Task No. 4

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

I. The purpose of the exercise

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

II. Introducing issues

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.

III. Literature

1. J. Ościk, "*Adsorption" (2-nd ed)*, PWN and Ellis Horwood Limited, 1982
2. P.W. Atkins, "*Physical chemistry*", 2001.

Theory

The adsorption phenomena.

Many physical and chemical processes occur at the boundary between two phases, while others are initiated at that interface. The understanding of phenomena occurring at such boundary surfaces is therefore often essential for explaining the mechanism of different physical or chemical processes

The role of surface phenomena is frequently underestimated or overlooked, although surfaces play the significant role in all natural sciences. The detailed knowledge of surface phenomena is therefore indispensable for all concerned with these sciences.

Between the molecules of all substances, irrespective of their state of aggregation, act Van der Waals or cohesive forces. Such forces are revealed only on several nanometers distance. The greatest distance between molecules at which cohesive forces still act is called the radius of molecular interaction.

In the bulk of the phase, intermolecular cohesive forces are balanced. In solids, liquids or gases the atoms, ions or molecules in the interface (surface layer) are exposed to the action of unbalanced forces due to both phases, these resultant forces acting normal to the phase boundary.

The unbalanced forces at the phase boundary, so-called surface forces, cause changes in the number of molecules (atoms, ions) to occur on the boundary surface as compared with the corresponding numbers within the neighboring (gaseous or liquid) phases. This change in concentration at the surface is referred to adsorption, and may be a physical process (physic-sorption) taking place due to van der Waals forces, hydrogen bonding, etc., or it may be due to chemical processes and the formation of chemical compounds (chemical adsorption or chemisorption). As a result of these processes, the balance of forces at the interface is partly or fully restored.

For any phase the surface molecules or atoms are in different 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.

The total internal energy 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:

$$U = u^m {*} m + u^s {*} A \tag{1}$$

where : m mass of the phase
            A surface area of the phase

From this equation we get the internal energy per unit mass (*U/m*):

$$U/m = u^m + u^s {*} C \tag{2}$$

where :   *U/m*   the surface area per unit mass called the specific surface area.

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

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, we can consider the process of adsorption in the following systems:

(1) liquid/gas   (3)   solid/liquid
(2) solid/gas   (4)   liquid/liquid

The adsorption excess.

The energy-saving 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 adsorbent is often used in chemical industry, e.g., for the separation and purification of chemical products.
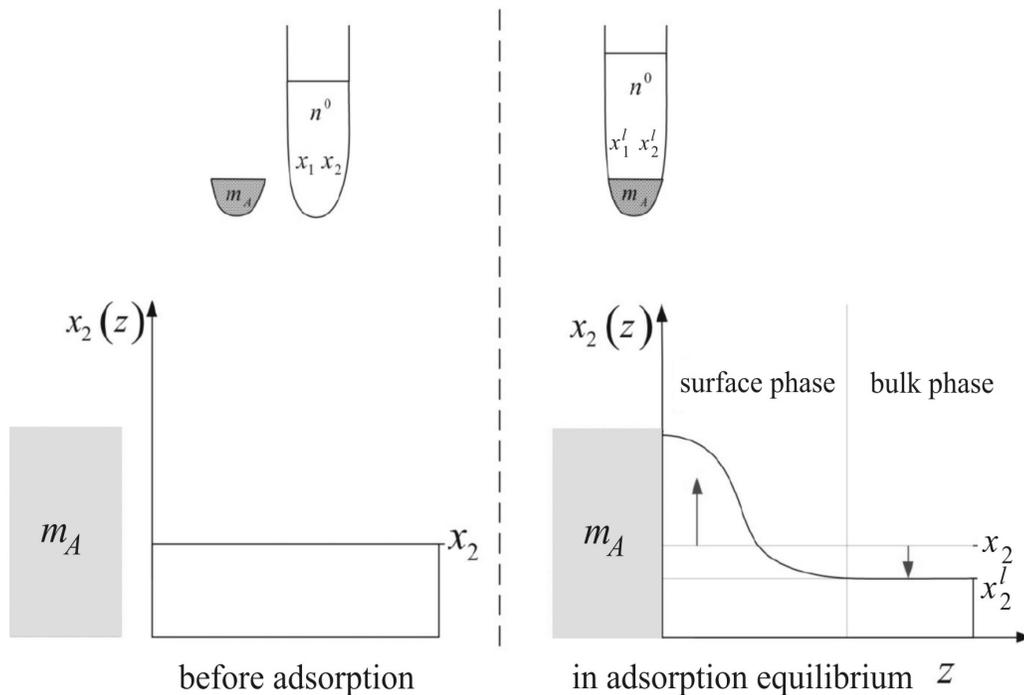

