III

DETERMINATION OF THE SPECIFIC SURFACE AREA OF SILICA GEL

I. Aim of experiment

The aim of the study is experimental determination of the surface area of silica gel via methylene blue adsorption from the Langmuir isotherm of adsorption.

II. Introductory issues

1. Definition of adsorption (physical and chemical adsorption).
2. Adsorption at the solid/liquid interface.
3. Adsorbents and their division.
4. Parameters characteristic of adsorbents:
   a) average pore diameter,
   b) specific surface area,
   c) total pore volume.
5. Determination of the specific surface area by physisorption.
   a) determination of the specific surface area from the BET isotherm.
   b) Langmuir theory and adsorption isotherm.

References:

1. J. Ościk, *Adsorption*, PWN Warszawa, 1982.
2. J. B. Condon, *Surface Area and Porosity Determinations by Physisorption, Measurements and Theory*, Elsevier, 2006.
3. D. Myers, *Surfaces, Interfaces, and Colloids: Principles and Applications*, John Wiley & Sons, Inc., 1999.
4. A. W. Adamson, A. P. Gast, *Physical Chemistry of Surfaces*, John Wiley & Sons, Inc., 1997.

III. Theoretical part

III. 1. Adsorption at the Solid/Gas and Solid/ Liquid Interfaces

Many physical and chemical processes occur at the boundary between two phases. The unbalanced forces at the phase boundary (the so-called surface forces) cause changes in the number of molecules (atoms, ions) to occur on the boundary surface in comparison with the corresponding numbers within the neighbouring (gaseous or liquid) phases. This change in concentration at the surface is called **adsorption.** In general, it is the process of accumulation of gases, liquids, or solutes on the surface of a solid or liquid. Molecules of **adsorbate** (substance that is adsorbed on the surface) are transferred from one phase (usually called volume/bulk phase) into the so-called surface phase which lies on the boundary of two physically, chemically or structurally different phases.
Adsorption can be most simply defined as the preferential concentration (i.e., location) of one component of a system at an interface, where the local (i.e., interfacial) concentration of one or more components of one or both phases is different from those in the bulk phases.

Where the interfacial concentration of the adsorbed species is greater than that in the bulk phase(s), one can refer to **‘‘positive’’ adsorption**, although the positive aspect is usually assumed. It is possible, however, for negative adsorption to occur. In such a situation, the concentration of a system component in the region of the interface will be less than that in one or both bulk phases. The result of **negative adsorption** can be to increase the interfacial energy of a system relative to a defined standard state.

Adsorption processes are usually classified according to the kind of phases constituting the interface, and according to the type of forces acting at this surface. Depending on the type of phases in contact, the processes of adsorption can be considered in the following systems:

liquid/gas
solid/gas
solid/liquid
liquid/liquid.

According to the type of forces acting at the interface, adsorption can be distinguished by:

- **physical adsorption** which involves intermolecular forces (van der Wals forces, hydrogen bonds, etc.),
- **chemical adsorption** (chemisorption) which involves valency forces as a result of the sharing of electrons by the solid (adsorbent) and the adsorbed substance (adsorbate).

Physical adsorption is characterized mainly by small heat of adsorption, reversibility of adsorption under certain conditions of pressure and temperature, adsorbed layers having thickness of several diameters.

Chemical adsorption possesses large heat of adsorption (of the same order as the heat of the relevant chemical reaction) and only monolayers are formed whose removal is very difficult and requires drastic measures.

III. 2. Adsorbents

When adsorption occurs on a solid, the solid is referred to as the **adsorbent** and the adsorbed material the **adsorbate**. Thus an adsorbent is a substance (usually porous in nature and with a high surface area) that can adsorb substances onto its surface by intermolecular forces.

Many adsorbents of different chemical character and geometrical surface structure are known. Generally adsorbents can be divided into two types:

- non-porous adsorbents,
- porous adsorbents.

Non-porous adsorbents **are obtained by precipitation of crystalline deposits such as** $BaSO_4$ or by grinding vitreous or crystalline solids. The specific surface area of these adsorbents is small and exceeds 10 m^2/g. However, more frequently it lies in the range of 0.1 to 1 m^2/g.

Finally, divided non-porous material can be obtained by incomplete combustion of organic substances - so called carbon black or organosilicon compounds – so called white carbon black, as well as by hydrolysis of orthosilicic haloanhydrides ($SiCl_4$, SiF_4) in strongly superheated steam – e.g. silica aerogels. Such materials composed of non-porous particles have the specific surface area of hundreds of square meters per gram and are used as fillers for polymers, lubricants, lakes, etc.

One of the non-porous adsorbents are graphitized carbon blacks obtained from normal carbon black by heating at 3000^{o}C in vacuum, in an inert gas or reducing atmosphere. In the case of thermal black the surface consists of the principal planes of graphite. The specific surface area of graphitized carbon blacks reaches several dozen square meters per gram.

