Task No. XI

Constants determination from the Freundlich equation of isotherm adsorption.

I. Goal of tasks

The goal of tasks is determination of parameters in the Freundlich isotherm equation on the basis of quantity of aniline in cyclohexane adsorption on the silica gel by the statistical method.

II. Theoretical problems

1. Adsorption:
   a) physical adsorption,
   b) chemical adsorption.
2. Adsorption equilibrium.
3. Theories of adsorption:
   a) Henry equation,
   b) Freundlich equation of adsorption isotherm,
   c) Theory and Langmuir equation of adsorption isotherm,
   d) Brunauer, Emmet and Telle (BET) multilayer theory of adsorption.

References:

1. J. Ościk, „*Adsorpcja*”, PWN Warszawa, 1979, str. 57–81.
2. R. Brdička, „*Podstawy chemii fizycznej*”, PWN Warszawa, 1970, 579–590.

III. Theoretical part

III. 1. Adsorption at the solid-vapour, solid-liquid interfaces

The phenomenon occurring at the interface consists in retention of substance in this area in a larger amount than inside the phase is called adsorption. The substance (**adsorbate**) undergoing adsorption is present in only one volume phase (vapour or liquid) and therefore adsorption is most often described as division of the substance between the volume phase and the surface phase. Adsorption proceeds almost always when vapours or liquids get into contact with solid (**adsorbent**). The larger specific surface area of the adsorbent is the grater adsorption is. Gas uptake in the volume of solid is also possible and this process is called **absorption**. It is often difficult to show differences between adsorption and absorption, therefore the technical term **sorption** is often used.

Depending on the kind of forces keeping particles adsorbed on the solid surface one can distinguish:

- **physical adsorption** conditioned by intermolecular interactions (van der Waals),
- **chemical adsorption** – chemisorption, specific adsorption proceeding due to chemical forces.

Physical adsorption is characterized by small heat of adsorption, invariability under suitable conditions of pressure and temperature, forming adsorption layers of the thickness about several diameters of adsorbate particles.

Chemical adsorption is characterized by large heat of adsorption, the same as chemical reaction, removing the adsorbed layer is very hard, the layers are usually monomolecular.

III. 2. Adsorption equilibrium

Adsorption equilibrium is established after considerable contact of the gas with the adsorbed surface, and can be presented in the general form:

$$f(a, p, T) = 0 \text{ lub } f(a, c, T) = 0 \qquad (1)$$

where: a is the quantity of substance adsorbed in the surface layer per 1g of the adsorbent, p is the equilibrium pressure of the gas in the bulk phase, c – the equilibrium concentration of substance in the volume phase and T is the temperature.

During the investigation of adsorption equilibrium one of the parameters is kept unchanged and depending on which parameter is kept unchanged one obtains:

- **adsorption isotherm** (T = const):

$$a = f\left(p\right)_T \qquad (2)$$

- **adsorption isobar** (p = const):

$$a = f\left(T\right)_p \tag{3}$$

- **adsorption isostere** (a = const):

$$p = f\left(T\right)_a \tag{4}$$

In the case of adsorption at the liquid-solid interface when c = const for the dependence corresponding to the adsorption isobar there is no special term. The adsorption isotherm is the most often used in adsorption equilibrium measurements because it is the most convenient method of research data presenting action. The adsorption isotherm is also elaborated theoretically to the largest exent.

III. 3. Adsorption on the homogeneous surface of adsorbent

III. 3.1. Henry equation

Adsorption equilibrium can be presented as follows:

Particle in the vapour phase ⇔ **Particle on the adsorbent surface (adsorption complex)**

In the case of homogeneous surface, the concentration in the surface layer is constant over the whole adsorbent surface, so for the adsorption equilibrium there is:

$$a = K_{a,p}\ p \tag{5}$$

or

$$a^s = K_{a^s,p}\ p \tag{6}$$

where: K is the constant at a given temperature.

These are dependencies analogous to the Henry equation. They describe gas solubility in liquids and show the simplest equation of adsorption isotherm called the Henry equation. Instead of total changes of the amount of the adsorbed substance a it is more often convenient to use quantity θ expressing the adsorbent coverage extent**:**

$$\theta = \frac{a}{a_m} = \frac{a^s}{a_m^s} \tag{7}$$

where: a_m and a_m^s are the total coverage of the adsorbent with the monomolecular layer of adsorbate.

