

Task V

COLLOIDAL SOLUTIONS AND NEPHELOMETRY

I. Aim of the task

The aim of the task is determination of velocity of sulphur sol formation during a reaction of hydrochloric acid with sodium thiosulphate and concentration of colophony sol by the nephelometric method.

II. Introduction

1. Characterization of colloidal systems.
2. Classification of colloidal systems.
3. Methods of colloidal system preparation.
4. Properties of colloidal systems.
5. Stability of colloidal systems – DLVO theory.
6. Optical properties of colloidal systems – nephelometry.
7. Velocity of chemical reaction.

References:

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III. Theory

III. 1. Characterization of colloidal systems

In 1861 Thomas Graham introduced the term **colloids** (Greek *kolla* – glue and *eidōs* – like) for the substances, which exhibited some common properties – a lower diffusion velocity than inorganic salts (crystalloids), but passed through a filter paper as distinct from macroscopic suspensions. He described two classes of matter: crystalloids and colloids. This classification differentiated between the substances that would diffuse through a membrane separating water from an aqueous solution (crystalloids), and those which would not (colloids). Faraday differentiated **colloidal substances**, whose solutions were “transparent”, but light passing through them could be observed as a bright smudge (the Tyndall effect). One of the most important observations was Faraday’s discovery that small particles could be detected by focusing light into a conical region. The further studies proved that every crystalline substance could be obtained in a colloidal form. The X-ray studies showed that a lot of typically colloidal substances had, in fact, a microcrystalline structure. When one claimed that the same substance could exhibit colloidal or crystalline properties, depending on the medium, such classification did not make physical sense. Graham used the term colloid to distinguish types of matter, but later it became apparent, that colloids are not separate types, but matter in a particular state of subdivision, in which effects connected with the surface are pre-eminent.

Nowadays the term “colloidal state” instead of “colloidal substances” is used as the matter state as common as the liquid state or the solid state. It is also hard to accept the Tyndall effect as characteristic of this state, because possessing sufficiently precise devices this phenomenon can be detected also in so-called true solutions. However, the definition based on the dispersal degree as a characteristic parameter of the colloidal state is still accepted.

Colloidal systems (in short **colloids**) are called **dispersed systems**, mostly binary, visible as physical homogeneous systems, although two components are not mixed molecularly. The colloidal system has a highly dispersed state in which single particles consist of aggregates of molecules. In contrast to pure homogeneous solutions, every colloidal system is a heterogeneous system consisting of at least two different phases: a **continuous phase** (or **dispersion medium**) and a **dispersed/disperse phase** (or **internal phase**). The dispersed phase consists of the colloidal particles with the dimensions from 1 to 100 nm, and even to 500 nm (0.5 μm) – the particles recognized by an ultramicroscope.

In the thirties Oswald introduced this classification according to the state of aggregation of the disperse phase and the dispersion medium. He gave such borderline values, below which there are the true solutions and above which the macroscopic suspensions exist. According to the state of aggregation classification is more suitable for general characterization of the variety of colloidal systems than other approaches. A disadvantage, however, is the adaptation of the state of the dispersed phase of different colloidal systems with the decreasing particle size. Based on thermodynamic criteria

it is very difficult to use the term “state” for the particles smaller than 0.1 nm that consist of no more than a few molecules.

Interpretation of these borderline values results from the fact that physical and chemical properties of the dispersed systems are determined by a state of interfacial surface. The colloidal systems consist of at least two phases. The problem: how many molecules must aggregate to a particle to obtain a new phase, is open. A single phase is homogeneous, i.e. it cannot contain any heterogeneities (fluctuations, defects), which could be treated as particles. Molecules at the interface always exhibit special properties, because they are within field of the molecular forces of neighbouring phases. Thickness of such surface phase, dependently on a structure of substance, is from 0.5 to 2 nm. As a particle cannot consist of only the surface layer, its dimension in all three spatial directions must be at least 1 nm.

III. 2. Classification of colloidal systems

The colloidal systems can be divided not only into these, in which particles of the dispersed phase have all three “colloidal” dimensions, but also those with “foliated” particles – one “colloidal” dimension and two macroscopic dimensions and “thread like” particles – two “colloidal” dimensions and one macroscopic dimension. It is one of the classifications of the colloidal systems.

III. 2.1. Classification of colloidal systems according to the phase state

The next essential classification is the classification according to the phase state of the dispersion medium and the disperse phase. Only two components in a gas phase cannot form the colloidal system, because they always mix molecularly. Other combinations are possible, therefore there exist 8 types of the colloidal systems.

