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## Review

# Effect of surface heterogeneity on adsorption on solid surfaces Application of inverse gas chromatography in the studies of energetic heterogeneity of adsorbents

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### Abstract

The paper presents a literature review of the chromatographic methods used for investigations of the heterogeneity of solid surfaces. Special attention is paid to inverse gas chromatography (IGC). Quantitative characteristics of heterogeneity of real solid surfaces including extreme models on adsorption centre topography of the “patch-wise” and “random” types are described. Analytical and numerical methods used for calculating the adsorption energy distribution function as a quantitative measure of surface heterogeneity are presented. Special attention is paid to the condensation approximation as well as to other approximations based on this assumption. IGC is presented as a quick, precise and effective method to characterise physicochemical properties of different kinds of adsorbents. Advantages of IGC over traditional methods of gas and vapour adsorption are shown. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Reviews; Inverse gas chromatography; Adsorbents; Surface heterogeneity; Adsorption isotherms

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## 1. Real solid surface

Real solid surfaces are characterised by different arrangement of atoms (molecules) on the surface and different chemical composition from the inside of the solid as well as by disappearance of crystallographic order. Only in some cases arrangement of the surface atoms is such as would result from extrapolation of the bulk phase crystallographic structure. These are surfaces of metals, some ionic crystals or graphite. Even here many defects of the surface structure are observed and the number of papers on the kind and way of formation of these defects is very large. Such a great interest is caused by the fact that the surface structure disorders play a significant role in catalytic processes.

Most actually existing surfaces are characterised by an average or a small degree of surface atom arrangement even if the interior of the solid phase is characterised by great arrangement of the crystallographic structure. An example is the powder formed during diamond grinding which gives the picture of the diamond structure in X-ray radiographic examination. However, in adsorption studies where the properties of its surface are essential it behaves like an amorphous active carbon [1]. The evidence for surface defects existence was obtained using many experimental techniques but the turning point was the pictures of the surface provided by means of microscopic methods using the tunnel effect [2].

This geometrical disorder and the chemically heterogeneous structure of real solid surfaces have a great effect on the adsorption processes occurring on it. With the progressing disappearance of the solid surface structure arrangement, the interaction between gases or solids adsorbing on the surface and the surface becomes more differentiated in various sites.

As well for high temperatures, the adsorbing molecules spend most time in the surrounds of the molecule–surface interactions potential local minima called adsorption centres. The smaller the extent of the solid surface atom arrangement is, the greater dispersion of the adsorption energy  $\epsilon$  on various adsorption centres, that is the values of adsorption potential in the local potential minima. This dispersion of adsorption energy is commonly called the surface heterogeneity. Its accepted measure is the

so-called distribution of adsorption energy  $\chi(\epsilon)$ , the probability density function for the adsorption energies  $\epsilon$ .

Heterogeneity of real surfaces is not a result of “careless preparation procedure” but one of the most fundamental properties of the surface. The evidence for it are computer simulations of solid surface formation carried out by Bakaev and other researchers as what was emphasized in the monograph by Rudziński and Everett [1]. The studies of the effect of adsorption energy dispersion on the behaviour of adsorption system have constituted one of the most dynamic world trends in the research on adsorption for the last few decades. Their results have been published in several hundred papers, several review articles and two comprehensive monographs [1,3].

The heterogeneous nature of solid surfaces is a result of both their way of formation and their past. Several basic mechanisms leading to such heterogeneity can be distinguished [4].

The initial smooth solid surface becomes rough after heating above certain temperatures due to shift of atoms or molecules from their equilibrium position in the solid system and their migration towards the sites of higher energy on the solid surface [1]. If after reaching equilibrium the solid is rapidly cooled, the structure is “frozen” in the metastable state characteristic of the temperature at which the surface has been formed. The surfaces obtained in this way maintain their structure in the presence of molecules adsorbed in the physical way but they can be modified through chemisorption. If the solid is formed by powder sintering, its structure is determined by the thermal treatment temperature [5,6]. Thermal treatment can lead to partial or total recrystallisation of the solid as in the case of graphitised carbons – carbon black [7,8]. Thin surface films are often spread by sputtering or condensation from the gaseous phase: the structures formed in this way are usually metastable and heterogeneous but with the temperature increase they can anneal to the state closer to equilibrium [9]. Heterogeneous surfaces can be formed through surface chemical reactions (e.g., through “etching”) or through the reactions with the component from the gaseous phase (e.g., through oxidation). Another important group of solids is formed by precipitation from the liquid phase or flocculation of the colloidal suspension [10–12].