Henry equation for the adsorption isotherm can be recorded introducing the notion for the coverage degree:

$$\theta = \frac{K_{a,p}}{a_m}\ p = \frac{K_{a^s,p}}{a_m^s}\ p \tag{8}$$

The surface coverage in the Henry area is proportional to the substance pressure in the vapour phase.

III. 3.2. Freundlich isotherm of adsorption equation

In 1895 Bedeker proposed an empirical equation for the adsorption isotherm in the form:

$$a = k\, p^{1/n} \tag{9}$$

where: k and n are the constants. This equation is known as the Freundlich adsorption isotherm equation, because Freundlich assigned great importance to it and popularized its use. For determination of k and n factors, characteristic of the adsorption isotherm the logarithm should be found from equation (9):

$$\log a = \frac{1}{n} \log p + \log k \tag{10}$$

In equation (10) *log a* is the linear function of *log p,* therefore the value n can be determined from the straight line inclination angle towards the abscissa, *log k* is the ordinate of the initial straight line. The n value is between 0.2 and 0.9 and increases with the increasing temperature approaching unity. The k value changes in a wide range depending on the adsorbent and the adsorbed substance. Contrary to the Lamgmuir isotherm the Freundlich isotherm is only empirical dependence and has a limited range of use. It can not be used to the rectilinear part of the isotherm occurring for low pressures, because there should be made an assumption $n=1$, for large values of pressure because the curve goes up indefinitely whereas the surface is finite thus leading to the state of saturation.

III. 3.3. Langmuir adsorption isotherm

In the years 1918-1918 Langmuir derived the adsorption theory. On the adsorbent surface there is a definite number of active sites (proportional to the surface area), at each of which only one molecule may be adsorbed. The bonding to the adsorbent can be either chemical or physical, but must be sufficiently strong to prevent from displacement of the adsorbed molecules along the surface. Thus we have localized adsorption as distinct from non-localized adsorption, where the adsorbate molecule can move freely along the adsorbent surface. We neglect interactions between the adsorbate molecules in the adsorber film. On the surface of the adsorbent a monomolecular adsorption layer is thus formed (monolayer adsorption).

Adsorbed particles in the bulk volume + **Active site on the adsorbent surface** = **Localized adsorption complex**

The equilibrium constant is given by::

$$K = \frac{a^s}{p\,a_o^s} = \frac{\theta}{p\theta_o} \tag{11}$$

where: a_o^s is the concentration of free active sites on the adsorbent surface, $\theta_o = a_o^s / a_m^s$ is the fraction of the surface covered with free active sites.

Of course:

$$a^s + a_o^s = a_m^s \text{ lub } \theta + \theta_o = 1 \tag{12}$$

Substituting into the equation a_o^s or θ_o from equation (12) we can write :

$$K = \frac{a^s}{p\left(a_m^s - a^s\right)} = \frac{\theta}{(1-\theta)p} \tag{13}$$

and after rearrangement:

$$\theta = \frac{K\,p}{1 + K\,p} \tag{14}$$

or

$$a^s = \frac{a_m^s\,K\,p}{1 + K\,p} \tag{15}$$

and

$$a = \frac{a_m\,K\,p}{1 + K\,p} \tag{16}$$

Equations (14–16) represent different forms of the Langmuir adsorption isotherm.

For low pressures in the gas phase $K_p \ll 1$, the Langmuir equation reduces to the Henry's equation. Hence adsorption initially increases linearly with pressure, after which this growth gradually decreases, and at a sufficiently high gas pressure adsorption assumes a constant value: the adsorbent surface becomes saturated with the monomolecular adsorbate layer.

Langmuir adsorption isotherm Fig. 1.

