Task 4

DETERMINATION OF EXCESS ADSORPTION ISOTHERM FROM BINARY SOLUTION ON SOLID BY STATIC METHOD

I. Aim of the task

The purpose of exercise is designation of the excess adsorption isotherm of n-butanol from binary solution (n-butanol – n-heptane) on the MCM-41 solid.

II. Introduction

1. The adsorption phenomena.
2. The adsorption excess.
3. Methods of adsorption excess determination.
4. Types of excess adsorption isotherm.
5. Actual adsorption.
6. Types of the adsorption isotherm from solution.

References:

1. P.W. Atkins, ‘*Physical chemistry*’, 2001.
2. J. Oscik, ‘*Adsorption*’, E. Horwood ; Halsted Press, Chichester : New York, 1982.
3. M. Jaroniec and R. Madey, *Physical Adsorption on Heterogeneous Solids*, Surface Science Letters, 210 (1989) A86.
4. W. Rudziński, D.H. Everett, *Adsorption of Gases on Heterogeneous Surfaces*, Academic Press, London, 1992.

III. Theory

III.1. The adsorption phenomena.

The role of surface phenomena is frequently underestimated or overlooked, although surfaces play the significant role in all natural sciences. Many physical and chemical processes occur at the boundary between two phases while others are initiated at that interface. The understanding of the phenomena occurring at interfacial surfaces is therefore essential for explaining the mechanism of many different physical or chemical processes.

For any phase the surface molecules or atoms are in higher energy state compared with those in the bulk phase. This additional energy, known as the surface energy, imparts to the surface region certain distinct features which differ significantly from those of the bulk regions of the phase. When two phases (e.g. solid and gas) are in contact the unbalanced forces at the phase boundary, so-called surface forces, are responsible for aggregation of gas molecules on the surface of solid. This in turn creates concentration gradient from the surface of solid to the bulk phase see Fig. 1. The described process is called **adsorption** and is defined by the IUPAC as '*an increase in the concentration of a dissolved substance at the interface of a condensed and a liquid phase due to the operation of surface forces*' [1]. In other words adsorption is a consequence of imbalanced forces present at the edge of the solid.

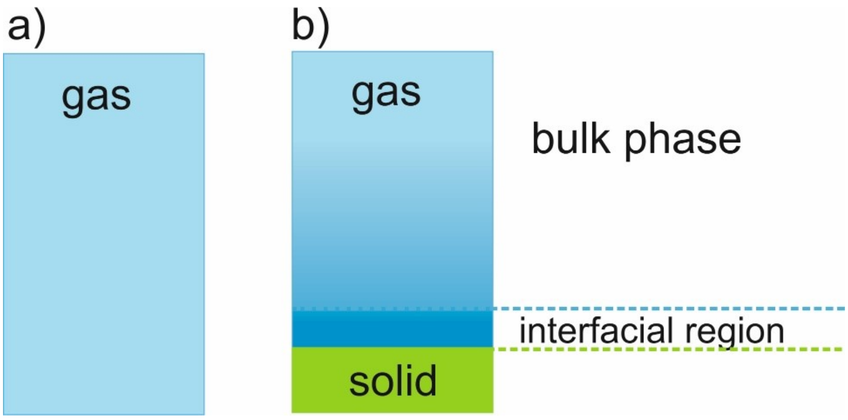


Fig. 1. Schematic concentration changes without (a) and with (b) adsorption occurrence. Darker color represents higher phase density.

When this change in concentration at the surface is caused by formation of chemical bonds at the interface the adsorption is called **chemisorption** (chemical adsorption) otherwise is referred to as **physisorption** (physical adsorption). The physisorption is driven mostly by van der Waals forces or hydrogen bonding. Both kinds of adsorption can occur in one system to partially or fully balance the forces at the interface. The adsorption processes can be classified based on the type of phases being in contact:

1. liquid/gas,
2. solid/gas,
3. solid/liquid,
4. liquid/liquid.

The total internal energy (U) of a given phase consists of two components: energy per unit mass (U^m) and energy per unit surface area (U^s) and is therefore described by equation:

$$U = (U^m \cdot m) + (U^s \cdot A) \quad (1)$$

where : m – mass of the phase,
A – surface area of the phase.

From this equation we get the total internal energy per unit mass:

$$\frac{U}{m} = U^m + (U^s \cdot C) \quad (2)$$

where : $C = \frac{A}{m}$ – the surface area per unit mass called **the specific surface area**.

For porous solids or high diminution systems, the specific surface area assumes large value and the surface energy (the interfacial energy) has significant effect on the properties of the given system.

