).

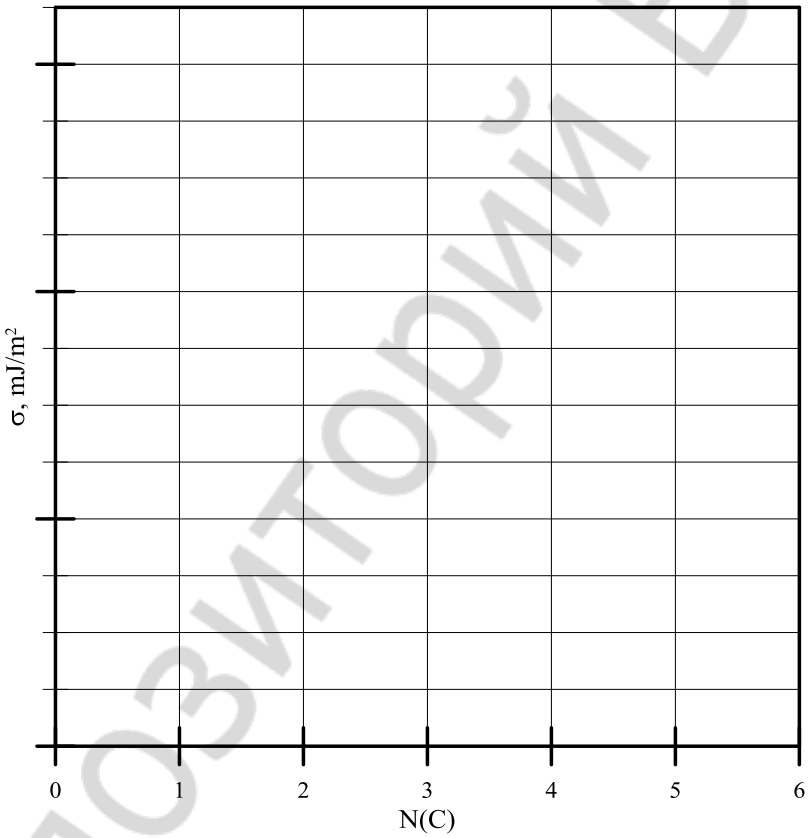

Figure 2. The dependence of surface tension on the number of carbon atoms in alcohol molecules

Conclusion: the dependence of surface tension of aqueous solutions on the length of hydrocarbon chain in alcohol molecules is _____

_____

Task 2. Determine the dependence of the solution surface tension on SAS concentration. Like in task 1 we should first calculate the number of water drops and the number of drops of the aqueous solution of amyl alcohol of the following concentrations: 0.01 M, 0.025 M, 0.05 M, 0.1 M, 0.2 M. The calculations should be started from solution with the lowest concentration.

We calculate the surface tension of aqueous solutions of amyl alcohol using the formula (2). This dependence of surface tension of alcohol aqueous solutions on its concentration can be represented graphically (figure 3).

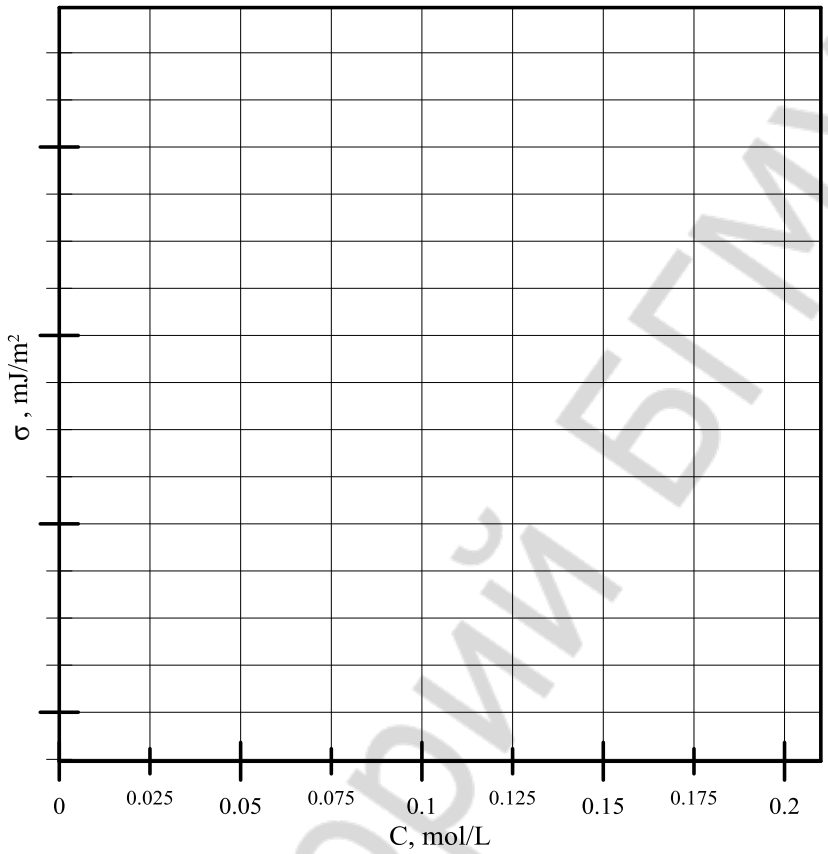

Figure 3. The dependence of surface tension of alcohol aqueous solutions on its concentration

Conclusion: the dependence of surface tension of amyl alcohol solutions on its concentration is _____
_____

Laboratory work 7. THE STUDY OF THE ADSORPTION OF MATTER FROM A SOLUTION ON A SOLID ADSORBENT

Objective: experimentally determine the amount of adsorption of acetic acid from the aquatic solution on the surface of coal.

Instruction. The essence of the work is to establish the contact between the solutions of known concentration and the adsorbent. As soon as the adsorption equilibrium between them is established we should determine the concentration of the equilibrium solution. The amount of adsorbed substance from the solution is determined using the difference in concentrations before and after the adsorption. Determining this difference for the solutions of different concentrations and knowing the adsorbent mass we get the data about the specific adsorption of a substance at different values of equilibrium concentrations. Using these data we draw the adsorption isotherm. In the present work the adsorption isotherm is satisfactorily described by Langmuir equation.