Surface structures formed by various mechanisms have a fractal character determined by the preparation conditions [13]. Dependence between the fractal and heterogeneous nature has been a subject of study [13].

Despite the complexity and variety of heterogeneous surface formation models, such surfaces possess similar adsorption properties. It means that the experimental adsorption isotherms obtained in different pressure ranges can be described by means of a small number of known empirical adsorption isotherms. It suggests that different mechanisms of surface formation constitute a statistical pattern, which is reflected in their adsorption properties. Some attempts are made to understand these mechanisms and associate them with the adsorption properties of the formed solid.

The computer studies of Bakaev and co-workers [14–17] confirm random topography on the oxide surface. Of course, there exists an extent of arrangement, which increases with farther penetration into the solid bulk phase. The most exterior layers of surface atoms (ions) can be amorphous while the interior ones can have an arranged structure.

Geometrical deformations of metal oxide surface and its energetic heterogeneity are very important in the catalytic reactions on the oxide surfaces. This phenomenon was investigated using various tech-

niques and the results are presented in the monograph by Somoryai [18] as well as in the paper by Hirschwald [19]. The latter is a review paper presenting the pictures of real oxide surfaces obtained by means of STM (scanning tunnelling microscopy) [20,21]. Fig. 1 presents, as an example, the picture of the surface obtained using this method. Darker and brighter fragments of the surface differ in height from one another.

## 2. Quantitative measure of heterogeneity

The commonly accepted quantitative measure of surface heterogeneity in the model of one-centre localised adsorption is the differential distribution of a number of adsorption sites among the corresponding values of adsorption energy, normalised to unity:

$$\int_{\Omega} \chi(\epsilon) d\epsilon = 1 \quad (1)$$

where  $\Omega$  is the physical domain of  $\epsilon$ .

For purely mathematical reasons,  $\chi(\epsilon)$  is often approximated by using the simple analytical function and it is assumed that  $\Omega$  accepts the values from the range of either  $(0; +\infty)$  or  $(-\infty; +\infty)$ . Such simplification does not provide significant errors in further theoretical calculations except some extreme physical areas [1].

For the real physical systems, the function  $\chi(\epsilon)$  has a rather complicated shape but in the first approximation it can be approximated by means of the simple quasi-Gaussian function [1]:

$$\chi(\epsilon) = \frac{1}{c} \cdot \frac{\exp\left(\frac{\epsilon - \epsilon^0}{c}\right)}{\left[1 + \exp\left(\frac{\epsilon - \epsilon^0}{c}\right)\right]^2} \quad (2)$$

This function assumes the maximum for  $\epsilon = \epsilon^0$ , but the width (variance) of the peak is described by the heterogeneity parameter  $c$  (variance  $\sigma$  is equal to  $\pi c / \sqrt{3}$ ).

The continuous line in Fig. 2 is the function  $\chi(\epsilon)$  for the argon adsorbed on rutile, obtained by averaging  $\chi(\epsilon)$  calculated using two different methods. It follows from the figure that  $\chi(\epsilon)$  is a smooth

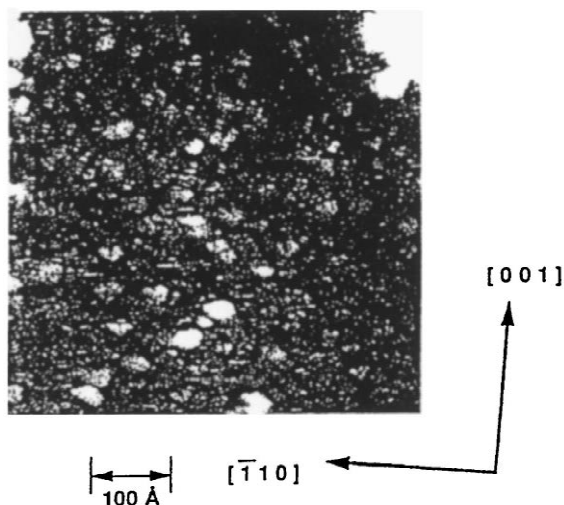


Fig. 1. Picture obtained by means of scanning tunneling microscopy [21] of the surface of titanium dioxide {100}.