Table. I. Types of colloidal systems and examples.

| Dispersion medium | Disperse phase | Technical name | Examples |
|-------------------|----------------|-------------------|---|
| Gas | gas | not existing | |
| | liquid | aerosol, | mist, fog, hairspray, cloud, condensing vapor |
| | solid | gasosol, aerosol | dust, smoke |
| Liquid | gas | foam, sol | gas bubbles in liquid – lather, fire extinguisher foam |
| | liquid | liosol, emulsion | milk, mayonnaise, gelatin solution, white/protein |
| | solid | lisol, suspension | metal sol, sulphide sol, $\text{Me}(\text{OH})_y$, Me_xO_y , printing ink, paint |
| Solid | gas | solid foam | insulating foam, pumice, gas occlusions in minerals |

| | | | |
|--|--------|-----------------------------|--|
| | liquid | solid foam, solid emulsion | bituminous road paving, ice cream, milky quartz |
| | solid | solid sol, solid dispersion | ruby glass (Au in glass), phosphate beads, NaCl crystals dyed by colloidal particles of metallic Na, some alloys |

The most common are colloidal systems with the liquid dispersion medium called **colloidal solutions** or **liosols** or more frequently **sols**.

III. 2.2. Classification of colloids according to behaviour of the disperse phase to the dispersion medium

According to behaviour of the disperse phase to the dispersion medium colloids can be divided into:

- **lyophilic** – particles of the disperse phase connect with molecules of the dispersion medium (solvate), which causes stability of the colloidal system (protein, tannin, synthetic polymers containing polar groups, e.g. polyvinyl alcohol, polyethylglycols),
- **lyophobic** – do not solvate (or solvate to a small extent), mainly stabilized by an electric charge.

III. 2.3. Classification of Bungenberg de Jong

A classification proposed by Bungenberg de Jong seems to be one of the most reasonable classifications:

- molecular colloids,
- phase colloids,
- association colloids.

Molecular colloids (lyophilic) consist of molecules with colloidal dimensions. These colloidal particles (molecules) are held together by chemical bonds. A colloidal character of the molecules results from a chemical structure, not from aggregation, hence an electric charge is not necessary to stabilize the colloidal solution. Solutions of proteins, nucleic acids, polysaccharides, polyisomers, gelatin, cellulose, latex and synthetic macromolecules are the examples of molecular colloids, which are called **colloidal bodies**. Individual macromolecules can also be collected into larger aggregates held together by non-covalent bonds, as in biocolloids.

Most macromolecular solutions consist of particles of varying size, that is, they are polydisperse. Therefore a molecular mass of the dissolved substance of the polydispersed system is given as a mean value.

One can distinguish mean molecular masses:

- numeral,
- weighed,
- viscous.

Mean numeral molecular mass (\bar{M}_n) is a ratio of total mass of all molecules and their number:

$$\bar{M}_n = \frac{\sum_i n_i M_i}{\sum_i n_i} \quad (1)$$

Mean numeral molecular mass \bar{M}_n represents a distribution of the total mass of the dissolved (dispersed) substance $\left(\sum_i n_i M_i\right)$ by all molecules $\left(\sum_i n_i\right)$.

Mean weighed molecular mass (\bar{M}_w) can be given by:

$$\bar{M}_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} \quad (2)$$

Mean weighed molecular mass is used when a share of heavier molecules affects the system properties.

Mean viscous molecular mass (\bar{M}).

Einstein derived a formula expressing a relationship of the colloidal solution viscosity η and the volume ratio of the dispersed substance Φ :

$$\eta = \eta_o (1 + 2.5\Phi) \quad (3)$$

The parameter Φ denotes the ratio of the total volume of the colloidal particles and the total volume of solution:

$$\Phi = \frac{Nv}{V_o} \quad (4)$$

where: N denotes the particle number, v – the single particle volume, and $V_o = Nv + V_{solvent}$.

Coefficient 2.5 in equation (3) refers to spherical particles, therefore this equation can be expressed in the form:

$$\frac{\eta - \eta_o}{\eta_o} = 2.5\Phi \quad (5)$$

The left side of the equation expresses so-called specific viscosity η_{sp} . Viscosity depends on the concentration of dispersed substance, therefore η_{sp} should be determined for infinitely small concentrations, that is, boundary viscosity η_{lim} :

$$\eta_{\text{lim}} = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} \quad (6)$$

This relationship is used for determination of mass of the colloidal particle from the Staudinger-Mark-Houwink formula:

$$\eta_{sp} = [\eta] = K \overline{M}_v^\alpha \quad (7)$$

where: K and α – the magnitudes characteristic of the solvent and the dispersed substance. They depend on temperature and interaction of particle(molecule)/solvent molecules. \overline{M}_v^α – the mean viscous molecular mass.