25 mL of acetic acid solution of the concentration indicated in the Table are poured using a graduated cylinder into six dry numbered flasks. Then 0.5 g of the activated carbon (previously grounded) are introduced in each flask simultaneously. The contents of the flask are stirred by circular motions for 10 minutes. Then the solutions are filtered through dry folded paper filter into separate tubes. 10 ml of the solution are taken from each filtrate using a pipette and transferred to the titration flasks. 2 drops of phenolphthalein indicator are added in each flask. Titrate each sample with the solution of sodium hydroxide (till the appearance of a slightly rosy color). The titration results are written down in the table.

Flask	**$C_{init}(CH_3COOH)$, mol/L**	**C(NaOH), mol/L**	**(V)NaOH, ml**	**$C_{eq}(CH_3COOH)$, mol/L**	**$\Gamma(CH_3COOH)$, mmol/g**
1	0.05	0.05			
2	0.025	0.05			
3	0.1	0.2			
4	0.2	0.2			
5	0.3	0.2			
6	0.4	0.2			

We calculate the equilibrium concentration of acetic acid using the formula:

$$C_{\text{eq}} = \frac{C_{\text{NaOH}} \cdot V_{\text{NaOH}}}{V_{CH_3COOH}}, \quad (1)$$

where V_{CH_3COOH} is the volume taken for titration.

Calculate acetic acid adsorption using the formula:

$$\Gamma = \frac{(C_{\text{init}} - C_{\text{eq}}) \cdot V_{\text{init}} \cdot 1000}{m} (\text{mmol/g}), \qquad (2)$$

where C_{init} is the concentration of acetic acid solution before adsorption, mol/L, C_{eq} is the concentration of acetic acid solution after the adsorption (equilibrium concentration), mol/L, V_{init} is the volume of acid solution taken for adsorption (in our case 0.025 L), m is the adsorbent mass (in our case 0.5 g).

In order to get the adsorption isotherm we should mark the equilibrium concentrations C_{eq} on the X-axis and the corresponding adsorption values Γ on Y-axis.

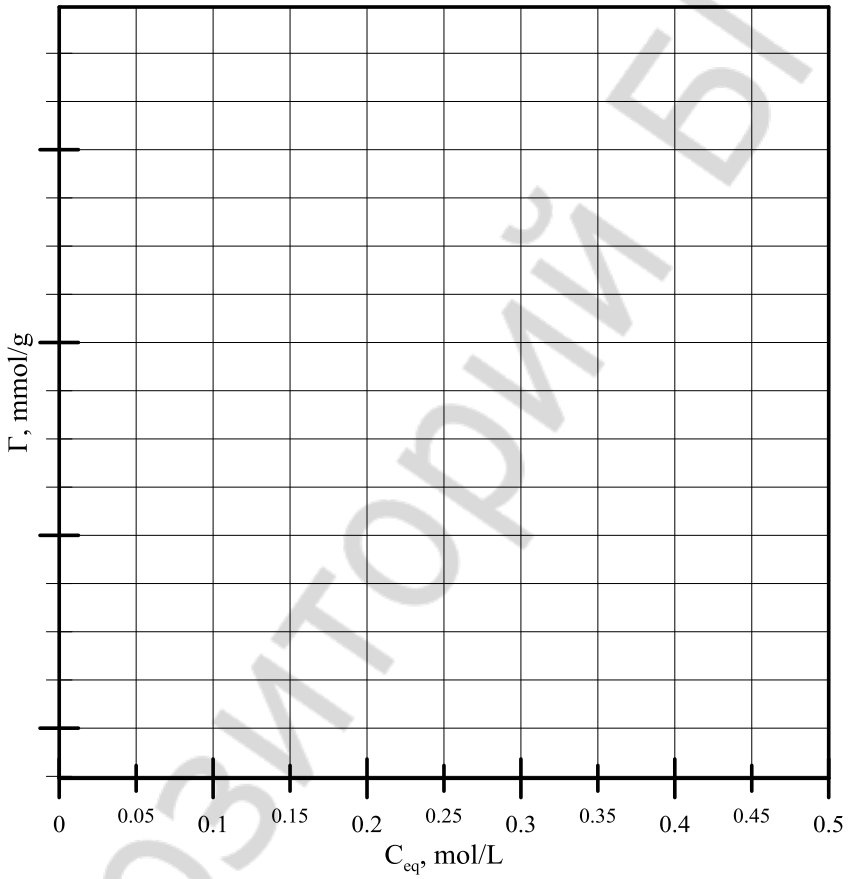

Figure 1. The adsorption isotherm

Conclusion: the dependence between the adsorption value of acetic acid from the solution on the surface of carbon and its equilibrium concentration is

Laboratory work 8. SEPARATION OF SERUM LIPIDS BY THIN-LAYER CHROMATOGRAPHY

Objective: to obtain a chromatogram of a mixture of serum lipids and to reveal in the extract the presence of cholesterol and stearic acid.

Instruction. The separation of blood serum lipids is based on their different solubility in a mobile organic solvent and in the immobile phase — water, fixed by a polar sorbent. In the result of a chromatographic process the mixture components are continuously rearranged between the mobile and immobile phases according to their distribution coefficients. That's why the mixture components move along the plate with different rate and migrate at different distances from the place of their application (start line).