III.2. The adsorption excess

The adsorption on solids from multi-component liquid mixtures is of the particular interest, since many industrial processes involve such mixtures. In spite of the increased application of zeolites, silica gels, aerogels, and other adsorbents with high adsorption capacity, the adsorption on solid is often used in chemical industry, e.g., for the separation and purification of chemical products.

The adsorption from solution, even in the case of the simplest binary solution is difficult process as compared to the adsorption of vapours, gases or pure liquids. The adsorption from solution is more complex and impossible to direct measurements. The solid surface is always covered with liquid mixture components and during adsorption only exchange of components between adsorbed layer and bulk solution is possible. Thus the increase of the one component concentration in surface layer in comparison to bulk phase is descriebed as **the adsorption excess** and not the real adsorption.

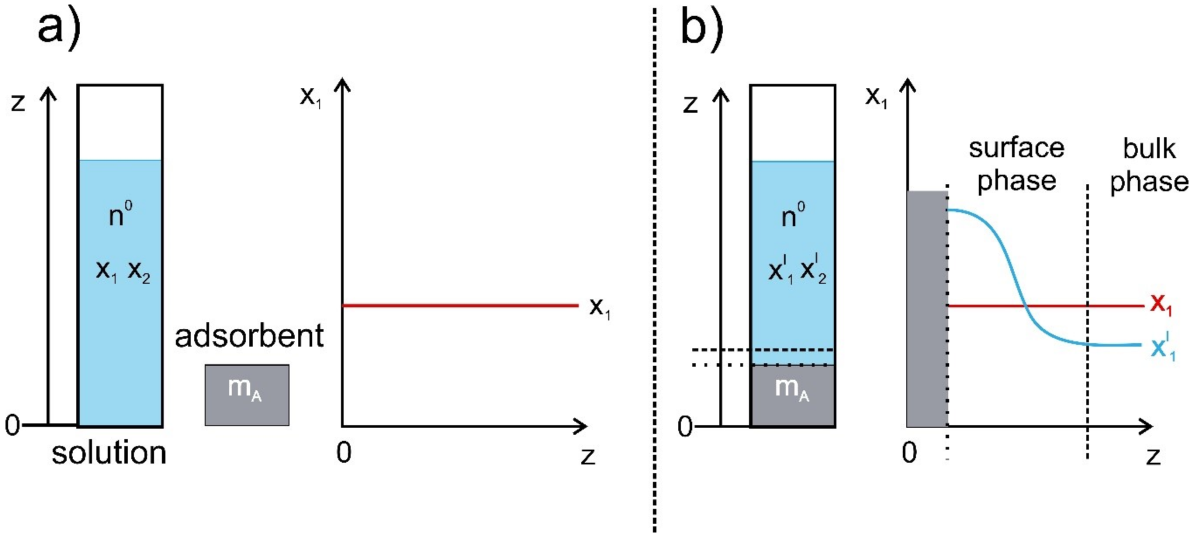


Fig. 2. Diagram of the adsorption from binary solution (formation of the surface excess) a) before adsorption, b) after adsorption equilibrium, x – molar fractions, z – the distance from the surface of adsorbent.

The adsorption excess ($n_1^{\sigma(n)}$) of component 1, being in contact with the mass of adsorbent (m_A) is given by the experimentally accessible values according to equation:

$$n_1^{\sigma(n)} = n^0 \cdot \frac{x_1 - x_1^l}{m_A} \tag{3}$$

where: $n_1^{\sigma(n)}$ – means the excess amount, expressed by number of moles of component 1 per 1 g of solid;
n^0 – the total amount of moles being in contact with solid $n^0 = n_1^0 + n_2^0$,
$(x_1 - x_1^l)$ – is a difference of the mole fraction of the component 1 before and after adsorption
m_A – the mass of adsorbent

Combination of a definite surface phase model with the mass balance equation for a liquid mixture–solid system allows to express, the adsorption excess of *i*-th component in terms of the mole fraction of the *i*-th component in the surface phase (index *s*) and the volume phase (index *l*) at the equilibrium.

$$n_i^{\sigma(n)} = n^s \cdot \frac{x_i^s - x_i^l}{m_A}, \quad i = 1, 2, 3, \dots, t \tag{4}$$

III.3. Determination of the adsorption excess

The surface excess can be measured by the static or the dynamic method. This division is based on the movement of both phases in contact in reference to each other (stirring does not count as motion). The static method is usually executed by flooding certain amount of solid sorbent with solution of known concentration in tightly closed and thermostated vessel. After equilibration (often after several hours) the concentration of components in solution is determined.