Porous adsorbents are used for the retention of gases and vapours, as active contacts or catalyst supports, for dehydration as well as adsorptive separation of mixture components. For their efficiency the specific surface area ranging from several hundred to one thousand square meters per gram is required. Such adsorbents are used in a granular form (tablets, granules, beads) with the mesh size of the grains usually ranging from 0.1 to 2 mm.

Porous adsorbents with the large specific surface area can be obtained by two main methods:

1. Construction of a rigid adsorbent skeleton of small, colloidal particles. The latter conglomerate or fuse at the sites of contact yielding a skeleton with a huge inner surface area – dried gels (xerogels) such as silica gels, aqueous Al_2O_3, activated magnesia.
2. Exposure of wide-porous or non-porous materials (coke, glass) to the action of active gases or liquids. For example, when acting on non-active carbon with oxygen-bearing gases (H_2O or CO_2) at 1123-1223K, part of the carbon undergoes combus-

tion as a result of which *active carbon* with a highly developed surface is obtained. Action with acids on sodium-boron glass removes the sodium-boron components and yields porous glass with pore dimensions similar to those of active carbon. The pore size depends on the heat-conditioning of the glass and final washing with aqueous NaOH and KOH solutions.

In both cases, porous solids, crystalline or amorphous, with a more or less developed surface area are obtained.

III. 3. Parameters characterizing structure of porous solids

Every porous material can be characterized by a few parameters describing its structure:

Average pore radius, R,

Average pore diameter (has dimension Å or nm) is a mean value of pore radii for a given porous material and indicates pore size distribution (PSD) as a function of their diameter.

Specific surface area, S,

Specific surface area of a porous material is a sum of the external particle surface area S_e and the inner surface area S_i and is usually defined as the surface area per unit mass of the material (m^2/g).

*External surface area***,** S_e is the geometrical area of porous particles per unit mass of the adsorbent and it is inversely proportional to the particle size.

Inner surface area, S_i is the area of the pore walls. Because as follows from the definition pores must be closed, S_i does not include walls of closed pores. Generally, the inner surface area is much bigger than the external surface area, e. g. for silica gels it is about a few orders of magnitude.

It should be taken into account that in general, the surface area is reversibly proportional to the average pore radius. The larger surface area, the smallest average pore radius.

Large surface area ($S > 500\ m^2/g$) indicates the presence of narrow pores, whereas small value of the surface area is characteristic of macroporous solids.

Total pore volume, V_p,

Total pore volume is the sum of volumes of all pores in one gram of adsorbent. If the surface wetting is completed it is independent of the kind of liquid.

Among the parameters described above, only pore volume V_p possesses physical meaning and can be easily measured. Pore radii and surface area can be determined based on appropriate model assumptions. Particularly the values of average radii for a given sorbent can be greatly doubtful due to model simplification used in calculations connected, among others, with pore shapes.

Regardless of the mentioned errors, knowledge of the parameters characterizing structure of porous materials is useful because of their practical application, e. g. in chromatography. However, to obtain precise pores structure a few independent methods should be used along with data standardizations.

According to IUPAC the following sizes characterize pores:

- **Micropores** with the dimension less than 2 nm,
- **Mesopores** have the size ranging from 2 to 50 nm,
- **Macropores** with the dimension larger than 50 nm.

The borderlines between different classes are not strict and depend on the shape of pores.

The effective radii of the widest pores are over **500 Å** and their surface area is from 0.5 to 2 m^2/g. Usually adsorption on their surface might be neglected. Moreover, also capillary condensation is very often assumed as immeasurable. Hence, macropores play a role of transport pores.

The effective radii of mesopores are between **20–500 Å** and are much bigger than adsorbing particles. On their surface monolayer and multilayer adsorption of vapour takes place ending with pores filling according to the capillary condensation mechanism. The low range (15-16 Å) of meniscus curvature radii corresponds to the borderline of Kelvin equation applicability. Surface area of mesopores changes from 10 to 500m^2/g. Adsorption in a mesopore range is a combination of physical adsorption on mesopore walls with physical condensation of adsorbate in pores, where meniscus reaches a critical radius. It is assumed that in this range all micropores are already filled-up and the monolayer is also filled.

Generally, in the mesopore region experimental isotherms measured on mesoporous solids display **hysteresis loops** (adsorption and desorption proceed along different paths). However, hysteresis is observed only when the menisci in the adsorption and desorption path are different in shape/diameter. Such situation is typical of open-ended cylindrical mesopores, bottle-shaped (ink bottle), or spaces between parallel sheets (slits). If cylindrical pore is closed at one end and does not contain any narrowing, the adsorption isotherm does not play hysteresis loop. The same is true for conical pores.

As the true pore diameter is a sum of 2 adsorbed layer thicknesses and meniscus diameter, the methods of data analysis use meniscus radii calculated from **Kelvin equation** (or its modifications including e.g. influence of meniscus radius on adsorbate surface tension - e.g. by Dubinin) and statistical layer thickness of adsorbate (often given by Harkins-Jura (HJ) or by Halsey / Frenkel-Halsey-Hill (FHH) equations).