Fig. 1 Diagram of the adsorption from binary solution (formation of the surface excess).

The adsorption from solution, as the simplest solution contains at least two components, compare to the adsorption of vapours, gases or pure liquids, is more

complicated and impossible to direct measurements. Owing to the assumed incompressibility of the liquid mixture, the adsorption volume is completely filled and only exchange of components in adsorbed layer is possible.

The amount increase of one component in surface layer compare to bulk phase is descriebed as **the adsorption excess**.

The adsorption excess ($n_2^{\sigma(n)}$) of component *2*, related to the mass of adsorbent (m_A), is a common quantity for the description of liquid-phase adsorption. It is given by the experimentally accessible values according to equation:

$$n_2^{\sigma\,(n)} \;=\; n_2^{\sigma}\,/\,m_A \;=\; n^0\,{}^*(x_2^{\,0} - x_2^{\,l})\,/\,m_A \tag{3}$$

where : $n_2^{\sigma\,(n)}$ means the excess amount, as number of moles of component *2*

n^0 the total amount of substances in bulk and adsorption phase
$n^0 = n_1^{\,0} + n_2^{\,0}$

$x_2^{\,0} - x_2^{\,l}$ difference in the mole fraction of the considered component "2" before and after adsorption.

Combination of a definite surface phase model with the mass balance equation for a liquid mixture–solid system allows to express, more general, the adsorption excess of *i*-th component as:

$$n_i^{\sigma(n)} \;=\; n_i^{\sigma}\,/\,m_A \;=\; n^s\,{}^*(x_i^{\,s} - x_i^{\,l})\,/\,m_A \;;\; i = 1, 2, 3, \ldots, t \tag{4}$$

in terms of the mole fraction of the *i*-th component in the surface phase (index *s*) and the volume phase (index *l*) at equilibrium.

Determination of the adsorption excess.

Surface excess can be measured by the static or dynamic method. The static method measures differences in the concentrations of a component 2 in starting solution and in solution being in equilibrium with the adsorbent. The concentration of the component of interest can be determined by various techniques such as chromatography, spectrophotometry, electrochemical methods, etc.

A simple way to measure adsorption from solution is flooding, in tightly closed containers, weighted amount of adsorbent with solutions of different composition. After equilibration adsorption (often from a few to several hours) the concentration of components in solution is measured.

By measuring the difference in concentration, caused by adsorption, for solutions of different starting concentrations, the surface excess of the asset according to equation (3). The relationship $n_1^{\sigma(n)} = f(x_1)$ exists, called excess adsorption isotherm.

Between methods of dynamic measurement of adsorption from solutions, the most popular is the method of leading analysis. This method counts on passing through a column,

containing adsorbent of mass m, a solution with a concentration c_1^i of component 1. Assuming, that a component 1 is adsorbed more strongly than component 2, its initial concentration in the eluent is equal to zero. As far as passing through a column of the input solution, the effluent starts to increase the concentration of a component 1 until its concentration in the solution of the input c_1^i. Dependence of the concentration of component 1 in the eluate from the volume of effluent is called breakthrough curve (Fig.2), and after its graphical interpretation can determine the retention volume (V_R).