The concentration of the solution can be determined by various instrumental analytic techniques (e. g. chromatography, spectrophotometry, voltammetry, etc.). By measuring the difference in concentration of a given component, caused by adsorption, for solutions of different starting concentrations, the surface excess of this component may be determined according to equation (3). The relationship $n_i^{\sigma(n)} = f(x_i^l)$ represents the so called **excess adsorption isotherm**.

The chromatographic method is the most popular dynamic method of determination of the surface excess values. This method is based on constant passing through column a binary solution with known concentration of component 1 (c_1^0 or x_1) filled with certain mass of adsorbent (m_A). Assuming, that the component 1 has greater affinity towards solid phase (is adsorbed more strongly) than the component 2, its initial concentration in the eluent is equal to zero. During the process amount of the component 1 in the effluent will increase up to the point when concentration of 1 at the end of column will be equal to c_1^0. The dependence of the concentration of component 1 in the eluate from the volume of effluent is called breakthrough curve and usually has characteristic *S* shape (Fig. 3.). From this curve in the middle of '*S*' **the retention volume** (V_R) can be obtained.

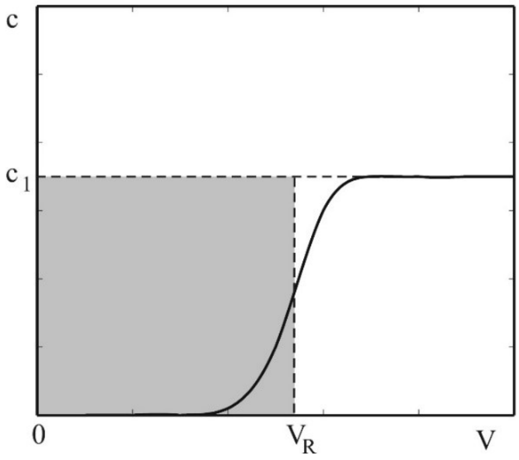


Fig. 3. Determination of the retention volume (V_R) in the dynamic method of the adsorption measurement from solution.

The value of excess adsorption ($n_1^{\sigma(v)}$), which in Figure 3 corresponds to the rectangular marked area, can be calculated according to the formula:

$$n_1^{\sigma(v)} = \frac{V_R \cdot c_1^0}{m_A} \tag{5}$$

or

$$n_1^{\sigma(n)} = \frac{V_R \cdot x_1}{V_{m,1} \cdot m_A} \tag{6}$$

where : $\boldsymbol{V_{m,1}}$- is the molar volume of the component 1 of the solution.

Breakthrough curves are determined for solutions of different concentrations of component 1, so the dependence of excess adsorption of component 1 on its concentration (c_1^l) or mole fraction (x_1^l) can be determined.

III.4. The excess isotherm of adsorption

The shape of adsorption isotherms from the liquid phase on solid may vary and is determined by many factors, among which the dominant role play the interactions of liquid mixture molecules with the adsorbent surface. Experimentally determined excess isotherms because of their shape can be ordered in five groups.