The adsorption process in micropores is much stronger than on relatively flat surfaces of meso- and macropores because the adsorbate molecule in the micropore is closely surrounded by pore walls. The basic parameter describing micropores is their total volume per unit mass, which is generally lower than 0.5 cm^3/g.

As the particle size is a parameter which is determined by its geometry, pore shape should be also taken into account during interpretation of the obtained experimental data. Pore shape is mainly unknown, but it could be approximated by the model (Fig.1). Three basic pore models exist:

a) cylindrical pores, circular in cross section,
b) ink-bottle pores having a narrow neck and wide body,
c) slit-shaped pores with parallel plates.

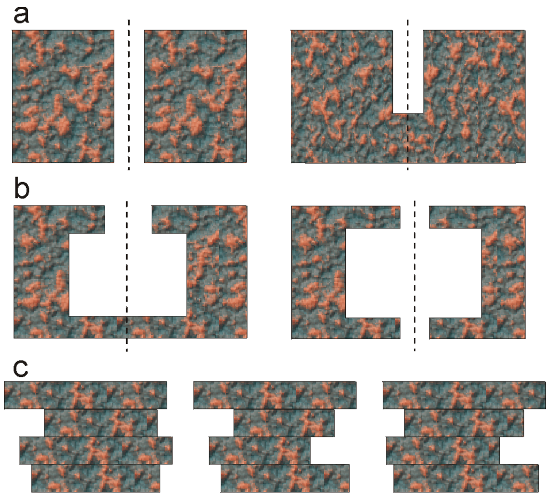

Fig. 1. Pore models: (a) cylindrical pores open at both ends and at one end (b) bottle-shaped („ink-bottle") pores; (c) slit-shaped pores.

The choice, which model is appropriate for a particular adsorbent usually is based on the cross-calculations of pore volume and surface area and comparison with the experimentally measured values.

The most popular pores model is that of cylindrical pores open at one or at two ends. The next one is the model of bottle shaped (ink-bottle) pores, being described by two radii: narrow bottleneck radius and that of the bottle bottom. The third pores model relates to pores with parallel walls.

Pore classification according to their size which was given above is associated with the mechanism of adsorption and capillary phenomena. Hence, porous adsorbent classification might be done in the same way giving: macroporous, mesoporous and microporous adsorbents.

Models of pores volume distribution are shown in Fig. 2. If distribution of pores is homogeneous, it is similar to the Gauss distribution curve (Fig. 2a). For many adsorbents pore volume distribution is heterogeneous. The simplest one is bimodal with two characteristic maxima of pore radius (Fig. 2b). In practice, a more complicated heterogeneous distribution curve can be also obtained as in Fig. 2c.

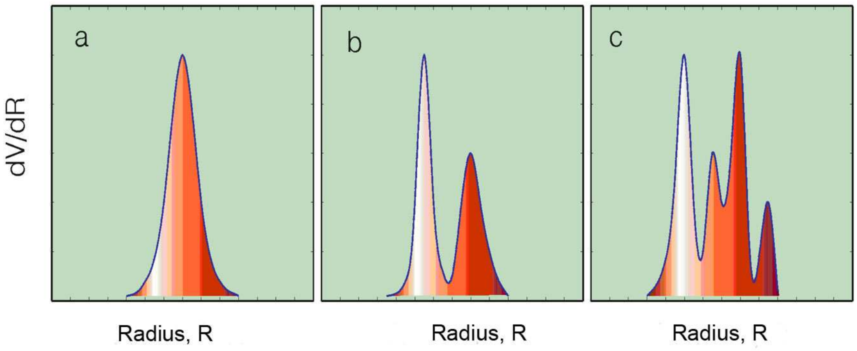

Fig. 2. Models of pores volume distribution as a function of their size (in a differential form dV/dD); a – homogeneous; b – bimodal; c – heterogeneous.

In the case of heterogeneous pore volume distribution interpretation of pore structure is difficult. Most of the wide pores can occur on the particle surface or between micrograins, whereas the narrower pores can be placed inside the grains being extension of the broader pores.

III. 4. Determination of the surface area by physisorption

Full knowledge of the adsorbent structure is very important due to its practical application. There are many methods of determining the structure of adsorbents (their specific surface area and porosity) by adsorption methods.

There are principally two methods extensively used to measure the adsorption isotherm:

- the volumetric method,
- the gravimetric method.

In both methods the adsorbent is kept at a constant temperature, usually near or at the boiling point of the adsorbate. The adsorptive pressure is increased step-wise and held constant for a period of time to allow the adsorption to occur and the temperature of the adsorbent to re-equilibrate. The length of time required depends upon the physical arrangement and the system being studied. Because in some cases re-equilibration might take hours, it is best to monitor the progress of the adsorption to determine when equilibrium is achieved. In the case of the volumetric system the adsorbed amount is measured by taking the pressure change and comparing this to that expected if the adsorbent were absent. In the case of the gravimetric measurement the amount adsorbed is indicated by the mass increment. A typical isotherm then is a plot of the amount adsorbed versus the adsorptive pressure. The pressure is usually expressed as a ratio of the adsorptive pressure p to the saturated vapour pressure over the bulk liquid p_o. The preferred unit for adsorbate amount is millimole or micromole of adsorbate per gram of adsorbent.