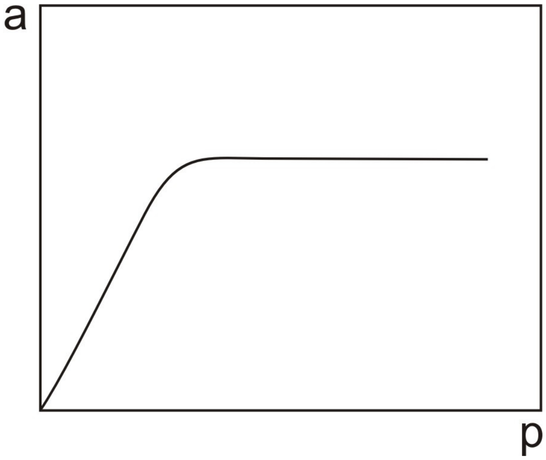

Fig. 1. Langmuir's adsorption isotherm

In general, the Langmuir isotherm describes best chemisorption and adsorption for a solution of comparatively large molecules such as dyes.

III. 3.4. Potential theory of adsorption

The Langmuir theory is based on the fundamental assumption that the adsorption layer is monomolecular. Eucken and Polanyi developed a method of polymolecular adsorption. Adsorption forces act at distances greatly exceeding the dimensions of a single molecule and they are not totally shielded by the first layer of adsorbate. Under these conditions the adsorption layer has a diffusional character and its density varies with the distance from the adsorbent surface. The potential theory depends upon the adsorption potential ε and the volume of the adsorption layer V^s.

The adsorption potential corresponds to the change of molar free energy connected with the change of vapour pressure from that over the pure liquid phase p_0 to the equilibrium pressure p at a given coverage of the adsorbent surface.

$$\varepsilon = RT \ln \frac{p_0}{p}$$

At the adsorbent there is a force field known as the adsorption potential field. In the surface space one can draw the anticipated equipotential surface. The cross-section of the surface layer is shown in Fig. 2.

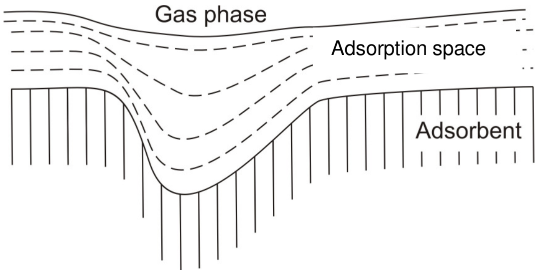

Fig. 2 Cross-section of the surface layer in terms of the potential theory

The equipotential surface is presented in the form of dashed lines. The spaces between every two equipotential surfaces have definite volumes. Therefore there is a relationship between the adsorption and the surface layer volume V^s:

$$V^s = aV_m$$

$$\varepsilon = f\left(V^s\right)$$

where $\boldsymbol{a}$ is the adsorption (in moles per gram of adsorbent), and $\boldsymbol{V_m}$ is the molar volume of liquid whose vapour is adsorbed (at the temperature of experiment)

III. 3.5. Brunauer, Emmet and Teller theory of multilayer vapour adsorption (BET)

In 1938 Brunauer, Emmet and Teller developed an interesting multilayer adsorption theory (BET). The principal assumption of the BET Theory is that the Langmuir equation applies to every adsorption layer: a molecule encountering an occupied site on the adsorbent surface does not leave that site immediately, but forms a short-lived adsorption complex. With the increasing vapour pressure to $\boldsymbol{p_0}$ the number of free sites on the adsorbent surface decreases, and therefore the number of active sites occupied by adsorbate molecules decreases as well since double, triple, etc. adsorption complexes are formed.

$$\theta = \frac{C\dfrac{p}{p_0}}{\left(1-\dfrac{p}{p_0}\right)\left[1+\left(C-1\right)\dfrac{p}{p_0}\right]} \tag{20}$$

or

$$a = \frac{a_m\, C\dfrac{p}{p_0}}{\left(1-\dfrac{p}{p_0}\right)\left[1+\left(C-1\right)\dfrac{p}{p_0}\right]} \tag{21}$$

where: C – the constant associated with the difference between the enthalpy of adsorption of the first layer Q_1 and the enthalpy of condensation Q_k $2.3 \log C = Q_1 - Q_k$.

Conventional measurements of the adsorbent specific surface area by the BET method are performed with the use of the low-temperature (78K) nitrogen adsorption isotherm, assuming that ω_m=0.162nm^2.

According to Brunauer five forms of isotherm for gases and vapours can be distinguished.