Task. The separation is carried out on the chromatographic plate «Silufol» which is an aluminum foil covered with a thin layer of silica gel with the admixture of starch. At the distance of 2 cm from the lower edge of the plate we mark a start line with a pencil (we do it carefully in order not to damage the sorbent layer) and at the distance of 10 cm from the start line we mark the finish line. With the help of a thin capillary we apply two drops (0.02 mL) of the solutions of cholesterol and stearic acid (witnesses) and the mixtures of components at the same distance from each other on the start line (figure 1). The plate is dried in the air and is placed into the desiccators with an organic solvent with the help of the pincers so that the solvent level should be lower than the place of substance application. Then we close the dessicator and after the mobile phase rises along the plate at 12 cm (till the finish line) we take the plate out of the dessicator and dry it in the air till the complete disappearance of the solvent. For the appearance of the stains on the plate we should put it into the vessel with crystalline iodine. Then it is taken out and after the evaporation of iodine excess the plate is watered and dried in the air. Then we measure the distances passed by the mixture of substances (L_1, L_2, L_3), «witnesses» and the organic solvent (L_{solv}).

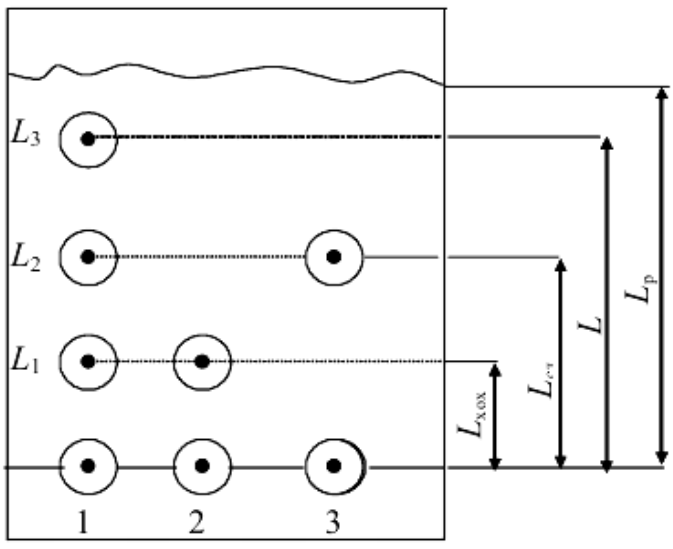

Figure 1. Determination of the retention index (R) at chromatography in the thin layer:
1 — investigated mixture; 2 — cholesterol; 3 — stearic acid

The retention indexes (R_1, R_2, R_3) are calculated using the formula:

$$R = \frac{L_1}{L_2}, \quad (1)$$

The results are written down in the table.

Mixture	**L, cm**	**R**
Investigated (1)	L_1 =	R_1 =
	L_2 =	R_2 =
	L_3 =	R_3 =
Cholesterol (2)		
Srearic acid (3)		

Conclusion: comparing R of «witnesses» to R_1, R_2, R_3 of the found substances in the mixture we can see the presence _____ _____ and absence _____ in the investigation mixture. According to the values of the retention indexes R_1, R_2, R_3 of the separate components of the separated lipid mixture _____ has the greatest polarity.

Laboratory work 9. PREPARATION OF COLLOID SOLUTIONS BY CONDENSATION AND THE STUDY OF THEIR OPTICAL PROPERTIES

Objective: to learn how to obtain colloid solutions by condensation and how to study the optical properties of colloidal solutions.

Reactants and devices. Tyndall apparatus, holder with test tubes, 0.01N KI, $AgNO_3$, H_2SO_4, $Na_2S_2O_3$, $K_4[Fe(CN)_6]$, $CuSO_4$ solutions, colophony solution in alcohol, water.

Task 1. To obtain colloid solutions by the methods of physical and chemical condensation (for sols obtained by the method of chemical condensation you should write the schemes of micelle structure).

Experiment I. The obtaining of sol of silver iodide.

In a test tube we pour $^1/_2$ of KI solution and then add $AgNO_3$ solution in the drop by drop manner at constant slow shaking till the formation of opalescent sol of AgI (a light luminous feculence):

$KI + AgNO_3 \rightarrow AgI + KNO_3$

The method of sol obtaining is _____

Draw the scheme of the micelle structure _____

Experiment II. The obtaining of sulphur sol.

We add 4–5 drops of H_2SO_4 solution to the solution of $Na_2S_2O_3$ ($^1/_2$ of the test tube). After some period of time (several minutes) we will see a slow formation of opalescent sol of sulphur:

$Na_2S_2O_3 + H_2SO_4 \rightarrow S + Na_2SO_4 + SO_2 + H_2O$

The method of sol obtaining is _____

Draw the scheme of the micelle structure _____

Experiment III. The obtaining of sol of copper (II) hexacyanoferrate.

We add $CuSO_4$ solution in the drop by drop manner to the solution of $K_4[Fe(CN)_6]$ ($^1/_2$ of the test tube) and shake it till the formation of sol of brick-red color:

$K_4[Fe(CN)_6] + 2CuSO_4 = Cu_2[Fe(CN)_6] + 2K_2SO_4$

The method of sol obtaining is _____

Draw the scheme of the micelle structure _____

Experiment IV. The obtaining of colophony sol by the method of solvent substitution.

We add 1–2 drops of alcohol solution of colophony to water ($^1/_2$ of the test tube) and shake the test tube vigorously. We can see the formation of milky white sol as colophony is insoluble in water.

The method of sol obtaining is _____

Task 2. To study the optical properties of the obtained colloidal solutions.

A prepared test tube with water or with electrolyte solution, for example, KI, and also the test tubes with the obtained colloid solutions should be placed through the upper hole in a black box with a source of light (a simplified Tyndall's apparatus without a focusing lens) one by one. If there is a colloid solution in the test tube, we will see a bright luminous beam of light (Tyndall's cone) passing through the solution. The obtained results should br written down in the form of the following table.

System	**Method of obtaining**	**Color, opalescence**	**Tyndall's cone**	**Conclusions**
Electrolyte solution				
Sol of silver iodide				
Sulphur sol				
Sol of copper (II) hexacyanoferrate				
Colophony sol				

Conclusion: based on the study of the optical properties of these solutions we can say that sols of _____ are colloid solutions because _____.

Laboratory work 10. DETERMINATION OF THE COAGULATION THRESHOLD OF ELECTROLYTE FOR SOL USING THE COLORIMETRIC METHOD

Objective: to learn how to determine experimentally the coagulation thresholds of electrolyte with the respect to a given sol using a photoelectric colorimeter.