In the case of **phase colloids** a colloidal particle is not a chemical molecule of a substance forming the disperse phase. Since atoms or molecules at or near the phase boundary have higher free energies than those in the interior of the phase, phase colloids have a large excess of free energy: the ratio of surface area to volume increases as the particle size decreases. Therefore dispersion colloids tend to form coarser aggregates (coagulation) with a loss of free energy in the process. Aggregation and disaggregation lead to formation of new particles of the same chemical character. They can be stabilized if the particles have a sufficiently strong electric charge; this is achieved by dissociation of surface groups or by preferential adsorption of ions with the same charge. Then the particles attract a shell of counter ions, which compensates for the electrical charge on their surfaces. Electrostatic repulsion occurs if the double layers of ions around two particles interpenetrate. This energy must compensate for the kinetic energy of the Brownian motion and the van der Waals energy. In practice, all dispersion colloids carry electric charges; metal colloids are usually negatively charged, whereas oxides are either negative or positive, depending on pH. Stabilization also occurs if the colloidal particles are highly solvated; in this case, their free energy decreases because of the solvation energy. Highly solvated colloids are often called lyophilic colloids. Finally, the addition of surface active compounds, such as tensides or macromolecules stabilizes

colloids. The tensides are called *dispersives*, *emulsifiers* or *foam stabilizers* and the macromolecules, *protective colloids*.

Association (micellar) colloids consist of aggregates formed by an association of molecules of dissolved substances. The material when dissolved in a liquid medium at low concentrations forms solutions on the molecular level which differ from other solutions only in quantitative terms. But as soon as a certain “critical” concentration range is surpassed, the dissolved molecules form aggregates, called “micelles” as a result of the interaction of van der Waals forces. These structures have colloidal dimensions and are called **association colloids**. This concentration range is indicated loosely by critical micelle concentration (**cmc**). Strictly speaking, a small number of micelles should be present in surfactant solutions even below the cmc: there is a dynamic equilibrium between micelles and single molecules. Character of this equilibrium depends on a concentration and a temperature of the solution. The association colloids include: soaps, detergents, tannins.

III. 3. Methods of colloidal system preparation

To obtain a colloidal fragmentation there can be applied two methods:

1. **dispersion methods** – the fragmentation of bigger particles to the colloidal dimensions (sizes) (1–100 nm). Compact matter must be divided by external forces.
2. **condensation methods** – the joining of molecules or ions to form larger clusters (aggregates).

Dispersion methods. Solids can be ground or broken, and liquids or gases can be dispersed by supersonic vibrations or centrifugal force. The other methods are: atomization by ultrasounds or temperature, lighting of metals immersed in liquid medium by UV or X-rays. Sols of metals can be obtained by atomization in Volt's arc (Bredig method). Peptization is the spontaneous dispersion of aggregates of colloidal particles, for example by an adsorption of ions from an electrolyte on particles of the solid phase. The particles thus acquire a similar electric charge and repel each other.

Condensation methods are mostly chemical methods. The most important methods for preparing dispersions from molecular size material are crystallization and polymerization. In both cases it is possible to control the process of nucleus formation and

particle growth to prepare mono-disperse solid particles to a high degree of approximation. Colloidal particles can be obtained either from highly concentrated (saturated or highly saturated) solutions by homogeneous seed formation, or from very dilute solution by heterogeneous seed formation. Polymerization or polycondensation reactions conducted under special conditions allow for participation of the sparingly soluble substance in the colloidal form (hydrosols of silver halide, metal sulphide, silicon acid). Hydrolysis of salt solutions leads to hydrosols of metal hydroxides and oxides. Sols of noble metals can be obtained by reduction of dilute salt solutions of these metals. There are also used oxidation reactions, for example the oxidation of hydrogen sulphide by sulphur dioxide or the oxidation of sodium thiosulphate by sulphuric acid lead to the colloidal sulphur. A decrease of solubility, that is transition of a given component from a medium in which it is soluble to a medium in which it is insoluble, is also the condensation method.

III. 4. Kinetic properties of colloidal systems

III. 4.1. Diffusion

Diffusion – the transport of gases, liquids or solids driven by differences in concentration. Diffusion occurs spontaneously, due to microscopic particle motion, and in a direction which tends to equalize concentration differences. Diffusion is connected with a kinetic motion of molecules, and depends on its size. Because molecules in colloidal systems are significantly larger than those in true solutions, the diffusion process in the colloidal solutions is slower. The most characteristic mechanic property is the **Browni-**

an motion, that is, random motion of small particles, such as dust or smoke particles, suspended in a gas or liquid. The Brownian motion of colloidal particles dispersed in water was first observed in a light microscope by Brown, a botanist, in 1827. Hence, that motion was called the Brownian motion. The Brownian motion consists of a series of movements of unequal magnitude and in arbitrary directions. In general, a dispersed particle is free to move in all three dimensions.