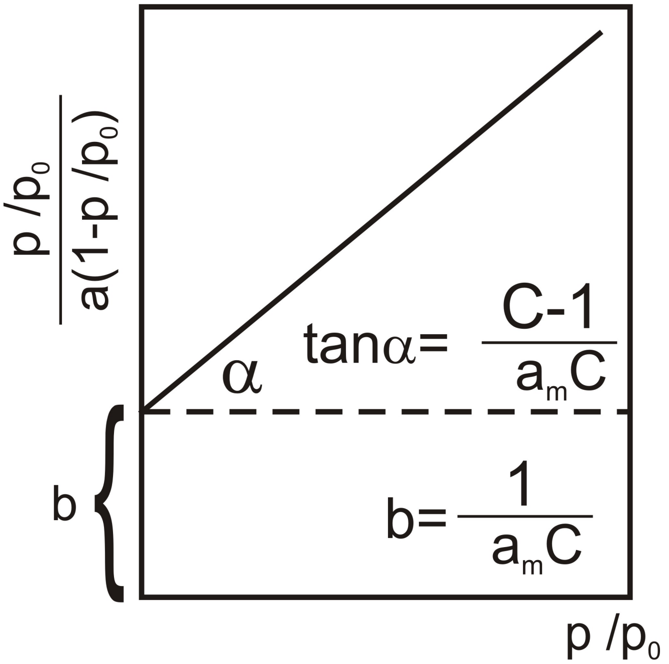

Fig. 3 Determination of the constants of the BET adsorption isotherm

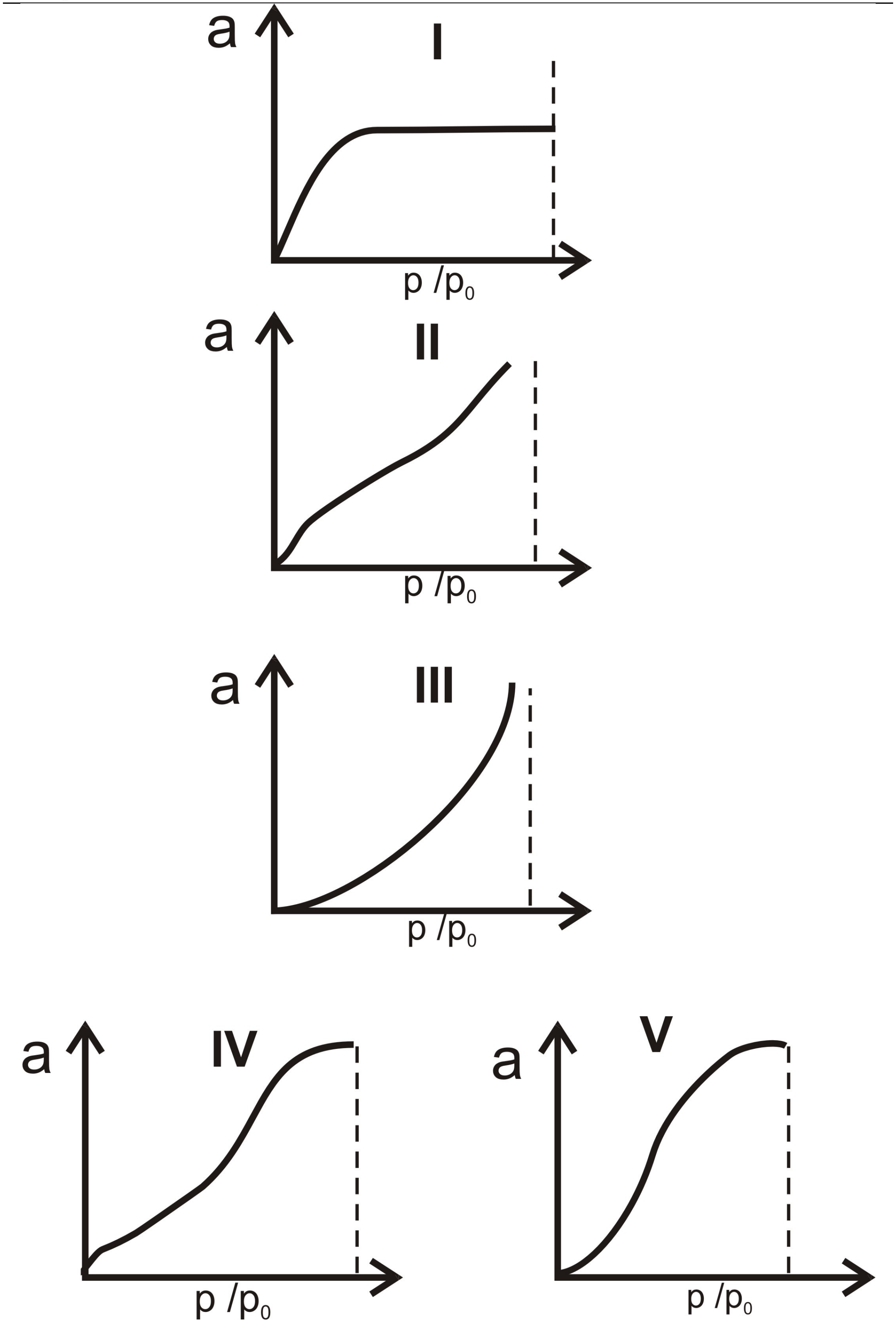

Fig. 4 Types of gas and vapour adsorption isotherms according to Brunauer

Type I corresponds to the Langmuir isotherm and is characterized by the fact that it tends monotonically to the limiting adsorption, probably attained on completion of the monomolecular layer.
Type II is very common in the case of physical adsorption, and is probably associated with the formation of a multimolecular adsorption layer. For instance for adsorption of benzene vapour on the graphitized carbon black.
Type III is rather uncommon, but is exemplified by adsorption of bromine on silica gel. It seems that in this case the absolute value of the heat of adsorption is equal to or smaller than the heat of condensation of the pure adsorbate.
Types IV and **V** correspond to Types II and III with the difference that the adsorption maximum is reached at a pressure lower than that of the saturated vapour p_0. It is believed that they both reflect the phenomenon of capillary condensation.
The BET equation encompasses the first three adsorption isotherm types. When $\left|\Delta_a H_m^s\right| >> \left|\Delta H_m^L\right|$, C is very large, so equation (21) reduces to:

$$a = \frac{a_m C\, p/p_0}{1 + C\, p/p_0} \tag{22}$$