The value of excess adsorption ($n_2^{\sigma(n)}$), which in Figure 2 corresponds to the hatched area of a rectangle, can be calculated according to the formula:

$$n_2^{\sigma(n)} \; = \; V_R * c_1^i \, / \, m \tag{5}$$

or

$$n_2^{\sigma(n)} \; = \; V_R * x_1^i \, / \, V_{m,2} * m \tag{6}$$

where : $V_{m,2}$ molar volume of second component of the solution

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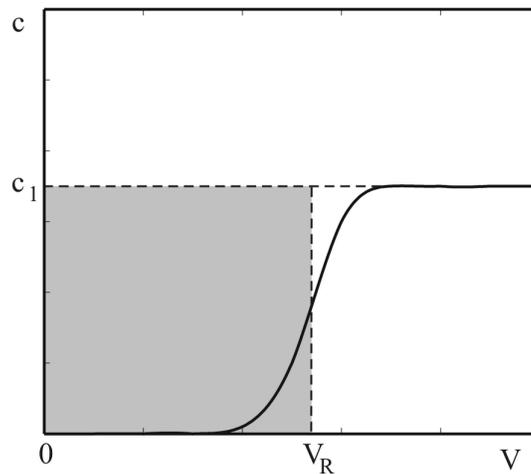

Fig. 2 Determination of the retention volume (V_R) in the dynamic method of the adsorption measurement from solution.

The excess isotherm of adsorption.

Experimentally determined excess isotherms can be ordered, in five groups, because of their shape. 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 surface of the adsorbent. The first three types of U-shaped adsorption isotherms are characterized by preferential adsorption of one component of the 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-isotherms and thy are characteristic for systems with high heterogeneity of solid surface. In consequence, no adsorption of only one dominant component is observed. The lack of surface excess for a particular composition of the starting solution (the intersection of the x-axi) is characteristic for these isotherms.
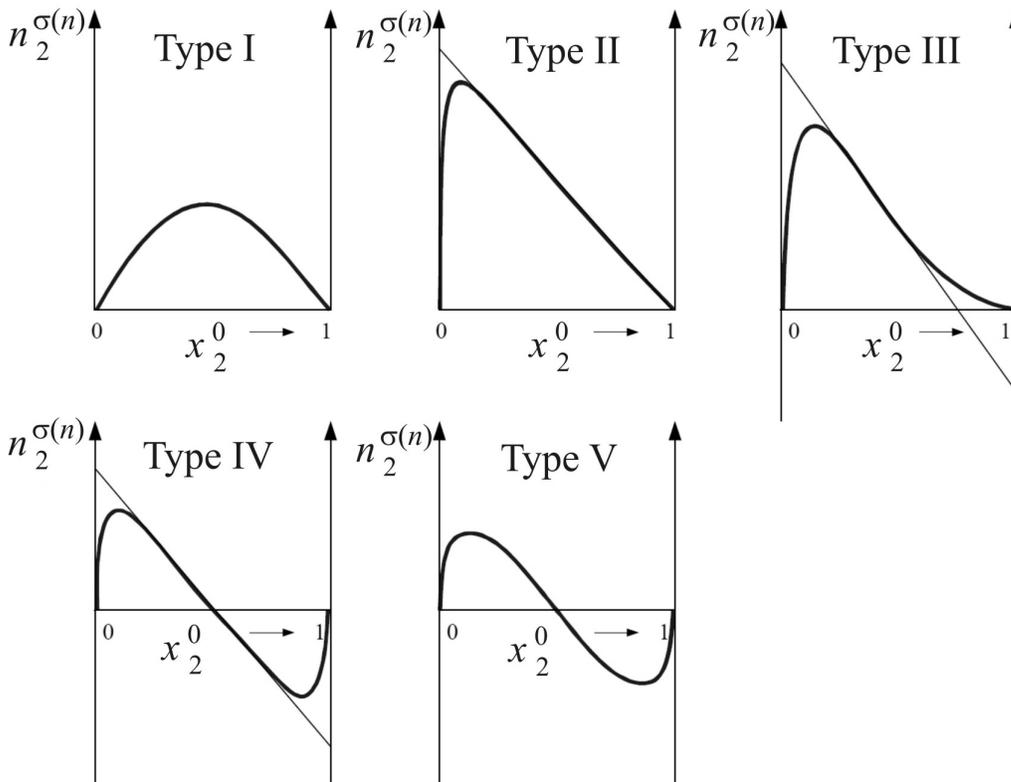

Fig. 3 Excess adsorption isotherms for a binary solution according to classification by Schay and Nagy.