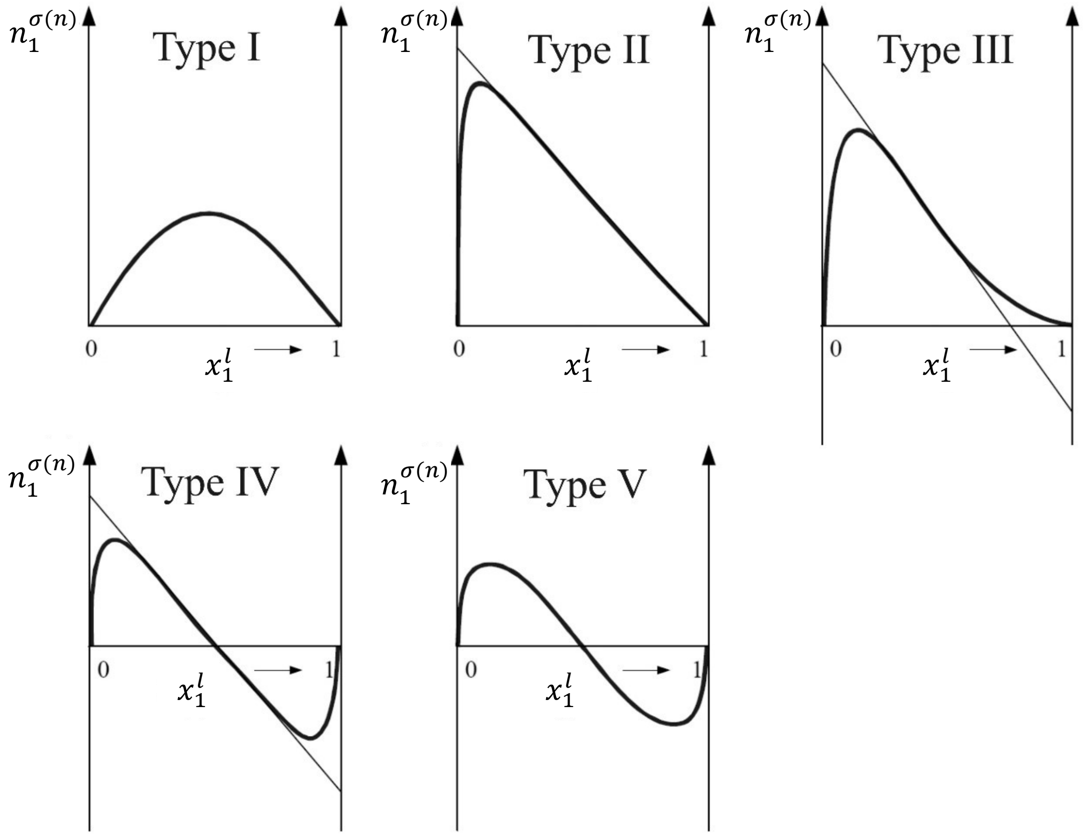


Fig. 4. Excess adsorption isotherms for a binary solution according to classification by Schay and Nagy.

The first three types (I-III) of 'upside-down' U-shaped adsorption isotherms are characteristic for preferential adsorption of the component 1 from the binary mixture in the whole range of concentration. The location of maximum isotherm is caused by the different interaction of constituent molecules of the solution with solid surface.

Types IV and V are called S-shaped isotherms and they are characteristic for systems with high heterogeneity of solid surface. In consequence, both components of binary mixtures are equivalently adsorbed. The surface excess of a given component depends greatly on the solution composition. Typically ca. in the middle of $n_i^{\sigma(n)} = f(x_i^l)$ graph for these two types of excess adsorption isotherms point $n_i^{\sigma(n)} = 0$ occur. **It means that concentration of both components in the interfacial region are equal to the composition of the bulk phase**. This effect is called **adsorption azeotropy**.

III.5. The absolute (individual) isotherm of adsorption

Excess isotherms do not provide redundant information about the actual quantities of components in the surface phase (n_1^s). Using the appropriate equations describing the adsorption process and based on the surface excess, absolute adsorption of a given component can be calculated. If the surface phase adsorption capacity is known ($\boldsymbol{n}^s$), the absolute adsorption can be calculated according to equation:

$$n_1^s = n_1^{\sigma(n)} + n^s \cdot x_1^l \tag{7}$$

where: n_1^s the absolute (individual) adsorption of component *1*, i.e. number of moles in the surface phase per 1 g of adsorbent;

$n_1^{\sigma(n)}$ the excess quantity as number of moles of component *1;*

n^s the surface phase adsorption capacity, i.e., the total number of moles of both components present in the surface layer $n^s = \sum_i n_i^s = n_1^s + n_2^s$

$\boldsymbol{x_1^l}$ the mole fraction of component *1* in the equilibrium.

The most important question is how to determine the surfaces phase or adsorption capacity. To assess $\boldsymbol{n}^s$, two classical most common methods are used: 1) the Schay and Nagy method and 2) the Everett method. Both methods take into account the material balance of components at the surface and volume phase.

III.6. Calculation of n^s according to Schay and Nagy method.

Schay and Nagy have assumed that, for the decreasing section of the excess adsorption isotherm, the surface excess $n_1^{\sigma(n)}$ can be a linear function of the mole fraction of component 1:

$$n_1^{\sigma(n)} = \mathrm{a} - \mathrm{b} \cdot x_1^l \tag{8}$$

The surface excess $n_1^{\sigma(n)}$ can be expressed as follows:

$$n_1^{\sigma(n)} = n_1^s - (n_1^s + n_2^s) \cdot x_1^l = n_1^s - n^s \cdot x_1^l \tag{9}$$

or

$$n_1^{\sigma(n)} = n_1^s - (n_1^s + n_2^s) \cdot x_1^l = n_1^s \cdot (1 - x_1^l) - n_2^s \cdot x_1^l \tag{10}$$

By comparing equations (8) and (9) we get:

$$n_1^s = a \qquad \text{and} \qquad n_1^s + n_2^s = n^s = b$$

Assumption of Schay and Nagy is valid only for physical adsorption, when the dimensions of the molecules of the solution components, are similar. The constants a and b in equation (8) represent the amounts of components in the adsorption layer if it is assumed that the composition of that layer is constant within the linear part of the adsorption isotherm (when it is linear at least within 0.3 mole fraction units) despite the bulk phase composition changes. The surface layer capacity is represented by intercepts of linear segment of isotherm and is given as intercept of extrapolated segment to $x_1^l = 0$. Despite some limitations, the Schay and Nagy method gives good results, especially for types II and IV excess adsorption isotherm.