This is the Langmuir isotherm, i.e. Type I isotherm. For values of C in the range 3 or 4 to several hundred, the BET equation yields isotherms corresponding to Type II. If C is equal to or smaller than unity, i.e. if $\left|\Delta_a H_m^s\right| << \left|\Delta H_m^L\right|$, the BET equation yields, according to Brunauer, isotherms of Type III. Such isotherms have been observed for halogen adsorption on carbon and silica gel as well as for adsorption of water and organic vapours on glass.
The BET adsorption isotherm is convenient for experimental use because it can be presented in a linear form and requires the selection of only two parameters. Agreement of this equation with the experimental data is, however, in a rather narrow range. For instance in the case of adsorption isotherms of Type II, plotted according to the BET equation in the linear form, the straight-line segment is obtained for the range of p/p_0 values of 0.005 – 0.3. in the range 0.3 to 0.5 the BET equation usually does not hold, because the difference between the constants plays a significant role which cannot be neglected. The adsorption predicted by the BET equation is usually too small at lower pressures and too large at high pressures.
If, due to limiting of the surface layer (e.g in a capillary), only *n* layers are formed in the adsorption process, then the BET isotherm has the form:

$$a = \frac{a_m C\, h\left[1 - (n+1)h^n + nh^{n+1}\right]}{(1-h)[1 + (C-1)h - C\, h^{n+1}]} \tag{23}$$

Where: $h = p/p_0$. When n=1, equation (23) becomes, for all values of C, the Langmuir equation with $C/p_0 = k$. If adsorption takes place on the free surface , then $n \to \infty$ and equation (23) reduces to equation (21).