Reagents and devices: photoelectric colorimeter, 100 ml flasks, burettes, $Fe(OH)_3$ sol, 0.0005 M K_2SO_4 solution.

Instruction. The optical density D (not to be confused with absorbance — A) is the difference in intensity of the transmitted light I_x and the incident light I_o.

When light passes through a colloid solution, its intensity decreases not only as a result of light absorption, but also due to opalescence. Therefore, the optical density depends on the degree of light absorption by the sol and on its ability to scatter light. The intensity of the scattered light increases with increase in linear particle sizes until the latter becomes equal to the wavelength of the transmitted light. After that, the brightness of the scattered light begins to decrease.

Since coalescence of sols leads to the process of particle coarsening, the intensity of the scattered light changes. Consequently, the optical density of the system also changes, which can be measured with a photoelectric colorimeter (FEC).

To find the coagulation threshold one has to build a graph based on the measurements of the optical density after the addition of different volumes of electrolyte solution to the sol (See sample on the leftmost figure) in the coordinates $D - V_{el}$. Using that graph one has to calculate several values of dD/dV and plot them against the volume (See sample on the rightmost figure).

$$dD/dV = \mathrm{tg}\varphi = a/b$$

The perpendicular dropped on the X-axis from the intersection point of the two curves corresponds to the minimal volume of electrolyte that causes coagulation. The coagulation threshold is found with the help of the formula:

$$\gamma = \frac{C_{\text{init}} \cdot V_x}{V_{\text{sol}}},$$

where γ is the coagulation threshold; C_{init} is the initial molar concentration of electrolyte; V_x is the volume of the electrolyte corresponding to the coagulation threshold (found graphically); V_{sol} is the volume of the sol.

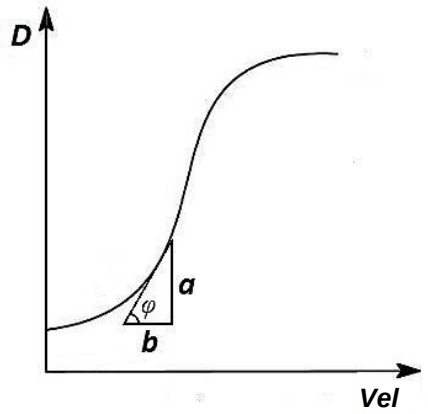

Figure 1. Dependence of the optical density (*D*) of sols on the volume of the electrolyte added (V_{el})

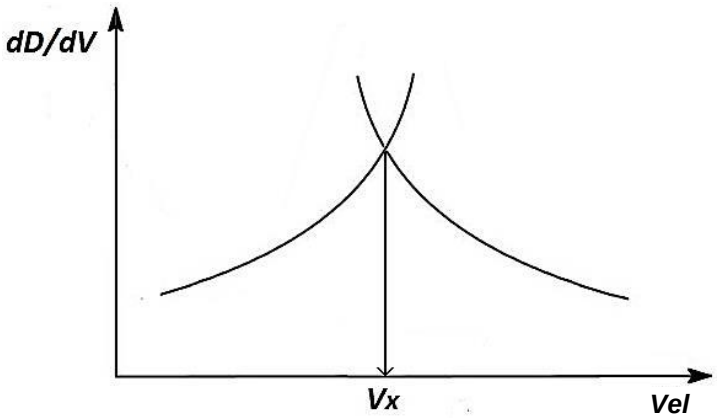

Figure 2. The plot of the derivative of D per V against V

Task.

1. To determine the electrolyte coagulation threshold with the respect to the sol by a colorimetric method, certain volumes of sol, water and electrolyte (see table) are thoroughly mixed in a flask. A 0.0005 M solution of K_2SO_4 is used as the electrolyte, and the coagulation threshold of this electrolyte is determined with the respect to the iron (III) hydroxide sol.

2. The optical density *D* is measured into special cuvettes. Measurements are made according to the instructions for working with the photoelectric colorimeter. The time interval between the addition of electrolyte to the sol and the measurement should be equal to one minute. Conduct eleven experiments, record the data in the Table.

	Flask number										
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
V($Fe(OH)_3$ sol), ml	0	10	10	10	10	10	10	10	10	10	10
V(H_2O), ml	5.0	4.5	4.0	3.5	3.0	2.5	2.0	1.5	1.0	0.5	–
V(0.0005 M K_2SO_4), ml	–	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
Optical density D											
d*V*											
d*D*											
d*D*/d*V*											