The graph in Fig. 4 presents practical calculations of surface phase adsorption capacity of n-butanol and n-heptane on solid. As shown in this figure, the total capacity is the sum of the surface phase capacity of the surface layer for the components of the mixture.

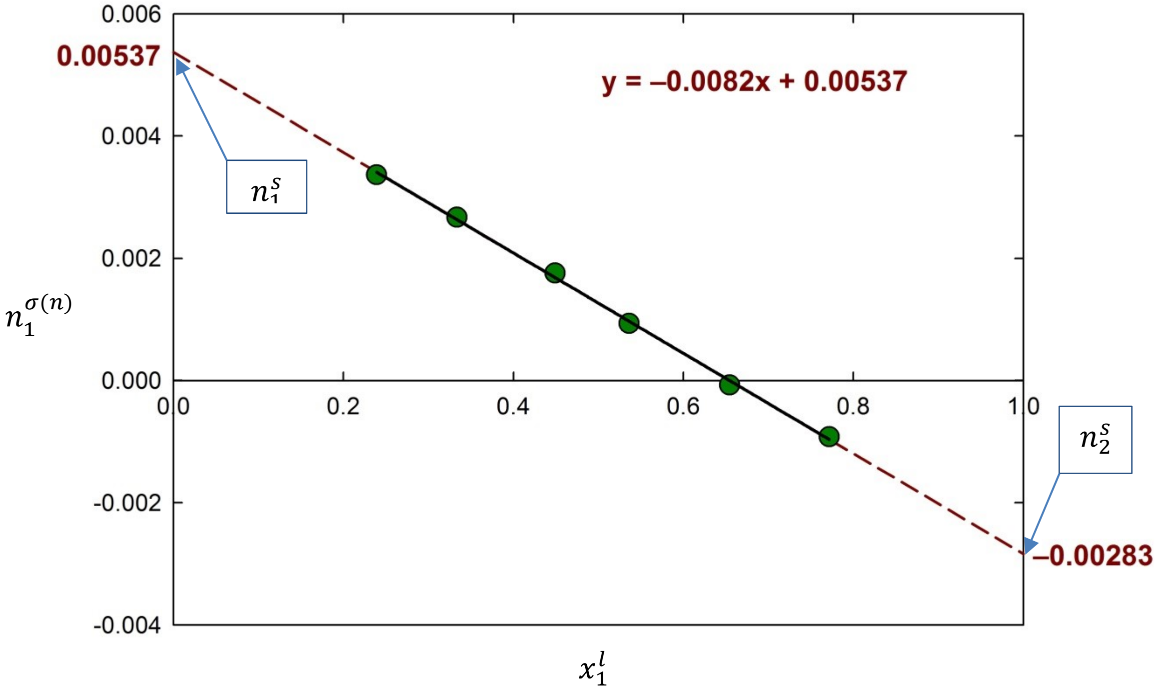


Fig. 5. Determination of adsorption capacity of surface layer by Schay and Nagy method.

III.7. Determination of n^s by Everett method

Another method of calculating of the total content of components in the surface layer has been introduced by Everett. This method can be used mainly for excess adsorption isotherms of types I and II.

Using the equation combining the excess adsorption and surface layer capacity in the following form:

$$\frac{x_1^l \cdot x_2^l}{n_1^{\sigma(n)}} = \frac{1}{n^s}\left(\frac{1}{K-1} + x_1^l\right) \tag{11}$$

where: $K = \frac{x_1^s \cdot x_2^l}{x_1^l \cdot x_2^s}$ is the equilibrium constant of adsorption.

and drawing a linear inverse of the surface layer capacity for adsorption of component 1, as a function of its mole fraction, it is possible to calculate surface phase adsorption capacity ***(n^s)***.

In case of physical adsorption K = const and left-hand side equation is a linear function of x_1^l (Fig. 5). Directional factor of this linear relationship is the inverse of the surface layer capacity $\boldsymbol{n^s}$, although some researchers have suggested a doubling of this value.