Actual adsorption isotherm.

Excess isotherms do not provide redundant information about the actual quantities of ingredients in the surface phase (n_2^s). Using the appropriate equations describing the adsorption process and based on the surface excess, actual adsorption can only be

calculated. If the surface phase adsorption capacity is known (n^s), the actual adsorption can be calculated according to equation:

$$n_2^{\ s} \ = \ n_2^{\ \sigma(n)} \ + \ \ n^s * x_2 \tag{7}$$

where : $n_2^{\ s}$ actual adsorption

            $n_2^{\ \sigma\ (n)}$ the excess quantity, as number of moles, of component *2*

            n^s surface phase adsorption capacity

            x_2 mol fraction of component 2

As we can not directly measure the actual adsorption, one can not directly measure the volume of the surface phase. The most important question is how to determine the volume of the surfaces phase or their adsorption capacity expressed as number of mmol adsorbate. When calculating n^s, two most commonly classical methods are used, taking into account the material balance of ingredients in the surface and volume phase.

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 $n_2^{\ \sigma(n)}$ can be a linear function of molar fraction of component 2:

$$n_2^{\ \sigma(n)} = a\text{-}bx_2 \tag{8}$$

The surface excess $n_2^{\ \sigma(n}$ can be expressed as follows:

$$n_2^{\ \sigma(n)} = n_2^{\ s} - (n_1^{\ s} + n_2^{\ s})x_2 = n_2^{\ s} - n^s x_2 \tag{9}$$

or

$$n_2^{\ \sigma(n)} = n_2^{\ s} - (n_1^{\ s} + n_2^{\ s})x_2 = n_2^{\ s}(1\text{-} x_2) - n_1^{\ s} x_2 \tag{10}$$

By comparing equations (6) and (7) we get:

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

Assumption of Schay and Nagy is valid only for physical adsorption, when the dimensions of the molecules, components of the solution, are similar. The constants *a* and *b* in equation (8) represent the minimum amounts of components in the adsorption layer if we assume that the composition of that layer is constant within the linear part of the adsorption isotherm (when it is linear within 0.3 mole fraction units) despite the changes of composition of the bulk phase. The method of Schay and Nagy gives good results, especially for types II and IV excess adsorption isotherm, despite the some limitations.

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.
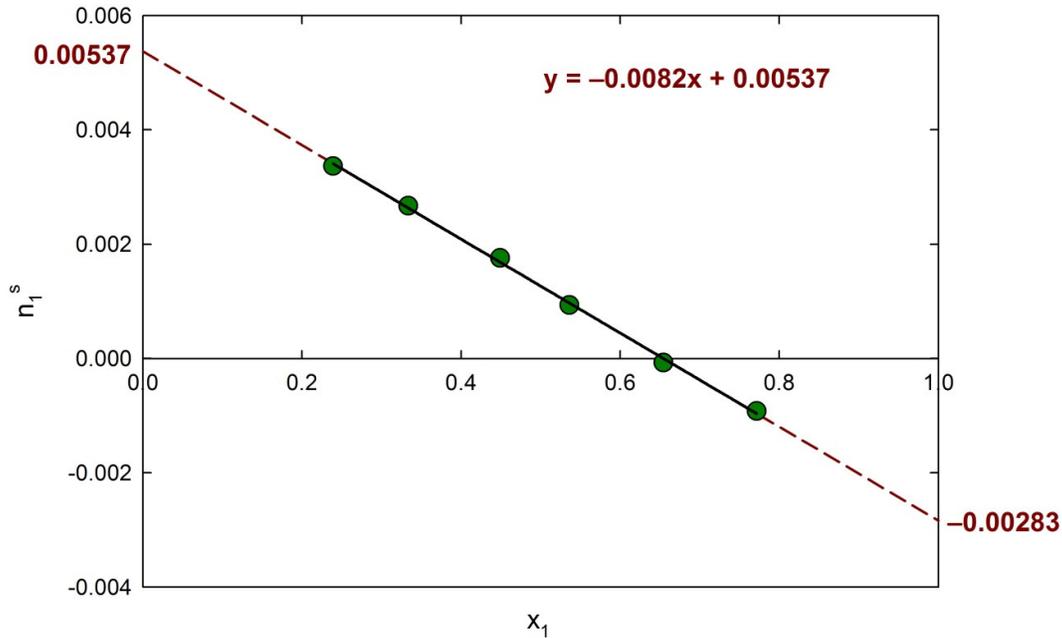