3. Calculate the values of d*D*/d*V* with the help of the results of the experiment (table).

4. Plot the dependence of d*D*/d*V* on V_{el}. Find the coagulation threshold.

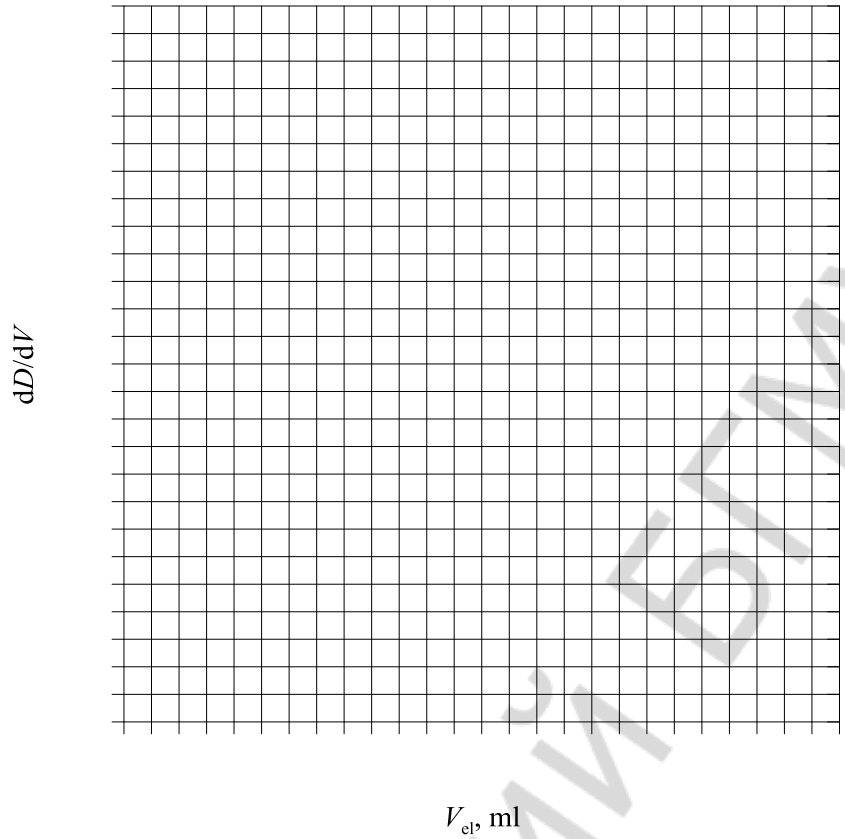

Figure 3. Dependence of d*D*/d*V* on V_{el}

5. The coagulation threshold is calculated by the formula:

$$\gamma = \frac{C_{init} \cdot V_x \cdot 1000}{V_{sol}} = \frac{\qquad\qquad}{\qquad\qquad} = \_\_\_\_\_,$$

where γ is the coagulation threshold, mmol/l; C_{init} is the initial molar concentration of electrolyte, mol/l; V_x is the volume of the electrolyte corresponding to the coagulation threshold, ml (found graphically); V_{sol} is the total volume of sol after the addition of water and electrolyte. In all the flasks it is equal to 15 ml. To express the coagulation threshold in mmol per liter one should multiply it by 1000.

Conclusion: the coagulation threshold of the K_2SO_4 solution with the respect to the iron (III) hydroxide sol γ = _____ was determined by _____ method.

Laboratory work 11. PREPARATION OF EMULSIONS, DETERMINATION OF THE TYPE OF EMULSIONS AND STUDY OF THEIR PROPERTIES

Objective: to get stable emulsions and determine their type; to study the inversion of the phases of the emulsion.

Reagents and devices: oil (liquid), water, 1 % solutions of K_2CO_3 and $CaCl_2$, solution of sudan (III), methylene blue solution, microscope, test tubes, slide glass.

Task 1. Obtain emulsion by dispersion method.

Experiment 1. Preparation of emulsion without emulsifier.

5 ml of distilled water is poured into a test tube, 5–6 drops of oil are added and shaken well until a white haze forms. The tube with the resulting emulsion is placed in a holder for subsequent observations.

Experiment 2. Preparation of an emulsion with an emulsifier.

5 ml of distilled water are poured into a test tube, 5–6 drops of oil are added, as well as 5–6 drops of a 1 % solution of K_2CO_3. The tube is shaken well until a milky white emulsion is formed. The tube should be kept in a holder for other tasks.

Conclusion: the emulsion obtained with / without emulsifier is more stable, because _____. Describe the resulting emulsions _____ _____.

Task 2. Determine the type of emulsion.

Experiment 3. Determination of the emulsion type by dilution method.

A. Put one drop of the emulsion made in the experiment 2 and one drop of water with a stick on the glass slide (side by side). Tilt the glass so that the drops touch.

The observed effect is _____ and the type of emulsion is _____.

B. 0.5 ml of oil, 5 drops of water and 5 drops of 1 % $CaCl_2$ solution should be poured together into a test tube. Shake the tube well until an emulsion is obtained. A drop of the resulting emulsion and a drop of water should be placed on the glass slide (side by side) and tilted. The observed effect is _____ and the type of emulsion is _____.

Experiment 4. Determination of the emulsion type by staining method.

3 drops of oil, 2 ml of distilled water, 2 drops of a 1 % solution of K_2CO_3 should be poured together into a test tube. Shake that tube strongly until the formation of emulsion. Then, one drop of sudan (III) solution and one drop of methylene blue solution are added.

Vigorously shake the tube for 1 or 2 minutes, put a drop of the resulting emulsion with a stick to the glass slide and examine it under a microscope. Draw an emulsion indicating the distribution of dyes (figure):

According to the Figure, the type of emulsion is _____. Save the emulsion for Task 3.

Task 3. To study the inversion of phases of emulsions.

Experiment 5. Half of the emulsion obtained in Experiment 4 should be poured into another tube together with 3 drops of oil and 4 drops of $CaCl_2$. After vigorous shaking of the tube for 1 to 2 minutes, study a drop of the resulting emulsion under a microscope. Draw an emulsion and determine its type.

The emulsion from experiment 4.	The emulsion from experiment 5.

According to the Figure, the type of emulsion is _____.

Conclusion: based on the results of experiments 4 and 5, the reason of the change in the type of emulsion is _____. The corresponding equations for the formation of a hydrophilic emulsifier and its conversion to a hydrophobic emulsifier are:

_____

_____

Laboratory work 12. CONDUCTOMETRIC DETERMINATION OF THE CRITICAL MICELLE CONCENTRATION

Objective: to get familiar with the method of the determination of the critical concentration of micelle formation.

Devices and reagents: educational-laboratory complex "Chemistry", graduated cylinders, scales, soap 2.25 g; volumetric flask per 1000 ml, distilled water.

Task. To determine the critical concentration of micelle formation, 7 solutions must be prepared.

Initial solution: 2.25 g of soap (M = 321 g/mol) should be added to a volumetric flask of 1000 ml. Then add distilled water to the mark.

Prepare solutions with the concentrations indicated in the table from the initial one and measure their electric conductivity (L) by the ELC "Chemistry". Solutions should be prepared immediately before the measurements to prevent the hydrolysis of the surfactant.

The measurement of electrical conductivity should be started from the solution No. 7. The results of conductometric measurements should be recorded in the Table together with the values of resistance R.