Each of these methods has advantages and disadvantages. Both isotherm measuring methods normally cool the sample to or below the boiling point of the adsorbate. The sample is then exposed to adsorptive gas while the gas pressure is measured. Since the temperature of the sample is known, usually by the use of a gas–liquid thermometer, then the vapour pressure of the adsorptive over its liquid is known and thus the ratio p / p_o can be calculated. This is the most precisely measured physical quantity, although p_o could be significantly off if the temperature of the sample is not carefully checked. This measurement is common to all the techniques.

The volumetric method is the most common measurement of the isotherm because it is the simplest and relatively inexpensive. It has the disadvantage of a greater uncertainty in the results. Because in this technique the amount of gas adsorbed is determined by measuring how much gas is used from a reservoir, several corrections need to be checked (the principal one is so called the “dead volume”). In this technique temperature measurements are very important.

The gravimetric method is more accurate and precise, however, equipment is more expensive and requires a little more skill and patience to operate. A balance that have *at least* a sensitivity of 10^{-6} is used. For example, if the normal load on the balance is about 1.0 g then it would normally be sensitive to 0.1 mg.

Calorimetric measurements are less common than those mentioned above and yield a different physical quantity. To be effective, the calorimetric method needs to be combined with either the volumetric technique, which is normal, or with the gravimetric technique which is a little more difficult for high-quality work. Both methods are used. Calorimetry measures the temperature change as the adsorption occurs. This along with a heat capacity measurements of the resultant adsorbate–adsorbent combination gives the heat of adsorption as a function of pressure. Less precise calorimetric measurements measure only the heat evolved which gives some idea of various adsorption mechanisms involved. Calorimetry is not widely used because accurate calorimetry is extremely difficult to perform and requires a great amount of time and effort.

A low-cost alternative to the volumetric is the **flow or carrier gas system**. The disadvantage of this method is that the results are very uncertain and normally do not give the isotherm. This technique is very similar to gas chromatography. A carrier gas, typically helium is used to carry adsorbate gas such as N_2. The sample is cooled down to the adsorption temperature (usually liquid N_2 temperature). During this cool-down, the adsorbate is adsorbed. A downstream detector, usually a heat conductivity detector, picks up the signal indicating that there is a decrease in the adsorbate. The sample is allowed to cool long enough for the signal to return to the baseline. The coolant is then removed or the sample heated up by some method. A reverse signal is then detected indicating the desorption of the adsorbate. A scheme of the type of signal is presented in Fig. 3.

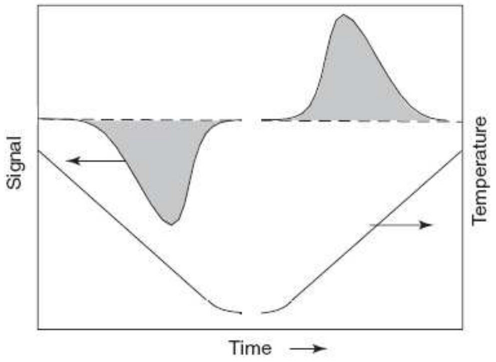

Fig. 3. Scheme of the signal observed for the flow system.

III. 5. Measuring the surface area from the isotherm

If the amount of material in one monolayer of adsorbate can be determined, then the surface area can be calculated from this. It is only necessary to know the average cross-sectional area of the adsorbate molecule. If n_m is the number of moles of adsorbate in a monolayer and ω the cross-sectional area of the adsorbate molecule, then the surface area, S, is given by:

$$S = n_m^s \, N_A \, \omega_m \tag{1}$$

where N_A is the Avogadro's number (6.022×10^{23} mol^{-1}).
Two problems are involved in it. Firstly, how to obtain n_m^s? Secondly, what is the value for ω? In the first instance some theory should yield n_m^s. The most widely used theory is the BET, which assumes that the adsorbate molecules settle on two types of specific

local sites, either a site on the adsorbent surface or on the top of another adsorbate molecule. The spaces of the sites are exactly those expected for close packing of the adsorbent molecules. Thus, the adsorptive solid phase spacing in the close-packed arrangement is used for ω.

According to Brunauer five principal forms of the adsorption isotherm for gases and vapours can be distinguished depending on the degree of adsorption (monolayer or multilayer), the mechanism of adsorption (physical or chemisorption), nature of the adsorbent surface (porous or nonporous), and relative strengths of adsorbate–adsorbent interactions (Fig. 4).