Fig. 4 Determination of adsorption capacity of surface layer by Schay and Nagy method.

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 relates mainly to excess adsorption isotherms of types I and II. Using the general equation of excess adsorption in form

$$\frac{x_1 x_2}{n_2^{\sigma(n)}} = \frac{1}{n^s}\left(\frac{1}{\alpha-1} + x_2\right) \tag{11}$$

where: $\qquad \alpha = \dfrac{x_1^s x_2^l}{x_1^l x_2^s} \qquad\qquad$ equilibrium constant of adsorption process

and drawing a linear inverse of the surface layer capacity for adsorption of component 2, as a function of its molar fraction, it is possible to calculate surface phase adsorption capacity (n^s).

In a case of ideal adsorption $\alpha = \text{const} = K$ and left-hand side equation is a linear function of x_2 (Fig. 5). Directional factor of this linear relationship is the inverse of the surface layer capacity n^s, although some researchers have suggested a doubling of this value.
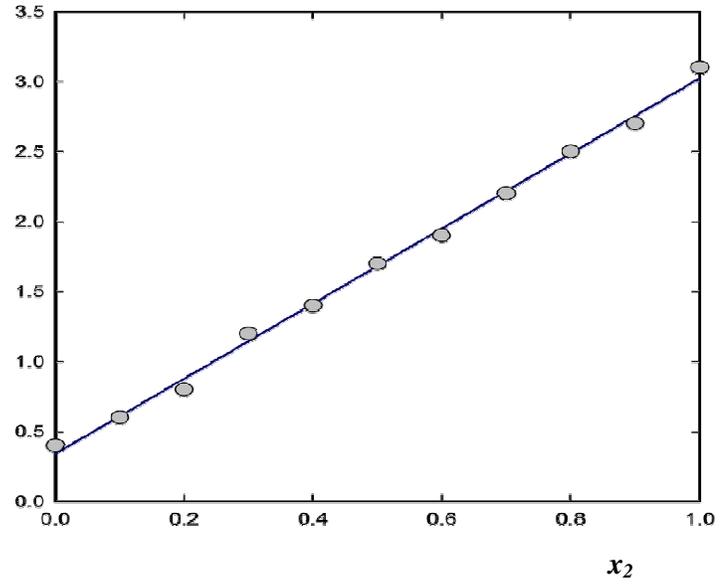
$$\frac{x_1^l \; x_2^l}{n_1^{\sigma(n)}}$$

Fig. 5 Determination of the adsorption capacity of the surface layer by Everett method.