The Brownian motion in dusts and fogs (aerosols) was first observed by the Polish scientist Badoszewski in 1881. The supporting theory was presented simultaneously by Einstein and Smoluchowski in 1905. Microscopic studies of Einstein and Smoluchowski led to the proof of the theory of Brownian motion and diffusion of colloidal particles. The Brownian motion was expressed by the mean square displacement during the same time interval:

$$\overline{x^2} = \frac{RT}{N_A} \frac{t}{3\pi\eta r} \quad (8)$$

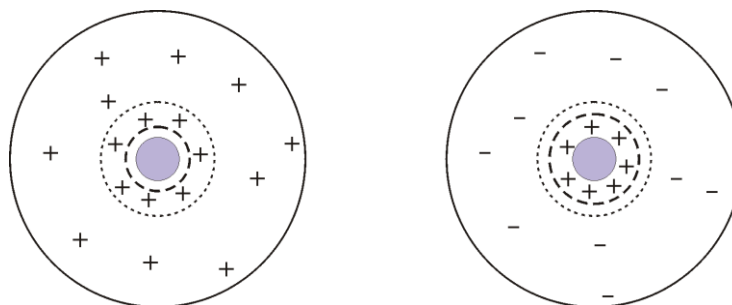
where: x – the direction during the time interval Δt , $\overline{x^2}$ – the square of mean view of the colloidal particle on the chosen axis, η – the viscosity coefficient, r – the colloidal particle radius, t – the observation time, and the other symbols have common meaning.

III. 4.2. Factors stabilizing colloidal systems

The factors which influence the stability of colloidal systems are:

- electric charge and its surface density,
- solvation of particles of disperse phase.

The first factor dominates in the case of the phase colloids, the second one in the case of the molecular colloids. A colloidal particle immersed in an electrolyte solution is usually charged owing to the adsorption of ions onto the particle surface and/or the ionization of dissociable groups on the surface. If two phases such as aqueous electrolyte solution and a metal come into contact, charge carriers (electrons or ions) are often



transferred between them. The charge carriers can either enter the aqueous phase or be adsorbed from it, leading to a potential difference between two phases. Mobile electrolyte ions with the charges of sign opposite that of the particle surface charges are called

counterions. The ionic cloud together with the particle surface charge forms an electrical double layer, that is, the layer consisting of an inner (adsorption) layer, firmly bound to the particle or solid surface, and an outer (diffuse) layer. The charges at the phase boundary are compensated by the same number of counterions in the aqueous phase. The rest of the counterions are found in the diffuse part of the double layer.

A particle consisting of a sparingly soluble aggregate and connected with its ionic layers is called a **micelle**. Depending on the adsorbed ions and pH of environment, the particle can be negatively or positively charged. Relative motion of the two phases causes a part of the diffuse double layer to be sheared off; the resulting potential jump at the shear plane is called the *electrokinetic potential* or *zeta potential*, that is, the potential which develops on the shear surface between the particle and the electrolyte solution, between the static (adsorption) layer and the mobile (diffuse) one. Under the influence of an external electric field, colloidal particles are divided along the shear plane. Then the particles with their adsorption layer migrate to one electrode and the diffuse layer to another one. The potential on the shear surface is smaller than the surface potential which is calculated from the number of charge carriers per unit of surface area.

The electric properties of the colloidal systems play an important role in the interactions between colloidal particles; determine stability of the colloidal systems.

III. 4.3. Stability of colloidal systems

A characteristic property of colloidal systems is the instability of their aggregates, which exhibit a tendency towards coagulation and flocculation.

Coagulation denotes aggregation of colloidal particles. The first step is the approach of particles, either through the Brownian motion or flow processes, to an equilibrium distance. This can lead, in a second step, either to loose aggregation (flocculation) or to a compact phase (coalescence). The approach of colloidal particles toward one another is subject to a number of forces: electrostatic repulsion due to interpenetration of their diffuse electrochemical double layers, van der Waals attractive forces, and steric repulsion which arises when the adsorption layers penetrate each other. The latter are caused by the oriented adsorption of solvent molecules, or by the adsorption layers of tensides or macromolecules. During coagulation the particles adhere to each other, the displacement of adhering dispersion medium takes place and the surface area of the particles is decreased. The Gibbs energy of the system also decreases.