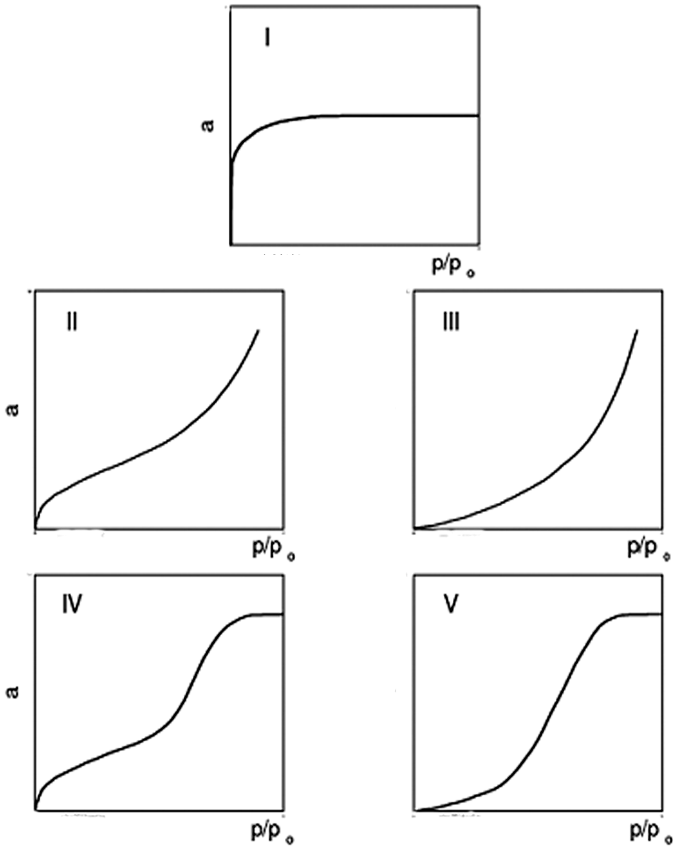

Fig. 4. Types of gas and vapour adsorption isotherms according to Brunauer.

Type I isotherm, corresponding to the Langmuir isotherm, is characterized by the fact that it tends monotonically to the limiting adsorption that is usually identified with the attainment of complete monolayer coverage. Such an isotherm can be found in chemisorption, where the system is limited to a monolayer and in the systems in which there is a strong nonspecific attractive interaction between the adsorbate and the adsorbent, but weak attraction between the absorbate molecules themselves. Such isotherm can also appear in the systems in which the solid has a very fine microporous structure.

Type II isotherm is typical of physical adsorption on nonporous solids. In contrast to type I, the adsorbate molecules in these cases also have relatively strong mutual interactions, which leads to the tendency for multilayer formation.

Types III and V isotherms are relatively rare and correspond to the systems in which the interaction between adsorbate molecules is stronger than that between the adsorbate and the adsorbent.

Type IV isotherm is obviously similar to type II and usually corresponds to the systems involving capillary condensation in porous solids. In this case, however, once the pores have become filled, further adsorption to form multilayers does not occur and the terminating plateau region results. This might indicate a relatively weak interaction between the adsorbate molecules.

If more complex isotherm classifications are available, they generally represent combinations and extensions of the five basic types described above.

III. 5.1. Determination of Surface Area from the BET Isotherm

The BET (Brunauer, Emmett and Teller) isotherm has been accepted as the general method for determining the surface area of finely divided solids by physical adsorption., It modified the Langmuir approach assuming the formation of a multilayer of adsorbed molecules. The BET model assumes that the adsorption of the first monolayer has a characteristic heat of adsorption H_A, but that subsequent layers are controlled by the heat of condensation of the vapor in question H_L. The linear form of the BET equation is given by:

$$\frac{p}{V(p_o-p)}=\frac{1}{V_m c}+\frac{(c-1)p}{V_m c p_o} \tag{2}$$

where V is the volume of adsorbed vapour at STP, V_m is the monolayer capacity at STP, p is the partial pressure of the adsorbate, p_o is the saturation vapour pressure of the adsorbate, and

$$c \approx exp\,\frac{(\Delta H_A-\Delta H_L)}{RT} \tag{3}$$

While the BET model for multilayer adsorption contains several potential sources of error due to the assumptions of the absence of lateral interactions between the adsorbed molecules, the constancy of the heat of adsorption (after the first monolayer), and the solid surface homogeneity, it generally produces useful results at pressures between 0.05 p_o and 0.35 p_o. It must be used with caution, however, for porous solids that show adsorption hysteresis, or when point B on the isotherm corresponding to V_m cannot be accurately determined.

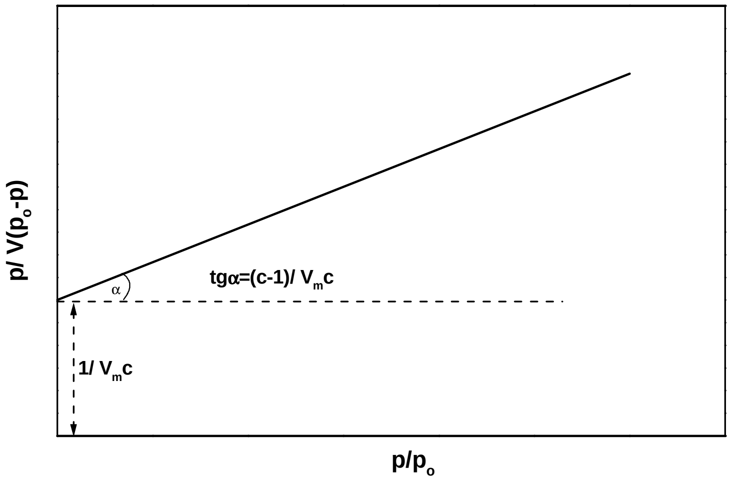

Fig. 5. Calculation of the constants from the the BET adsorption isotherm equation.