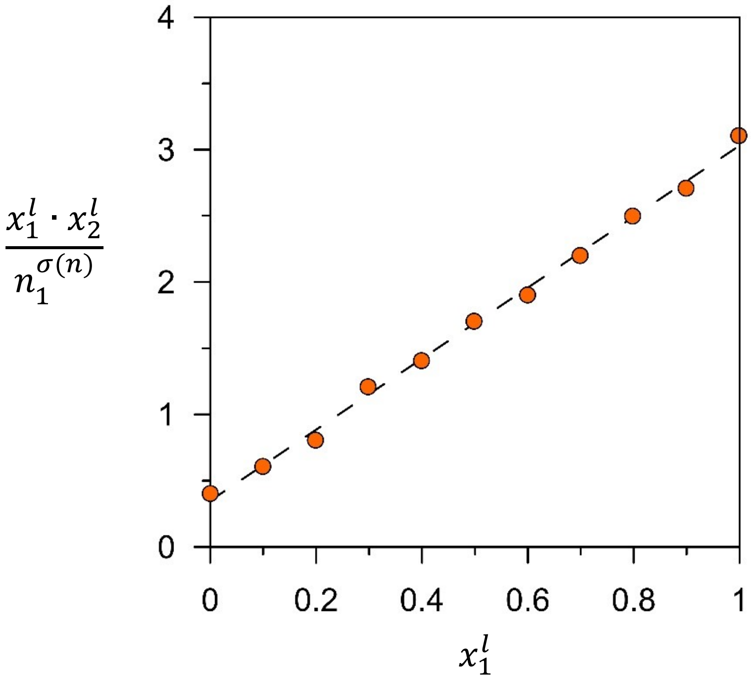


Fig. 6. Determination of the adsorption capacity of the surface layer by Everett method.

The absolute adsorption isotherms of components 1 and 2, corresponding to different excess adsorption isotherms shown in Fig. 4, are presented in Fig. 7.

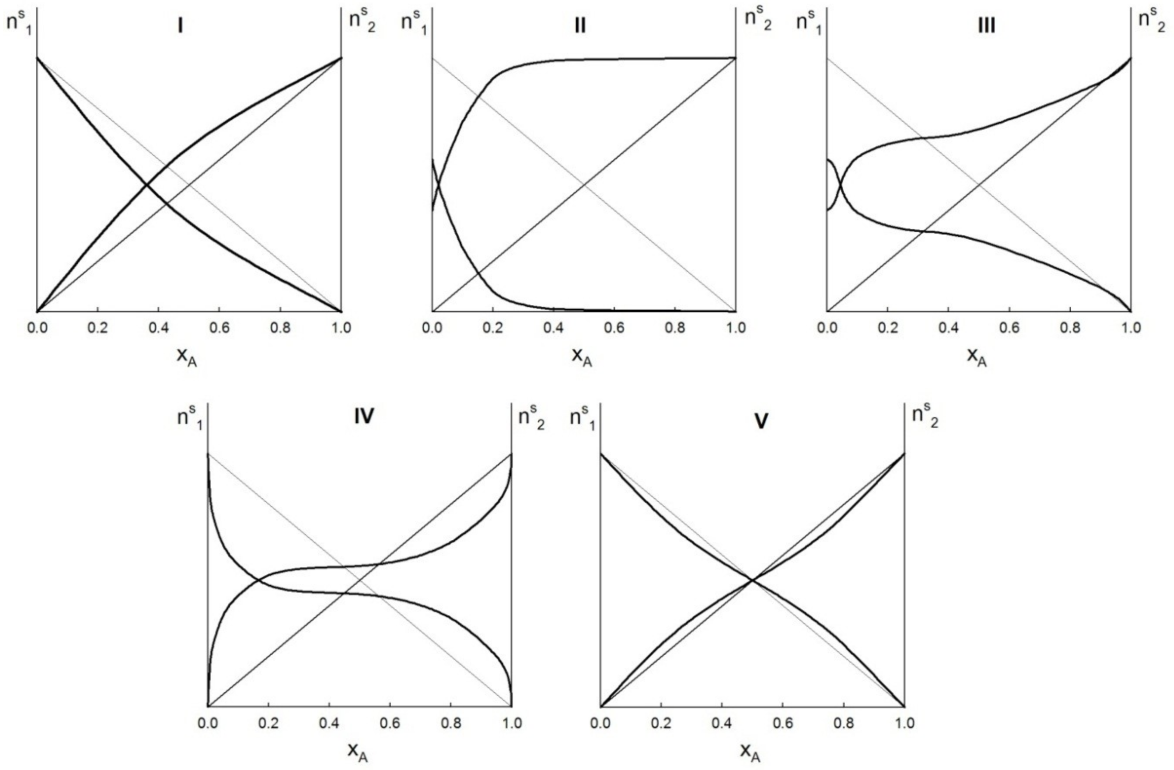


Fig. 7. Absolute adsorption isotherms of components 1 and 2 corresponding to the appropriate excess adsorption isotherm.