The actual adsorption isotherms of components 1 and 2, corresponding to different excess adsorption isotherms shown in Fig. 3, are presented in Fig. 6.
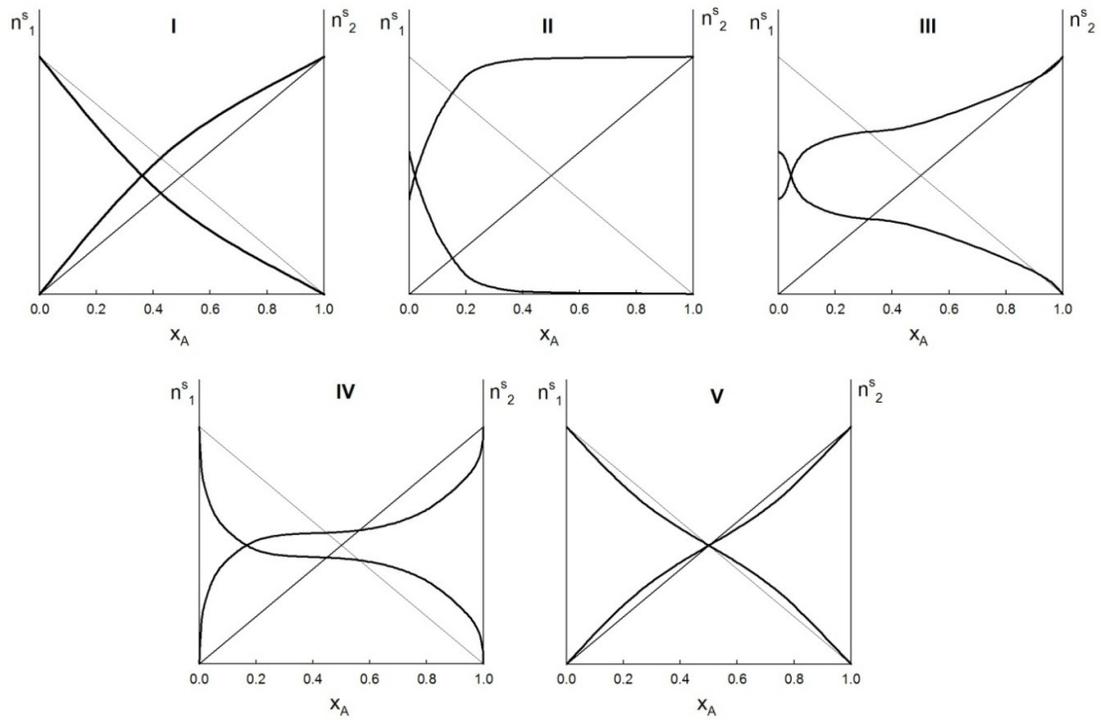

Fig. 6 Actual adsorption isotherms of components 1 and 2 corresponding to appropriate excess adsorption isotherm

The calculation of the thickness of the surface layer.

The surface excess [eqn. (1)] may be written in terms of the adsorbed phase mole fractions of component 2:

$$n_2^{\sigma(n)} = n_2^{\sigma} / m_A = n^0 * (x_2^0 - x_2^l) / m_A \qquad (3)$$

Assuming the restrictive model of the monolayer for the adsorbed phase of a binary solution, we have:

$$1/n^s = x_1^s/m_1 + x_2^s/m_2 \qquad (12)$$

where :
- n^s — the number of molecules in the surface phase
- x_1^s, x_2^s — molar fraction of component 1 and 2 in surface layer
- m_1, m_2 — capacity of monomolecular layer for component 1 and 2

Considering, that the surface phase consists of τ layers of adsorbed molecules, the mole fraction of component 1 in surface phase can be expressed:

$$x_1^s = a_1^0/\tau + x_2^s * a_2^0 / \tau = a_s / n^s \qquad (13)$$

where :
- a_i^0 — the molar cross-sectional area of the adsorbed molecule
- a_s — specific surface area of the solid

Combination of eqn. 3 and 13 yields:

$$x_2^s = \left(\tau * x_2^l + a_1^0 (n_2^{\sigma(n)}) / ma_s \right) / \tau - (a_2^0 - a_2^0)(n_2^{\sigma(n)}) / ma_s) \qquad (14)$$

Since x_2^s must not be exceed one, and more restrictively, dx_2^s/dx_2^l must always be positive for the stability of the adsorption system, one can check the thermodynamic consistency of a model in which τ layers are assumed and physically realistic values of a_1^0, a_2^0 and a_s are chosen. In this way a minimum thickness, τ_{min} , of the adsorbed layer can be found, below which unacceptable values of x_2^s are obtained.