No. of solution	**$C_м$, mol/L**	**L, mS**	**R = 1/L, Ω**
Initial solution № **1**	0.0070		
solution № **2** (50 ml sol-n № 1 + 50 ml H_2O)	0.0035		
solution № **3** (50 ml sol-n № 2 + 50 ml H_2O)	0.00175		
solution № **4** (50 ml sol-n № 3 + 50 ml H_2O)	0.00087		
solution № **5** (50 ml sol-n № 4 + 50 ml H_2O)	0.000437		
solution № **6** (50 ml sol-n № 5 + 50 ml H_2O)	0.000218		
solution № **7** (50 ml sol-n № 6 + 50 ml H_2O)	0.000109		

Based on the calculated data, build the plot of R against C. Find the critical micelle concentration with the help of the plot. To make it, continue the straight sections of the curve until their intersection, drop the perpendicular from the intersection point to the X-axis and find the value of CMC.

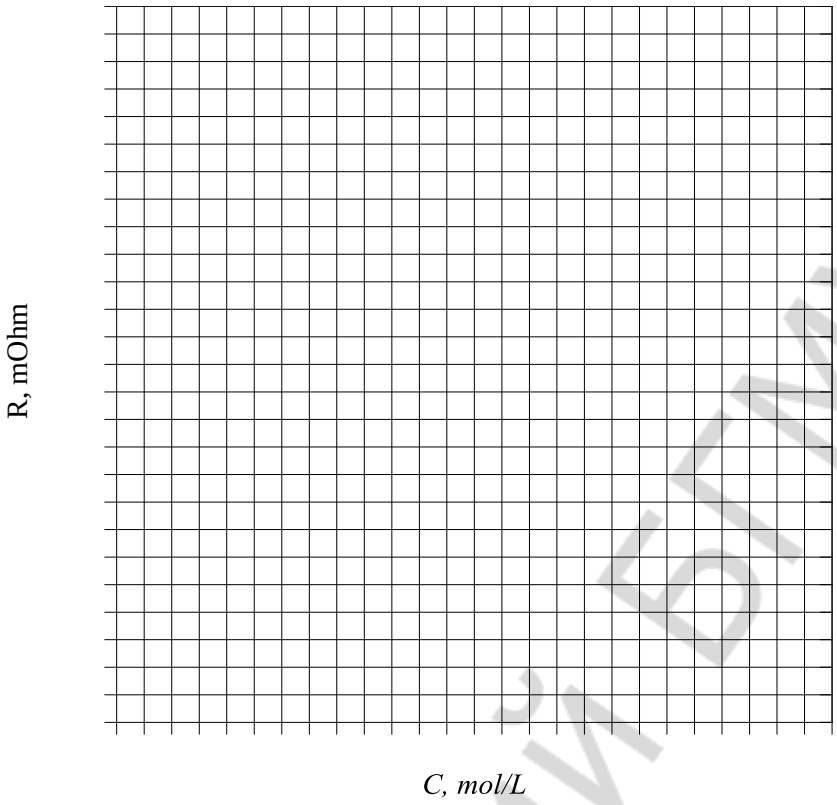

Figure 1. Dependence of the resistance *R* on concentration C

Conclusion: the critical micelle concentration determined by the conductometric method is _____.

Laboratory work 13. DETERMINATION OF THE ISOELECTRIC POINT OF THE PROTEIN

Objective: to learn how to determine isoelectric point of the protein.

Task. 1 ml of acetate buffer with pH 3.2; 4.1; 4.7; 5.3; 6.2 are poured into each of the five tubes. 0.5 ml of a protein (gelatin) solution with a mass fraction from 0.5 to 4 % and 4 ml of alcohol should be poured together in each tube. The contents of the tubes should be thoroughly mixed, the degree of turbidity of the samples is estimated against a dark background and qualitatively evaluated on a five-point scale. In the case of low turbidity in all the tubes, 0.5 ml of acetone is added to each of them. The maximal turbidity will be noticed in the tube with the maximal coagulation of the protein. The closer the pH to the pI, the stronger the coagulation.

Record the results in the table.

pH	**3.2**	**4.1**	**4.7**	**5.3**	**6.2**
Degree of turbidity					
Turbidity intensity (on a five-point scale)					

Conclusion: on the basis of this work, the isoelectric point of gelatin is equal to _____.

Laboratory work 14. EFFECT OF pH ON THE SWELLING OF GELATIN. THE SALTING OUT OF GELATIN FROM THE SOLUTION

Objective: experimentally confirm the dependence of the degree of swelling of the protein on the pH; to study the effect of electrolytes on the solubility of proteins.

Task 1. To determine the dependence of the degree of swelling of gelatin on the pH.

0.5 ml of gelatin powder is added to dry measuring tubes (10 ml). Then the following solutions are added until the top label in each tube: first — 0.1 M hydrochloric acid solution, second — $1 \cdot 10^{-5}$ M HCl solution, third — $1 \cdot 10^{-5}$M solution of NaOH, fourth — 0.1 M sodium hydroxide solution. The contents of the tubes are mixed with a stick. Do not forget to wash the stick with distilled water and to wipe after the mixing in each tube. After 30 minutes, the volume of the swollen gelatin is determined and the degree of swelling is calculated by the formula:

$$\alpha = \frac{V - V_0}{V_0},$$

where α is the degree of swelling; V_0 is the initial volume of the polymer, ml; V is the volume of the swollen polymer, ml.

The obtained data is added to the table.

System	pH	Volume of the polymer		Degree of swelling (α)
		initial (V_0)	swollen (V)	
0.1M HCl solution				
$1 \cdot 10^{-5}$M HCl solution				
$1 \cdot 10^{-5}$M NaOH solution				
0.1M NaOH solution				

The plot of the degree of swelling of the protein on the pH of the medium is constructed.