IV. Experimental part

A. Apparatus and reagents

1. Apparatus: spectrophotometer Helios UV–VIS.
2. Equipment:
   - quartz cuvettes,
   - calibrated flask 10 cm^3 – 1 piece,
   - glass bottles with covers 15 cm^3 – 6 pieces,
   - pipette 25 cm^3 – 1 piece,
   - automatic pipette 0-20 µl,
   - funnel for pouring silica gel.
3. Reagents:
   - dried silica gel Si-100 with graining 0.063–0.2 mm and weight about. 1 g in a glass ampoule,
   - aniline solution in cyclohexane of the concentration 0.5 M in a bottle with a proportioner,
   - aniline solutions for the calibration curve of the concentrations: **$0.5\cdot10^{-4}$, $1.0\cdot10^{-4}$, $1.5\cdot10^{-4}$, $2\cdot10^{-4}$, $2.5\cdot10^{-4}$, $3\cdot10^{-4}$, $3.5\cdot10^{-4}$ i $4\cdot10^{-4}$ M.**

B. Task procedure

1. Prepare aniline in cyclohexane solutions.
2. Using the analytical balance weigh a sample of silica gel, pour it through a dry funnel to the prepared aniline solution.
3. Carry out the adsorption process for 60 min. mixing repeatedly the bottle with silica gel, do not allow the silica gel to stay on the bottle walls
4. Using a spectrophotometer Helios measure absorbance of aniline solutions of known concentration to the calibration curve, next measure absorbance of solution in the bottle with silica gel (solution after adsorption).

C. Apparatus operating instructions

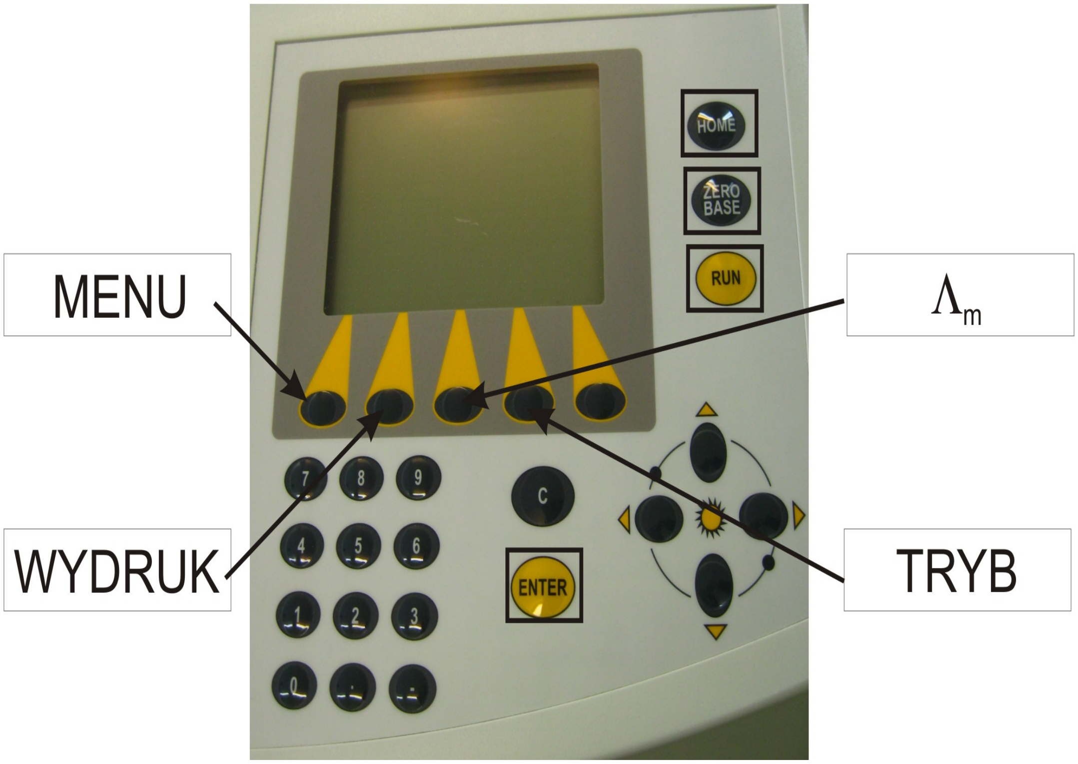

Fig. 1. Helios spectrophotometer

Turn on the apparatus pushing the start key to the back of apparatus cover. Wait about 3 min. till the end of optical tests.