However, it is always possible to achieve the thermodynamic consistency, for $\tau = 1$, 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. 7 illustrates the correlation of x_2^s depending on x_2^l for different values of τ in the system n-dodecane – n-butanol – activated carbon. The present results show that, in this system, the minimum thickness of the surface phase (τ_{min}) is 3.
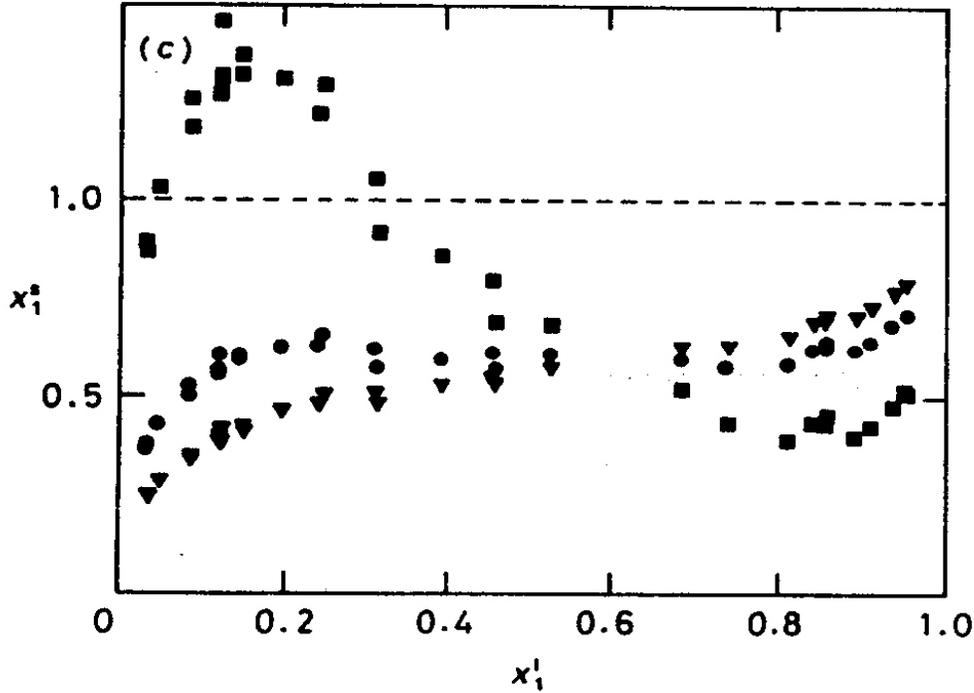
Fig. 7 Calculation of the thickness of the surface layer corresponding to appropriate excess adsorption isotherm as a surface mole fraction for different τ. $\tau=1$ (■), $\tau=2$ (•), $\tau=3$ (▼)

The estimation of non-ideality in the surface phase.

Another important aspect of the thermodynamic compatibility of experimental data is the determination of activity coefficient in the bulk (γ^l) and surface (γ^s) phase. In an ideal system, activity coefficient of components should be constant throughout the range of concentrations.

By measuring the surface tension of the appropriate solution and the value of the activity coefficient of both components of this solution in the bulk phase, we can determine the value of the activity coefficient in the surface phase according to following equation:

$$\ln\gamma_i^s = \ln\Box\frac{x_i^l\gamma_i^l}{x_i^s} - \left.\frac{\left(\sigma-\sigma_i^0\right)a_s}{RT}\right. \tag{15}$$

where:
	γ_i^s	activity coefficient of component i in the surface phase
	γ_i^l	activity coefficient of component i in the bulk phase
	x_i^s	mole fraction of component i in the surface phase
	x_i^l	mole fraction of component i in the bulk phase
	σ	surface tension of appropriate solution
	σ_i^0	surface tension of pure component i
	a_s	specific surface area of the solid
	R	molar gas constant
	T	temperature of measurements