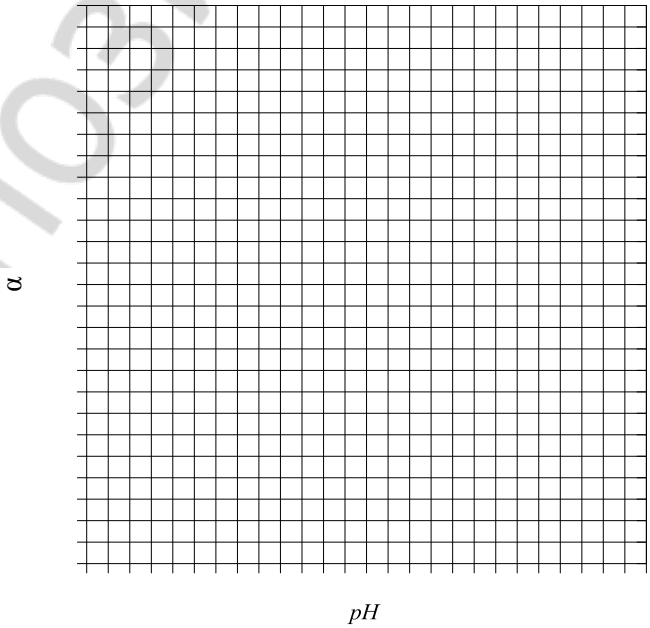

Figure 1. Dependence of the degree of swelling of the protein on the pH of the medium

Conclusion: with the increase of the pH of the medium, the degree of swelling of gelatin is _____.

Task 2. To salt out gelatin from its water solution.

A saturated solution of ammonium sulfate is poured into the solution of the protein (gelatin) in a test tube until the protein formation of precipitate. Then, add water to the test tube until the complete dissolving of the precipitate.

Conclusion: the precipitation of protein and its dissolution are due to _____.

Laboratory work 15. DETERMINATION OF THE RELATIVE MOLECULAR MASS OF POLYGLUCIN BY THE VISCOSIMETRIC METHOD

Objective: to determine the relative molecular mass of polyglucin by the viscosimetric method.

Devices and reactants: a viscometer, a stop-watch, solutions of polyglucin with different mass fractions: 0.03, 0.04, 0.05, 0.06, respectively.

Instruction. The determination of viscosity by the liquid flow method is based on the measurement of the outflow time of the same volumes of solution and solvent through the same capillary at the same temperature. That is why it is possible to calculate the relative viscosity based on the outflow times only. According to Poiseuille's law, the volume of liquid *V* flowing through the capillary tube is directly proportional to the time of flowing τ, the pressure of the column of liquid *p*, the fourth power of the capillary radius *r* and inversely proportional to the capillary length *l* and viscosity η:

$$V = (\pi \cdot \tau \cdot r^4 \cdot \rho)/(8 \cdot l \cdot \eta)$$

So, the viscosity is:

$$\eta = (\pi \cdot \tau \cdot r^4 \cdot \rho)/(8 \cdot l \cdot V)$$

where η is the viscosity; *r* is the radius of the capillary; *p* is the pressure of the column of liquid; *t* is the time of fluid outflow; *V* is the volume of the liquid; *l* is the length of the capillary.

To measure viscosity by this method, capillary viscometers are used, representing modified versions of the Ostwald viscometer. For a given viscometer, the length of the capillary *l* and its radius *r*, as well as the volume of the outflow fluid *V*, are constant. Consequently, they can be replaced by a constant *k*:

$$\frac{\pi \cdot r^4}{8 \cdot l \cdot V} = k,$$

Then the equation takes the form:

$$H = k \cdot \tau \cdot \rho.$$

According to this equation, at a constant pressure of a liquid column, the viscosity is proportional to the outflow time. In this case, the relative viscosity is expressed by the following equation:

$$\eta_{rel} = \eta/\eta_0 = (k \cdot \tau \cdot \rho)/(k \cdot \tau_0 \cdot \rho_0) = (\tau \cdot \rho)/(\tau_0 \cdot \rho_0),$$

where η_{rel} is the relative viscosity; η is the viscosity of the HMC solution; η_0 is the viscosity of the pure solvent.

If the fluids flow under the influence of their own gravity at equal altitudes of the liquid column, then the ratio of pressures can be replaced by the ratio of the densities.

For rather dilute solutions of biopolymers, the densities of solvent and solution are considered to be equal, and the relative viscosity is calculated by the simple formula:

$$\eta_{rel} = \tau/\tau_0,$$

where τ is the flow time of the dilute biopolymer solution; τ_0 is the flow time of the pure solvent.

Measure the outflow time for the solvent and solutions with different polymer concentrations, calculate relative, specific and reduced viscosities for these solutions, plot the graph of the dependence of the reduced viscosity of η_{spec}/C on the concentration C. The straight line should be extrapolated to the Y-axis and the value of the characteristic viscosity [η] should be found. Then the relative molecular weight of the polymer should be calculated from the Mark–Hauwink–Kuhn equation.

Polyglucin is a product of acid hydrolysis of native dextran $(C_6H_{10}O_5)_n$ — that is a polysaccharide of bacterial origin. A solution of polyglucin with a mass fraction of 6 % and a relative molecular weight in the range from 40,000 to 60,000 in a physiological solution of sodium chloride is used as a blood substitute.

Task. The dried Ostwald viscometer (figure 1) is installed strictly vertically in a water thermostat at a certain temperature. 10 ml of distilled water (solvent) are poured into a wide elbow (1) of the viscometer. With the help of a rubber pear, transfer the water into a narrow knee (2), the level should be 1–2 cm above the top mark (3), and let the water freely pass into the wide knee of the viscometer.

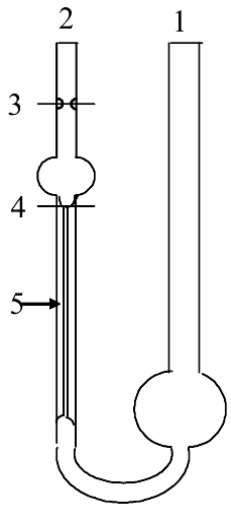

Figure 1. Ostwald viscometer

As soon as the water level is at the top mark, turn on the stopwatch. When the water level is at the bottom mark (4), stop the timer and record the time of water flow through the capillary (5). Repeat the measurement at least three times. Then the water is poured out through a wide elbow and the viscometer is rinsed with the most dilute polyglucin solution. Determine the flow time through the capillary of the viscometer for polyglucin solutions, starting with the solution of the lowest concentration. For each solution, the measurements are repeated at least three times. For calculations, take the mean of flow time calculated from three measurements. All the results of measurements and calculations should be recorded in the table.