III.8. Calculation of the thickness of the surface layer

The surface excess [eqn. (4)] may be written in terms of the adsorbed and bulk phase mole fractions of component 1:

$$n_1^{\sigma} = n^{s} \cdot \left(x_1^{s} - x_1^{l}\right) \tag{12}$$

The thickness (number of molecular layers) τ in the surface phase may be expressed as follows:

$$\boldsymbol{\tau} = \frac{\boldsymbol{n_1^s \cdot a_1^0 + n_2^s \cdot a_2^0}}{\boldsymbol{S_{BET}}} \tag{13}$$

where:

a_i^0 – the molar cross-sectional area, $a_i^0 = \omega_i \times N_A$ (ω_i – is an area occupied by adsorbate molecule on the solid surface, N_A –Avogadro Number),

S_{BET} – the specific surface area of the solid,

Considering, that the surface phase consists of $\boldsymbol{\tau}$ layers of adsorbed molecules, the mole fraction of component 1 in surface phase can be expressed:

Combination of eqn. 12 and 13 yields:

$$\boldsymbol{x_1^s} = \frac{(\tau \cdot x_1^l) + a_2^0 \cdot \left(\frac{n_1^{\sigma(n)}}{s_{BET}}\right)}{\tau - (a_1^0 - a_2^0) \cdot \left(\frac{n_1^{\sigma(n)}}{s_{BET}}\right)} \tag{14}$$

Since $\boldsymbol{x_1^s \le 1}$, and more restrictively, $\boldsymbol{dx_1^s / dx_1^l}$ must always be positive in whole concentration range. This way, one can check if mono- or multilayer surface phase is realistic for a given system. Additionally it can be evaluated whereas the thermodynamic consistency of a model in which $\boldsymbol{\tau}$ layers are assumed and physically realistic values of a_1^0, a_2^0 and a_s are chosen properly. In this way a minimum thickness, $\boldsymbol{\tau_{min}}$, of the adsorbed layer can be found, below which unacceptable values of $\boldsymbol{x_1^s}$ are obtained.

However, it is always possible to achieve the thermodynamic consistency, for $\boldsymbol{\tau} = 1$, by choosing smaller values of a_1^0 and a_2^0 . If we assume a different structure for the adsorbed phase, for instance one where the adsorbed molecules are oriented perpendicularly to the surface, thus occupying smaller areas than as considered above, it is possible to find realistic values of a_i^0 which are consistent with an adsorbed monolayer.

Fig. 8 illustrates the correlation of $\boldsymbol{x_1^s}$ depending on $\boldsymbol{x_1^l}$ for different values of $\boldsymbol{\tau}$ in the system n-dodecane – n-butanol – activated carbon. The present results show that, in this system, the minimum thickness of the surface phase ($\boldsymbol{\tau_{min}}$) is 3.

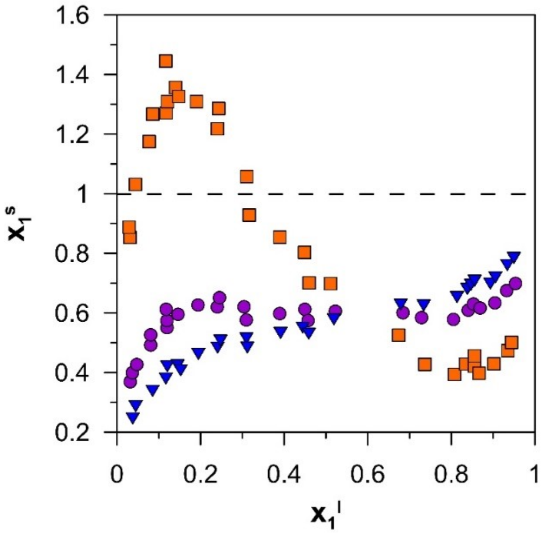


Fig. 8 Calculation of the thickness of the surface layer corresponding to appropriate excess adsorption isotherm as a surface mole fraction for different **τ**. **τ** =1 (squares), **τ** =2 (dots), **τ** =3 (inverse triangles). (based on [2]).

References to the *Theory*

[1] https://goldbook.iupac.org/,
[2] A.M.G. Dasilva, V.A.M. Soares, J.C.G. Calado, Thermodynamics of Adsorption from Solution, J Chem Soc Faraday T, 87 (1991) 755-760.