Push the button **MENU** and select METODY and approve **ENTER,** from the available methods select WIDMO XI approve **ENTER,** next read pushing **ENTER.** Insert a quartz cuvette with cyclohexane into the apparatus and push **ZERO BASE.** After setting zero, solutions for the calibration curve can be measured. Put the solution with the lowest concentration into the apparatus and push **RUN,** after spectrum plotting push **POKAŻ WYNIKI,** write down the values of maximizes. In the same way plot the spectra of other solutions for the calibration curve. DO NOT PUSH ZERO BASE AFTER EVERY MEASUREMENT.

Push buttons **HOME** and **λm** from the apparatus keyboard, select the wavelength for the second maximum from the calibration curve solutions and approve **ENTER.** Investigate absorbance of the solutions after adsorption putting next solutions into the apparatus and write down the wavelength.

D. Method of task achievement

From the base solution of aniline in the cyclohexane (concentration 0.5 M/dm^3) take a sample **1 cm^3** of solution and pour in to the calibrated flask, volume 10 cm^3, complete with cyclohexane to the mark. Pour out the solution from the calibrated flask to bottle No. 1. Analogously prepare the next solution samples in turn: **2, 4, 6, 8, 10 cm^3** base solution of aniline in cyclohexane. These are the solutions for adsorption of the concentration c_0 (concentration should be calculated during data elaboration)

Using the analytical balance weigh the ampoules with dried silica gel, next pour out gel into the suitable solution using a dry funnel. Weigh empty ampoules with covers again.

The adsorption process must be carried out for one hour with occasional mixing. After settlement of adsorption equilibrium using an automatic pipette 10 μl of solution should be poured into the calibrated flask and completed with cyclohexane to the mark. Next measure absorbance using a spectrophotometer.

When the adsorption balance is fixed, measure absorbance solutions for the calibration curve concentrations: **$0.5\cdot10^{-4}$, $1.0\cdot10^{-4}$, $1.5\cdot10^{-4}$, $2\cdot10^{-4}$, $2.5\cdot10^{-4}$, $3\cdot10^{-4}$, $3.5\cdot10^{-4}$, $4\cdot10^{-4}$ M.** The measurements should be made using a spectrophotometer and operation instruction of the apparatus.

When the measurements are over, pour out solutions after adsorption (without silica gel) to the container marked „ZLEWKI – aniliny i cycloheksanu” To the bottles with silica gel pour water and pour out to the container with the inscription „ZLEWKI – żelu z aniliną”. Rinse the bottles using small amounts of acetone and pour out to the container with the inscription „ZLEWKI acetonu”.

E. Data elaboration

1. Prepare a graph of calibration curve $A = f(c_1)$ to determine the linear equation using the method of least squares.
2. Using $A=f(c_1)$ equation calculate solution concentration after adsorption for individual concentration of aniline based on the measured values of absorbance for the equilibrium solutions (c). Remember about diluting the solution 1000 times (**10 μl to 10 cm^3).**

3. Calculate the total amount of aniline, n^s adsorbed for each concentration per 1 g of absorber using the equation:

$$n^s = \frac{V(c_o - c)}{m} \tag{22}$$

where: V – the volume of solution used for adsorption (dm^3), c_o – the solution concentration before adsorption (mol/dm^3), c – the balanced concentration (mol/dm^3), m – silica gel mass(g).

4. Make a graph of adsorption isotherm of aniline from cyclohexane on silica gel $n^s = f(c)$.
5. Using the graphical method determine the constants k and n from the Freundlich adsorption isotherm. For this purpose prepare the graph $\log n^s = f(\log c)$. It should be a straight line. From the angle of inclination (θ) determine n using the equation:

$$\frac{1}{n} = tg\,\theta \quad that\ is \quad n = \frac{1}{tg\,\theta}$$

and from the point of intersection with Y-axis determine log k.

The results should be given in the form of tables:

Table I. Calibration curve

No.	1	2	3	4	5	6	7	8
Concentration, $c_1 \cdot 10^{-4}$ (mol/dm^3)	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Absorbance								

Table II. Adsorption isotherm

Flask number	c_o (mol/dm^3)	Absorbance after adsorption	c (mol/dm^3)	Gel mass (g)	Quantity of adsorption n^s (mol/g)	log c	log n^s
1							
2							
3							
4							
5							
6							

6. Write down *n* and *k*.
7. Add all graphs.