Flocculation is a process, in which the approach of colloidal particles to one another occurs in the presence of a flocculating agent, which provides countercharges for the colloidal particles. Flocculation in aqueous suspensions is usually achieved by the addition of suitable inorganic electrolytes with polyvalent cations or macromolecular organic flocculants. There are two main stages of flocculation: destabilization of the colloid and transport of the particles to one another. The particles do not touch each other because they are separated by solvent molecules. The particles in an aggregate called **flocculant** lose their individual kinetic properties and the flocculant moves as the entirety. During flocculation the surface is not decreased. The flocculant particles can be separated easily by mixing and adding suitable substances. Flocculation is the reversible process.

One distinguishes between attractive forces (van der Waals forces) which lead to an approach of the particles, and repulsive forces (e.g., electrostatic forces), which hinder that approach. The lyophobic sols are mainly stabilized by electrostatic repulsion, therefore they are sensitive to the addition of electrolytes, which generally reduce the electrostatic repulsion, which causes precipitation of the colloidal particles – coagulation (transition sol → gel). The fastest coagulation takes place at the point of zero charge (PZC) or at the isoelectric point (IEP). To stabilize the dispersed system, the repulsion forces between the particles must be larger than the attraction ones. Attraction and repulsion are the results of the intermolecular forces.

In the 1940s, Derjaguin, Landau, Verwey and Overbeek developed a theory of colloidal stability now known as the **DLVO theory**. This theory has made it possible to discuss the stability of lyophobic colloids quantitatively. The DLVO theory is based on the interaction due to overlapping of electrical double layers and London-van der Waals forces between colloid particles. A starting point of the DLVO theory is an assumption, that the total energy of the system is a sum of electrostatic energy U_e and dispersive energy U_D , that is, the stability of colloid particles depends on the total potential energy of interaction:

$$U = U_e + U_D \quad (9)$$

and

$$U = \frac{8k^2 T^2 \varepsilon_0 \varepsilon a}{e^2 z^2} \exp(-\kappa d) \left[\frac{\exp \frac{z e \psi_\delta}{2kT} - 1}{\exp \frac{z e \psi_\delta}{2kT} + 1} \right]^2 - \frac{H a}{12d} \quad (10)$$

where: k – the Boltzmann constant, T – the absolute temperature, ε – the relative electrical permittivity, ε_0 – the electrical permittivity of a vacuum, a – the particle radius, e – the elementary charge, z – the valence, $1/\kappa$ – the thickness of diffuse layer (screen parameter), d – the distance between particles, ψ_δ – the potential induced by the diffuse layer in the charge layer, H – the Hamaker constant.

If two charged particles in a dispersion medium approach each other, their diffuse double layers permeate and the repulsion between two identical double layers always develops due to the accumulation of ions in the diffuse layer.

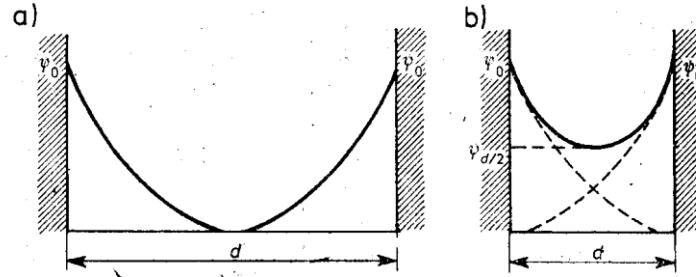


Fig. 1. Schematic representation of the electric potential versus distance for two not disturbed double layers (a) and two permeating double layers (b).

Fig. 1a represents the electric potential that single double layers have in the absence of interactions. However, if both diffuse double layers permeate, the charge and potential distribution are varied because of equilibrium disturbance between the attraction of the interfacial charge and the calorific movement of counterions. The potential between the particles $\psi_{d/2}$ consists of additive potentials, which would occur there in the absence of the second/latter particle and assuming that the potential of double layer of the particle is constant. With permeating, the charge of double layer decreases – the surface ions disappear because of the neutralization of counterions. However, if the surface charge is constant, the potential of diffuse double layer changes. Both ways lead to the same expression for the interaction energy between two particles. The repulsion energy depends on:

- the potential of diffuse double layer,
- the potential between two particles,
- the concentration of ions,
- the charge of ions.