The monolayer capacity V_m allows for the calculation of the surface area based on the area occupied by each adsorbed gas molecule. If a plot of $p/V(p_o - p)$ versus p/p_o is linear over the pressure region mentioned above, from the slope of the line $a = (c-1)/V_m c$ and the intercept $b = 1/V_m c$ the monolayer capacity V_m of the solid can be calculated and thereby its specific surface area *S*:

$$V_m = \frac{1}{a+b} \tag{4}$$

$$S = \frac{V_m k}{m} \tag{5}$$

$$k = \frac{N_A \omega}{M_v} \tag{6}$$

where m is the sample weight, N_A is the Avogadro's number, ω is the area per molecule of the adsorbed gas, and M_v is the gram molecular volume of gas (22.400 L at 0^oC).

The adsorbate most commonly employed for BET surface area determination is nitrogen, which has an effective area per molecule ω of 0.162 nm^2 at the liquid nitrogen temperature (77 K).Other useful gases are argon (ω=0.138 nm2) and krypton (ω=0.195 nm^2).

The BET isotherm was developed primarily to describe the type II isotherm shown in Fig. 3, such as is found for the adsorption of relatively inert gases (N_2, Ar, He, etc.) on polar surfaces ($c \approx 100$). However, it reduces to type I (Langmuir isotherm) when restricted to the monolayer coverage ($\Delta H_A >> \Delta H_L$), and describes type III isotherms in the unusual situation where the adsorption of the first monolayer is less exothermic than that of the subsequent layers (e.g., $c < 1$) resulting in low adsorption at low values of p/p_o.

III. 5.2. Determination of the solid pecific surface area by the method of dyes adsorption using the Langmuir isotherm equation

Among many methods applied for determination of specific surface area, the method based on the dyes adsorption (e.g., methylene blue, Ponso 2R) is also applied. This method includes dye adsorption from the solutions of the increasing concentration. Then the dye loss in particular solutions is measured and the adsorption isotherm is found out.

In 1916 Langmuir presented the adsorption isotherm for adsorption from the gaseous phase, which in general holds best in the case of chemisorption and adsorption from solutions of comparatively large molecules such as dyes.

The Langmuir isotherm is probably the best known of all isotherms describing adsorption, and often serves as a basis for more detailed development. In the case of adsorption from solutions pressure is replaced with concentration.

The Langmuir adsorption isotherm equation presents „real" adsorption dependence on the solution concentration, while experimentally we can measure only excess adsorption. Although for dilute solutions it can be assumed that excess adsorption is equal to real adsorption. As the adsorbent surface is porous and energetically heterogeneous, monolayer adsorption is doubtful. It is shown by the results obtained by means of this method that are generally smaller compared to other methods, e.g. N_2 thermal desorption.

In order to obtain the adsorption isotherm Langmuir assumed that on the adsorbent surface there are a definite number of active sites, in each of which only one molecule can be adsorbed. In accordance with this fact on the surface of the adsorbent a monomolecular adsorption layer is thus formed (**monolayer adsorption**). The bonding to the adsorbent can be either chemical or physical, but must be sufficiently strong to prevent displacement of the adsorbed molecules along the surface – **localized adsorption**. If p, $T = const$, adsorption equilibrium is achieved:

molecule in bulk phase + **active site on the adsorbent surface** = **localized adsorption complex**

The equilibrium constant is given by:

$$K = \frac{a^s}{p\,a_o^s} = \frac{\theta}{p\theta_o} \tag{6}$$

where: a_o^s, a^s are respectively the concentration of the free and occupied active sites on the adsorbent, $\theta = a^s / a_m^s$ – the surface coverage of the adsorbent, a_m^s – the quantity corresponding to the complete coverage of the adsorbent surface by a monomolecular film of a given adsorbate, $\theta_o = a_o^s / a_m^s$ is the fraction of the surface covered with free active sites.

Because:

$$a^s + a_o^s = a_m^s \text{ or } \theta + \theta_o = 1 \tag{7}$$

equation (6) can be written as:

$$K = \frac{a^s}{p\left(a_m^s - a^s\right)} = \frac{\theta}{(1-\theta)p} \tag{8}$$

and after rearrangement:

$$\theta = \frac{K\,p}{1 + K\,p} \tag{9}$$

or

$$a^s = \frac{a_m^s\,K\,p}{1 + K\,p} \tag{10}$$

We can also write

$$a = \frac{a_m\,K\,p}{1 + K\,p} \tag{11}$$

Equations from 9 to 11 represent different forms of the **Langmuir adsorption isotherm**. The Langmuir adsorption isotherm is shown in Fig. 6.