The examples of changes in activity coefficients for components of the volume (γ_1^l, γ_3^l) and surface phase (γ_1^s, γ_3^s) as a function of mole fraction (x_1), calculated according to eqn. 15 for the system: n-dodecane (1) and n-butanol(3) on activated carbon, are shown in Fig. 8.
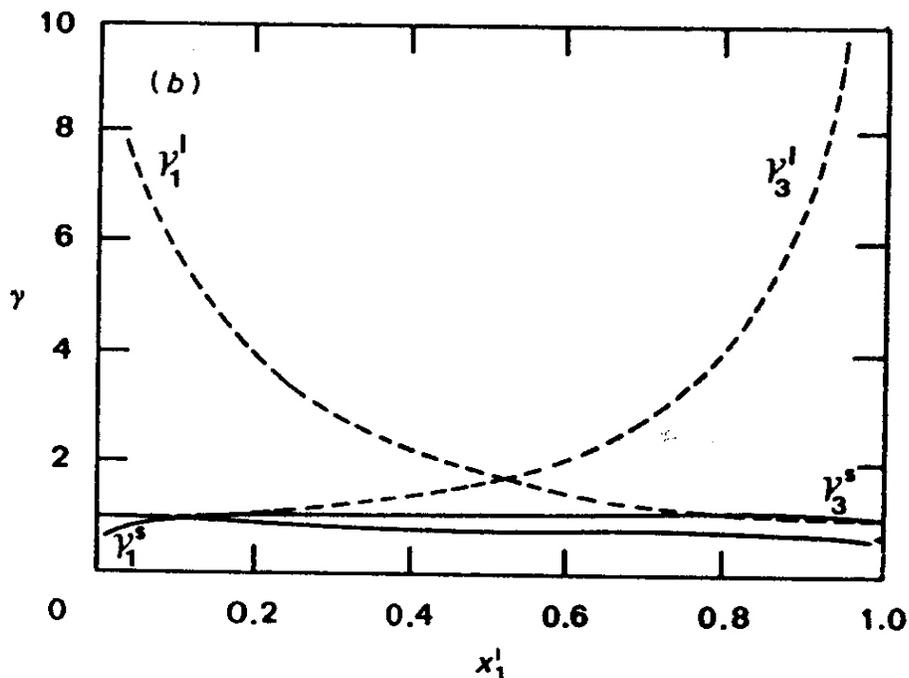

Fig. 8 Dependence of the activity coefficient in bulk and surface phase on molar fraction

As it can be seen from this graph, the stability of the activity coefficient of both components in the surface phase shows an increase of ideality of the surface phase compared to the bulk phase.

Experimental

A.   Equipment and reagents

1. Instrumentation:
· Gas-chromatograph HP-5890 Series II equipped with micro-TCD.
· Column 1m*2mm packed with Hayesep Q 80/100 mesh.
· Integrator 3394A
· Micro-syringe 5 µl.

2. Equipment:
· Glass vessels (2 mL) 5 pcs.
· Calibrated glass vessels (25mL) 5pcs.

3. Reagents:
· n-butanol p.a.
· n-heptane p.a.
· MCM-41 home-made adsorbent.

Fig. 8 Gas-chromatograph HP-5890 Series II.

B.   The execution of exercise

Prepare five standard solutions of n-butanol in n-heptane with different specific molar fraction.

Prepare five ampoules with a specific portion of the adsorbent (~ 100 mg).

To a specific portion of the adsorbent in an ampoule, add a certain amount of standard solution (~ 1 ml).

Hold ampoules in thermostat at constant temperature ~ 25°C, to achieve adsorption equilibrium (~ 1 hour).

Determine the concentration of components of standard solution, before and after adsorption, by gas chromatography. Perform measurements at 170°C. Inject of 0,8 μl of appropriate solution in "empty needle" mode. For each concentration, measurements should be repeated three times.

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.

Calculate the surface excess for each standard solution and next draw a graph of the surface excess (mmol/1g of adsorbent) on molar fraction (x_1^0) of n-butanol.

Calculate the capacity of the surface layer of investigated adsorbent according to Everett and Schay-Nagy method.

Finally, draw the actual adsorption isotherm of n-butanol on MCM-41 solid.