The electrostatic interaction energy between two spherical particles with a radius a can be written:

$$U_e = \frac{a\kappa}{z^2} f(\Psi_\delta, \Psi_{\delta/2}) \quad (11)$$

If the electrical double layers permeate each other only to a small extent, that is, in the case of a weak interaction, to calculate the electrostatic energy of interaction the approximation can be applied:

$$U_e = \frac{8k^2 T^2 \epsilon_0 \epsilon a}{e^2 z^2} \exp(-\kappa d) \left[\frac{\exp\left(\frac{ze\psi_\delta}{2kT} - 1\right)}{\exp\left(\frac{ze\psi_\delta}{2kT} + 1\right)} \right]^2 \quad (12)$$

To characterize the electrostatic interaction in dispersed systems, knowledge about the potential of diffuse double layer and the content of electrolyte solution, that is,

ion concentrations and valency of counterions, is needed. To calculate the electrostatic interactions, the potential ψ_δ of particles is required. Unfortunately, this potential practically cannot be measured or calculated (only it can be determined for a few cases). Therefore, instead of ψ_δ the zeta potential ζ is used ($\Psi_\delta \approx \zeta$) despite that the position of shear plane and the structure of liquid within this plane are unknown.

Considering equation (12) in view of intermolecular forces, one can claim that the electrostatic energy exponentially decreases with the distance. At near and remote distances the attraction forces should dominate. Fig. 2 presents the dependence of the energy U on the distance for given values of the potential ψ_δ of spherical particles.

Appearance of the maximum indicates the energetic barrier making the colloidal particle joining (flocculation) difficult. If the thermal energy of particles is greater than the energetic barrier, each collision results in joining the particles, that is, coagulation. The height of the energetic barrier depends on the ψ_δ value, which depends on the adsorption of potential creating ions, surface active ions and electrolyte concentration. The effect of the electrolyte comes from screening of the particle charge by the electrolyte ions, which can be expressed by the Debye parameter $1/\kappa$.

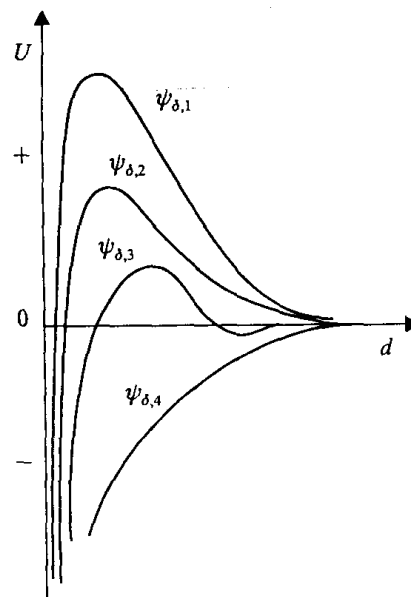


Fig. 2. Dependence of the interaction energy on the distance for spherical particles for given values of the potential ψ_δ .

As a result of intermolecular interactions particles approach each other up to a given distance, which corresponds to the total energy. If the liquid layer is between particles, they can be divided by using mechanical work (mixing). This process is called peptization. **Peptization** is the spontaneous dispersion of aggregates of colloidal particles. The particles thus acquire a similar electric charge and repel each other.

The repulsion energy is dependent on the potential value, but this effect is limited. At high potentials a part of the formula, dependent on the potential, approaches 1.

In Fig. 3 an effect of potential on the electrostatic repulsion energy for flat particles at 20 nm and ionic strength 10^{-3} M is presented.

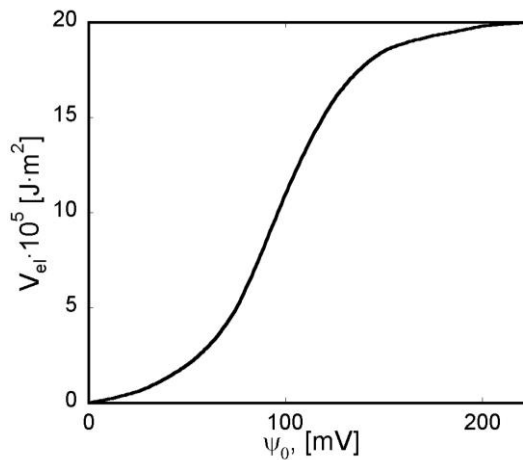


Fig. 3. Effect of the potential of the diffuse electrical double layer on the repulsion energy.

III. 4.4. Optical properties

The optical properties of colloidal systems are essential. A light beam passing through a solution can be absorbed or scattered. In case of true solutions mainly light absorption appears but in case of colloidal solutions **light scattering** is more important.

The **medium** is called **optically homogeneous** if its refractive index is not dependent on spatial coordinates and it is constant in the whole medium volume. Optically homogeneous medium does not scatter the light.