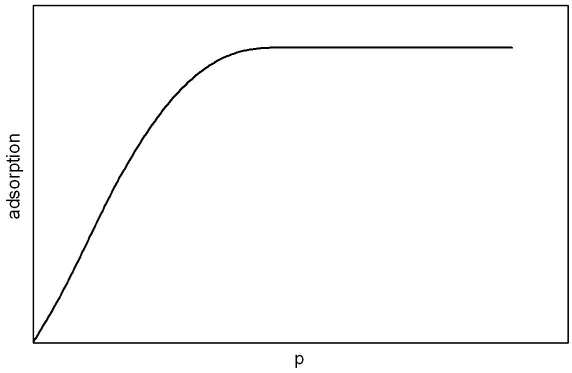

Fig. 6. Langmuir adsorption isotherm

The Langmuir adsorption isotherm equation can be written in the form of linear equation:

$$a=\frac{a_m K p}{1+K p} \Big/ \cdot (1+K p) \tag{12}$$

$$a\,(1+K p)=a_m K p \Big/ a \tag{13}$$

$$1+K p=a_m K \frac{p}{a} \Big/ a_m K \tag{14}$$

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

Fig. 7 shows the plot of p/a versus p, when the Langmuir equation is applicable (straight line), permitting the calculation of the constants a_m and K.

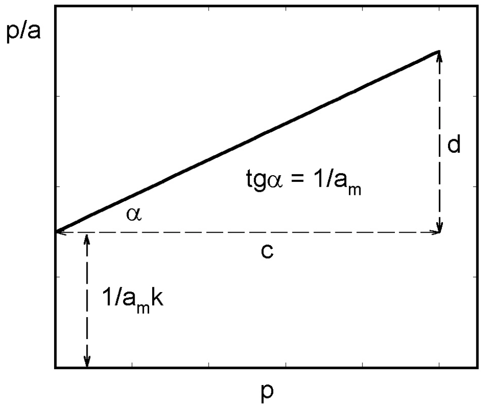

Fig. 7. Calculation of the constants from the Langmuir adsorption isotherm equation

The quantity a_m or a_m^s, the amount of adsorbate covering the surface area of the adsorbent in a monomolecular film (mole/g), is known as **the monolayer capacity**.

As mentioned earlier, in the case of adsorption from solution, pressure is replaced with concentration in equilibrium. Hence equation (9) can be written:

$$\theta = \frac{K\,c}{1 + K\,c} \tag{16}$$

If n^s is a number of moles of the substance adsorbed on the surface of adsorbent of *m*, and n_m^s is a number of adsorbate moles required to form monolayer, then the surface coverage can be expressed as:

$$\theta = \frac{n^s}{n_m^s} \tag{17}$$

In this case equation (11) can be written as:

$$\frac{c}{n^s} = \frac{1}{n_m^s}\,c + \frac{1}{K\,n_m^s} \tag{18}$$

If the plot of c/n^s against c is linear, $1/n_m^s$ can be calculated from its slope and ordinate $1/K\,n_m^s$:

$$\frac{1}{n_m^s} = tg\,\alpha \quad that\,is \quad n_m^s = \frac{1}{tg\,\alpha} \tag{19}$$

If the area occupied by one molecule in the monolayer is known ω_m (for methylene blue $\omega_m = 1.2 \cdot 10^{-18}$ m^2), determination of n_m^s based on the above equation allows to calculate specific surface area of adsorbent *S* (m^2/g) from the equation:

$$S = n_m^s\,N_A\,\omega_m \tag{20}$$

IV. Experimental

A. Equipment and chemical reagents

1. Measuring apparatus: spectrophotometer ”CECIL 1011”.
2. Equipment:
   - 25 ml volumetric flask– 6 pieces,
   - 100 ml bottle– 6 pieces,
   - volumetric pipette of volumes 5 and 10 ml,
   - one-size 5 ml pipette – 1 pieces,
   - plastic cuvette – 2 pieces.
3. Reagents:
   - methylene blue solution for adsorption of the concentration $1.25 \cdot 10^{-2}$ M,
   - methylene blue solution for a calibration curve of the concentration $1.5 \cdot 10^{-3}$ M,
   - dried silica gel 100 of the particle size 0.063–0.2 mm; about 0.5 g of gel samples in glass ampoules.

B. Scheme of experiment

1. Preparation of methylene blue solutions for adsorption and a calibration curve.
2. Weighing silica gel samples.
3. Conducting adsorption for 60 min. (mixing bottle contents several times).
4. Absorbance measurements of the solution for a calibration curve and that above the adsorbent (solutions after adsorption), by means of a spectrophotometer.

C. Operation of the device

I. The way how to start working of a spectrophotometer ”CECIL 1011”

Switch on the spectrophotometer 10 min. before starting the measurements (the bottom is placed at the back of the apparatus). On the display there appears the captions **CAL**, and then **AUTO** – the apparatus is reset automatically.