		Flow time, s				η_{rel}	η_{spec}	η_{red}, cm^3/g
		τ_1	τ_2	τ_3	τ_{av}			
Water								
***C*(polyglucin), g/cm^3**	0.03							
	0.04							
	0.05							
	0.06							

Relative, specific and reduced viscosities of the solutions are calculated by the formulas:

$$\eta_{rel} = \tau/\tau_0 \qquad \eta_{spec} = \frac{\eta - \eta_0}{\eta_0} = \frac{\eta}{\eta_0} - 1; \qquad \eta_{red} = \frac{\eta_{spec}}{C}.$$

The graph of the dependence of η_{spec}/C on the concentration C is plotted (figure 2). The segment cut off by a straight line on the Y-axis corresponds to the characteristic viscosity [η].

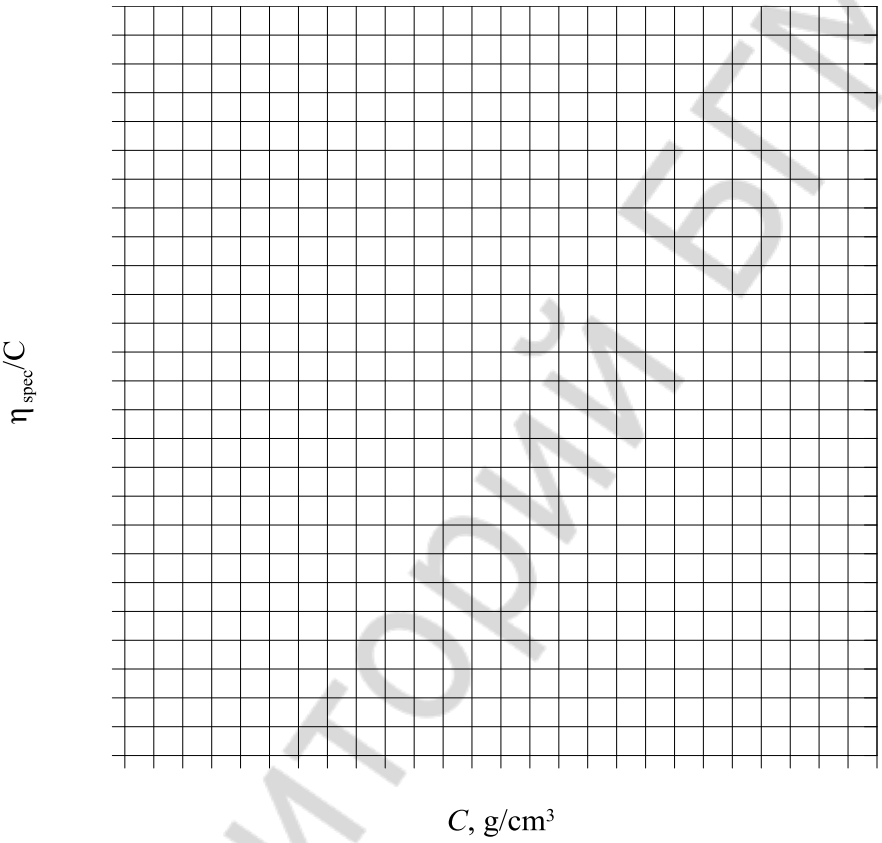

Figure 2. The dependence of η_{spec}/C on the concentration C

The relative molecular weight of the polyglucin is calculated by the way of the substitution of the value of [η] in the Mark–Hauwink–Kuhn equation: $[\eta] = K \cdot M \cdot \alpha$. For water solutions of polyglucin, the constants K and α are respectively equal to: $9.66 \cdot 10^{-2}$ cm^3/g and 0.5.

$$M = \frac{[\eta]}{K \cdot \alpha} = \text{\_\_\_\_\_} = \text{\_\_\_\_\_}.$$

Conclusion: the solution of polyglucin with the relative molar mass _____ is used as a blood substitute.

LITERATURE

1. *Барковский, Е. В*. Общая химия : учеб. пособие / Е. В. Барковский, С. В. Ткачёв, Л. Г. Петрушенко. Минск : Вышэйшая школа, 2013. 639 с.

2. *Медицинская* химия = Medical Chemistry : учеб. / В. О. Калибабчук [и др.]. 3-е изд., испр. Киев : Медицина, 2015. 224 с.

3. *Atkins, P*. Atkins' Physical Chemistry / P. Atkins, J. de Paula. 10th ed. Oxford University Press, 2014. 500 p.

4. *Kontogeorgis, G. M*. Introduction to Applied Surface and Colloid Chemistry / G. M. Kontogeorgis, S. Kiil. Wiley, 2016. 388 p.

5. *Buxbaum, E*. Biophysical Chemistry of Proteins : An Introduction to Laboratory Methods / E. Buxbaum. Springer, 2011. 510 p.

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Учебное издание

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ФИЗИЧЕСКАЯ ХИМИЯ РЕАЛЬНЫХ И КОЛЛОИДНЫХ РАСТВОРОВ

PHYSICAL CHEMISTRY OF REAL AND COLLOID SOLUTIONS

Практикум

На английском языке

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Подписано в печать 05.01.18. Формат 60×84/8. Бумага писчая «Снегурочка».
Ризография. Гарнитура «Times».
Усл. печ. л. 16,04. Уч.-изд. л. 8,02. Тираж 26 экз. Заказ 17.

Издатель и полиграфическое исполнение: учреждение образования
«Белорусский государственный медицинский университет».
Свидетельство о государственной регистрации издателя, изготовителя,
распространителя печатных изданий № 1/187 от 18.02.2014.
Ул. Ленинградская, 6, 220006, Минск.