The **medium** is called **optically nonhomogeneous** if the refractive index is different in all points of medium because of e.g. the density fluctuation and the presence of particles of an additional substance. The light scattering in the medium, in which the heterogeneities are smaller than $(0.1-0.2)\lambda$, where λ is the light length, is called the **Rayleigh scattering** or the **Tyndall effect**.

In 1857 M. Faraday discovered that a beam of light is scattered when it passes through a colloid or true solution. In 1863 J. Tyndall stated that the scattered light is polarized. If an electromagnetic wave propagates through the medium, the molecules or atoms of the medium are polarized, and the positive and negative charge centers vibrate with respect to each other. This constitutes an oscillating electric dipole which emits light of the same wavelength as the exciting light. In an isotropic crystal, in which all the atoms are in their rest positions, scattered light is not emitted, because for each volume element which emits light, there is another which emits light 180° out of phase with the first; the scattered light is thus quenched by interference. However, if the polarization of the light emitted from microregions (such as colloidal particles) varies, scattering is observed. Scattered light is measured by **nephelometry** based on the Tyndall effect.

III. 4.5. Nephelometry

Nephelometry is an optical method for quantitative determination of the solid fraction in suspensions or aerosols from the intensity of light scattering. In analytical chemistry the methods for determining the amount of cloudiness, or turbidity, in a solution are based upon measurement of the effect of this turbidity upon the transmission and scattering of light. Turbidity in a liquid is caused by the presence of finely divided suspended particles. If a beam of light is passed through a turbid sample, its intensity is reduced by scattering, and the quantity of light scattered is dependent upon the concentration and size distribution of the particles. In nephelometry the intensity of the scattered light is measured at the angle of 90 or 45° to incident light, while, in turbidimetry, the intensity of light transmitted through the sample is measured.

Classical light scattering theory was derived by Lord Rayleigh and is now called the **Rayleigh theory**. The Rayleigh theory applies to small particles. By small particles, we mean particles whose size is much less than λ or the wavelength of the light that is being scattered. Intensity of the scattering light I_r scattered by spherical and colourless particles can be related with intensity of the incident light I_o by the equation:

$$I_r = 24\pi^3 I_o \left(\frac{n_1^2 - n_2^2}{n_1^2 + 2n_2^2} \right)^2 \frac{Nv^2}{\lambda^4} \quad (13)$$

where: n_1 and n_2 are the refractive indices of the disperse phase and the dispersion medium respectively, N is the general number of scattering particles, v the particle volume, λ the wavelength of incident light.

For the colloidal solutions with a different dispersion degree and the general number of particles per volume unit, the above relationship can be presented in the simpler form:

$$I_r = k \frac{zv^2}{\lambda^4} \quad (14)$$

where: k is the constant of proportionality, and z the number of particles per volume unit.

The ratio of intensity of scattering lights I_{r_1} and I_{r_2} for two suspensions with a different particle size of the dispersed phase, is proportional to the particle size of both sols v_1 and v_2 :

$$\frac{I_{r_1}}{I_{r_2}} = \frac{v_1}{v_2} \quad (15)$$

which allows for determination of the colloidal particle sizes.

In the case of two colloidal systems containing particles of similar size, the ratio of intensity of the scattering lights is proportional to their concentrations, which can be expressed by:

$$\frac{I_{r_1}}{I_{r_2}} = \frac{c_1}{c_2} \quad (16)$$

Using formula (16) one can find the concentration of the studied sol if intensity values of scattering lights and concentration of standard sol are known. It gives possibility to apply the nephelometry in quantitative analysis.

The Tyndall effect was applied for an ultramicroscope construction. The ultramicroscope is a device used to study colloidal-size particles that are too small to be visible in an ordinary light microscope. The light scattered by the particles is measured, which makes them appear spherical regardless of their actual shape. In the older versions, the sample is observed perpendicular to the incident light. In the newer versions, the forward separation at small scattering angles is measured, so the primary beam must be blocked. If the particles flow through the lighted volume, their number and size can be analyzed. The particles, usually suspended in a liquid, are illuminated with a strong light beam perpendicular to the optical axis of the microscope. These particles scatter light, and their movements are seen only as flashes against a dark background; their structure is not resolved. The ultramicroscope is used for determination of the diffusion coefficient, density of colloidal system, coagulation velocity and particle radius. Some of the colloidal solutions exhibit the stronger light absorption than the light scattering. The absorption measurement allows for an evaluation of concentration of the disperse phase and tracking of the coagulation process. The colour of colloidal systems depends on the dispersion degree and can differ in transmitted and scattered light.