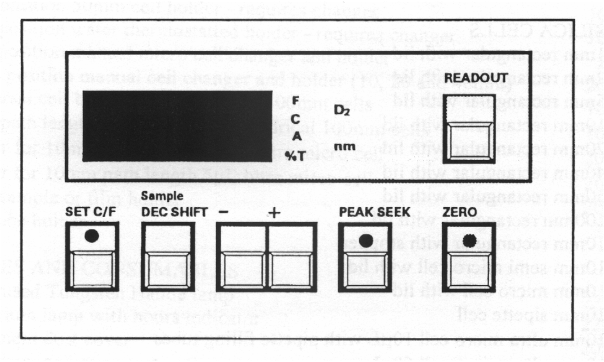

Fig. 8. Display of the „CECIL 1011” spectrophotometer

II. Setting the required wavelength

1. Place the plastic cuvette filled with distilled water (reference liquid) under the metal lid. Keep the cuvette on the top.
2. Press the button **READOUT** as long as the caption **nm**. appears on the right side of the display. Then, using the **–/+** buttons fix the wavelength to 500 nm (wait 15 s for the apparatus stabilization).

3. Using the **READOUT** button start measuring absorbance (light **A**) and press **ZERO** to set zero absorbance for water.
4. Replace the cuvette with water with that containing the most concentrated solution for a calibration curve.

The most precise measurements of the dependence $A = \mathrm{f}\,(c)$ can be obtained if the Lambert-Beer law is obeyed. This means that for a given wavelength absorbance can not be larger than 1. If the obtained absorbance value is higher than 1, the wavelength should be changed to obtain the absorbance smaller than 1. To achieve this repeat the points from II-1 to II-4 starting e.g. with the wavelength 495 nm.

III. Absorbance measurements

1. After establishing the required wavelength put in the cuvette containing distilled water and illuminate **A** using **READOUT** button. Then press **ZERO**.
2. Take out the cuvette with water and put the cuvette with the measured solution (in the order from the most diluted to the most concentrated one).
3. For long lasting measurements control absorbance for the reference liquid from time to time.
4. Take out the cuvette and wash carefully with distilled water.
5. Switch off the spectrophotometer.

D. Experimental setup

1. Adsorption

Prepare the solutions for adsorption from the solution of the concentration **$1.25{\cdot}10^{-2}$ M**. For this purpose take respectively: **1, 2, 3, 4, 5** and **6** ml solutions and transfer into the 25 ml volumetric flasks. Then add distilled water until the bottom of the meniscus touches the graduation line. Pour the obtained solutions into glass bottles.

Dried silica gel is in glass ampoules. To obtain its precise mass, weigh the closed ampoules, pour silica gel into the prepared solution and weigh the empty ampoule with the cork again.

To obtain the adsorption equilibrium leave the bottles with their contents for 1 hour, shaking every few minutes. In the same time take the absorbance measurements of a calibration curve.

2. Calibration curve

Take respectively **1, 2, 3, 4, 5** and **6 ml of $1.5{\cdot}10^{-3}$ M** methylene blue solutions and transfer them into the 25 ml volumetric flasks. Add distilled water until the bottom of the meniscus touches the graduation line.

3. Absorbance measurement

Measure absorbance of solutions for a calibration curve according to point III – Absorbance measurements. Write down the wavelength for which the measurements were taken. Before the absorbance measurement for the solutions after the adsorption, take 5 ml of the solution above the adsorbent, put into the 25 ml volumetric flask and distilled water until the bottom of the meniscus touches the graduation line.

E. Results and conclusions

1. Make the calibration curve (model curve) $A = f(c_1)$.
2. Calculate the equation for the model curve using the method of the smallest squares.
3. Based on the calibration curve determine concentration of the solutions after adsorption. Remember that the obtained concentration should be multiplied by 5 because before the absorbance measurements the solutions in equilibrium were diluted 5 times.
4. Calculate the amount of the methylene blue adsorbed on 1g of silica gel.

   For the particular solutions, calculate the amount of the dye adsorbed on silica gel (n^s) using the equation:

$$n^s = \frac{V(c_o - c)}{m} \tag{16}$$

   where: V – the volume of the solution used for adsorption (mol/ml), m – the mass of silica gel (g).
5. Calculate c/n^s for every solution in equilibrium and make the graph $c/n^s = f(c)$.
6. From the slant angle of the straight line calculate the monolayer capacity n^s_m – equation (14).
7. Knowing the monolayer capacity calculate the specific surface area of silica gel S using equation (15).
8. Present the obtained results in tables:

Calibration curve

Flask number	1	2	3	4	5	6
Concentration, c_1 (mol/ml)						
Absorbance, A						

Adsorption

Flask number	c_0 [mol/ml]	Absorbance A	c [mol/ml]	Gel mass [g]	n^s [mol/g]	c/n^s
1.						
2.						
3.						
4.						
5.						
6.						

9. Prezent the obtained values:
   - monolayer capacity n^s_m,
   - the specific surface area of silica gel.
10. Present a graph of calibration curve and adsorption isotherm.