IV. Experimental

A. Equipment and reagents

1. Instrumentation:

- Gas-chromatograph HP-5890 Series II equipped with micro-TCD.
- Column 1 m×2 mm packed with Hayesep Q 80/100 mesh.
- Micro-syringe 5 µl.

2. Equipment:

- Glass vessels (4 mL) 10 pcs.
- Calibrated glass vessels (25 mL) 5pcs.

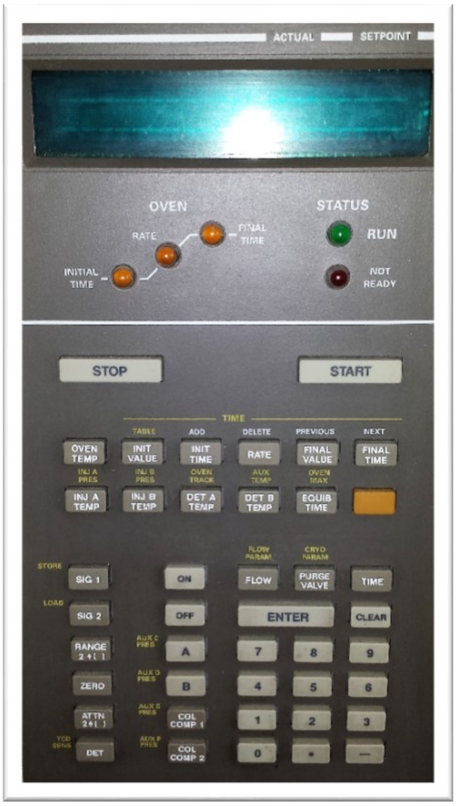
3. Reagents:

- n-butanol p.a.
- n-heptane,
- MCM-41 or Si 40.

B. Preparation of the gas chromatograph for the measurements

1. Turn on the fume hood in room 240 (during the analysis gasous hydrogen released from the device)
2. Turn on the main hydrogen valve (it’s at the top of the hydrogen cylinder).
3. Set **the gas pressure at 0.4 MPa** by screwing the reducer valve (the red knob).
4. Turn on the PC and the chromatograph (ON/OFF buton is on the right side of the device).The chromatograph will do the *autocheck* procedure (wait for a few minutes).

Fig 9. Gas-chromatograph HP-5890 Series II



5. To set the oven temperature on the front panel press **OVEN TEMP** → introduce desired temperature from numeric keyboard → **ENTER**. In case of error press CLEAR and reintroduce desired oven temperature. The oven should be heated at a heating rate equal to 20°C per 10 min.

6. Press **OVEN TEMP → 60 → ENTER** (wait for 10 min.)
   a. **OVEN TEMP → 80 → ENTER** (wait for 10 min.)
   b. **OVEN TEMP → 100 → ENTER** (wait for 10 min.)
   c. **OVEN TEMP → 120 → ENTER** (wait for 10 min.)
   d. **OVEN TEMP → 140 → ENTER** (wait for 10 min.)
   e. **OVEN TEMP → 170 → ENTER** (wait for 10 min.)
7. Turn on **TCD REF** valve on (two full anti-clockwise twists) the front panel of the gas chromatograph. Wait for 3-4 min.
8. Run **LP-Chrom** software.
9. Press **DET → A → ON**.
10. The gas chromatograph is now ready for analysis.

C. The execution of exercise

1. Prepare five standard solutions of n-butanol in n-heptane with different specific molar fraction.
2. Prepare five ampoules with a specific portion of the adsorbent (~ 100 mg).
3. To a specific portion of the adsorbent in an ampoule, add a certain amount of standard solution (~ 1 ml).
4. Hold ampoules in thermostat at constant temperature ~ 25°C, to achieve adsorption equilibrium (~ 1 hour).
5. Determine the concentration of components of standard solution, before and after adsorption, by gas chromatography. Perform measurements at 170 °C. Inject of 1.0 μl of appropriate solution in 'empty needle' mode. For each concentration, measurements should be repeated three times.
6. On the basis of these results, plot a graph of the peak area on the concentration of n-butanol in standard solution. Using this graph determine concentration of n-butanol in all solutions after adsorption.

C. Analysis of results.

1. Calculate the specific surface excess amount ($n_1^{\sigma(n)}$) for each standard solution and next draw a graph of the surface excess (mmol/1g of adsorbent) on the mole fraction ($\boldsymbol{x_1^l}$) of n-butanol.
2. Calculate the capacity of the surface layer ($\boldsymbol{n^s}$) of investigated adsorbent according to Everett and Schay-Nagy method.
3. Finally, draw the absolute adsorption isotherm of n-butanol on Si 40 or MCM-41 solid according to the material which was investigated during the experiment.