IV. Experimental

A. Devices and materials

1. Device: Turbidimeter HI88713.
2. Equipment:
 - beaker – 50 cm³ – 2 u,
 - Erlenmayer flask – 100 cm³,
 - measuring flask – 100 cm³,
 - measuring flask – 25 cm³ – 6 u,
 - graduated pipette: 5 i 10 cm³,
 - full pipette: 5 cm³ – 2 u,
 - cuvette.
3. Materials: aqueous solutions: 0.02 and 0.05 M HCl and solutions: 0.01 and 0.25 M Na₂S₂O₃; colophony solution in alcohol – 2%.

B. Program

1. Preparation of the spectrophotometer for measurements.
2. Preparation of the reaction mixture (HCl + Na₂S₂O₃).
3. Measurement of turbidity of the reaction mixture (HCl + Na₂S₂O₃) as a function of time.
4. Preparation of a basic solution of colophony and solutions to obtain a calibration curve.
5. Measurement of turbidity of the colophony solutions for the calibration curve and a solution of an unknown concentration (given by a demonstrator).
6. Development of the results.

C. Use of devices

1. Turbidimeter HI88713

The HI88713 Turbidimeter with high measurement accuracy works consistently with ISO 7027 standards.

The range of turbidity measurements is: 0.00 to 1000 FNU (formazine nephelometric units) in FNU mode, 10-4000 FAU (formazine suppression units) in FAU mode, 0.00 to 4000 NTU (nephelometric turbidity units) in proportional NTU mode and 0.00 to 1000 NTU in non-proportional NTU mode.

Round (25 mm) cuvettes are made of special optical glass that guarantees repeatability of measurements. The instrument is calibrated for turbidity at 5 points (<0.1; 15; 100; 750; 2000 NTU).



Fig. 4. Turbidimeter HI88713, HANNA Instruments.

To conduct measurements there are needed to:

- turn on the nephelometer using the ON / OFF switch on the device back,
- fill the cuvette up to the 10 mL mark,
- insert the cuvette into the measuring cell,
- close the cover of the device,
- press the READ button and read the NTU value,
- when taking measurements in time, before each reading, press the READ button,
- after completing the measurements, remove the cuvette from the cell,
- repeat the activities for other samples.

The lid of the instrument should be closed during measurements!

D. Methods

1. Pour 5 cm³ of 0.05 M HCl and 0.025 M Na₂S₂O₃ to the beakers of 50 cm³ volume. Assume a moment of mixing of these two solutions from two beakers as $t = 0$ [min]. In the next step, put the studied solution into the pure cuvette, place it in the measuring cell and conduct a measurement in the above way. Measure the turbidity value starting from $t = 2$ min. after mixing both solutions, first every minute, and later every 2 min, and at the end of the experiment (when *NTU* changes are small) every 5 min. Repeat the second series of experiments for the 0.02 M HCl and 0.01 M Na₂S₂O₃ solutions.
2. Put 10 cm³ of the colophony solution in alcohol into the Erlenmeyer flask with distilled water (about 50 cm³ of water) mixing intensively. Leave the solution for 15 min, next

pour to a measuring flask (100 cm³) and fill to the mark with distilled water. The obtained colophony sol contains 10⁻³ g of the disperse phase in 1 cm³. In the measuring flask of 25 cm³ volume, prepare 5 solutions with the concentrations c [g/cm³] given by the demonstrator from Table I. Calculate how much colophony solution (cm³) should be used to obtain the required concentrations.

Table I.

| Number of sample | Number of series | 1 | 2 | 3 | 4 | 5 |
|---|------------------|-----|-----|-----|-----|-----|
| $c \cdot 10^{-4}$ [g/cm ³] | I | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 |
| | II | 0.2 | 0.6 | 1.0 | 1.4 | 1.8 |
| | III | 0.4 | 0.8 | 1.2 | 1.6 | 2.0 |

The demonstrator prepares a sample of the colophony sol of unknown concentration. The measurement of the turbidity value of the prepared samples should be conducted in the above way.

E. Results and conclusions

- Put the obtained values of turbidity for the solution of sulphur sol in the table:

| $c_{\text{HCl}} =$ | $c_{\text{Na}_2\text{S}_2\text{O}_3} =$ |
|--------------------|---|
| t [s] | NTU |
| | |

and present as graphs of the dependence $NTU = f(t)$ for both series (on one plot).

- Draw the turbidity curve of the colophony sol as a function of the solution concentration and based on this calibration curve determine the concentration of the sample prepared by the demonstrator. Include the results in the table:

| $c \cdot 10^{-5}$ [g/cm ³] | NTU |
|--|-------|
| | |

- Draw the conclusions about the velocity of the sulphur sol formation in the reaction of hydrochloric acid with sodium thiosulphate from the obtained results and write an equation of the reaction.