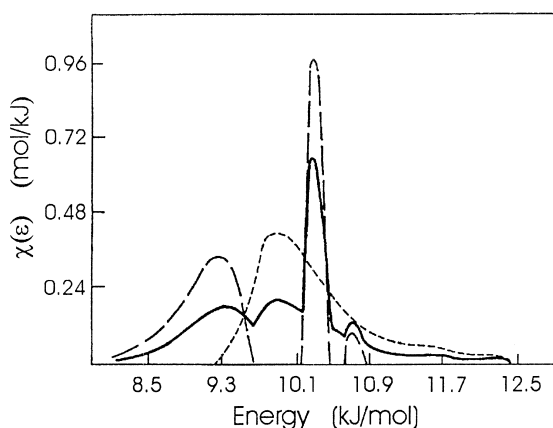


Fig. 2. Function of energy distribution  $\chi(\epsilon)$  for the Ar rutile system at 85 K studied by Drain and Morrison [96]. The broken line presents the function calculated by Rudziński and Jaroniec [73] and the strongly broken line presents the function calculated by Dormand and Adamson [70]. The continuous line presents the mean value of these two functions.

function similar to the Gaussian function. Such a function is real for adsorption of both argon and water because the interactions with oxygen on the surface take place in both cases. In the case of monolayer adsorption using such a function leads to the Langmuir–Freundlich isotherm (an empirical equation of this kind was first taken into account by Bradley [22] and Sips [23,24] and it is often called the Bradley–Sips equation) which is probably the most common isotherm used for description of the experimental data at rather low surface coverage when the effect of multilayer adsorption can be still neglected. Using the simple function  $\chi(\epsilon)$  is generally necessary to avoid a large number of unknown parameters. This procedure is characteristic of most theoretical papers on adsorption on solid heterogeneous surfaces.

This energetic heterogeneity of the surface that is change of the depth of the local potential minima while passing from one to adsorption site to another results from the structural surface heterogeneity. The local minima of adsorption energy depend on the configuration of solid atoms (ions) in their vicinity. This particular configuration affects also the adsorption potential minima of the closest surrounding of adsorption sites. The correlation degree between the adsorption energies of the closest neighbours

depends on the kind of the solid under consideration (i.e., on the arrangement extent) as well as on the conditions under which the solid was formed.

### 3. Assumed topographies of the adsorbent surfaces

When the interactions between the adsorbing molecules cannot be neglected, besides the adsorption energy distribution  $\chi(\epsilon)$ , the way in which the adsorption centres of various energies are distributed on the solid surface should be taken into account. In the hitherto studies of adsorption on the heterogeneous surfaces two models of surface topography were considered.

The first one is of the “patch-wise” type where the adsorption centres of the same properties are grouped in large patches on the surface. It is generally assumed that these patches are so large that they constitute independent thermodynamic adsorption subsystems being in the thermal and material contacts (the exchange of adsorbate molecules between these subsystems is possible). In further studies it is assumed that the conditions of the system in which two interacting molecules are adsorbed on two different patches make the negligible contribution to the thermodynamic properties. Fig. 3A presents a diagram of the patch-wise type surface. This model was for the first time used by Ross and Olivier [25].

The other model of surface topography assumes that the adsorption sites of various adsorption energy are distributed on the surface in a “random” way. This type of surface topography is shown in Fig. 3B. This completely random distribution of centres causes that in the surrounding of any adsorption centre probability of finding any other centre is the same. As a result, the microscopic composition of the adsorbed phase in the surrounding of any centre is the same and identical to the average composition of the phase on the whole solid surface. The model was worked out by Hill [26].

The “patch-wise” and “random” surface topography represent two boundary cases. It seems that the surface should be characterised by so called “intermediate” surface topography (intermediate properties between the extreme physical situations) where

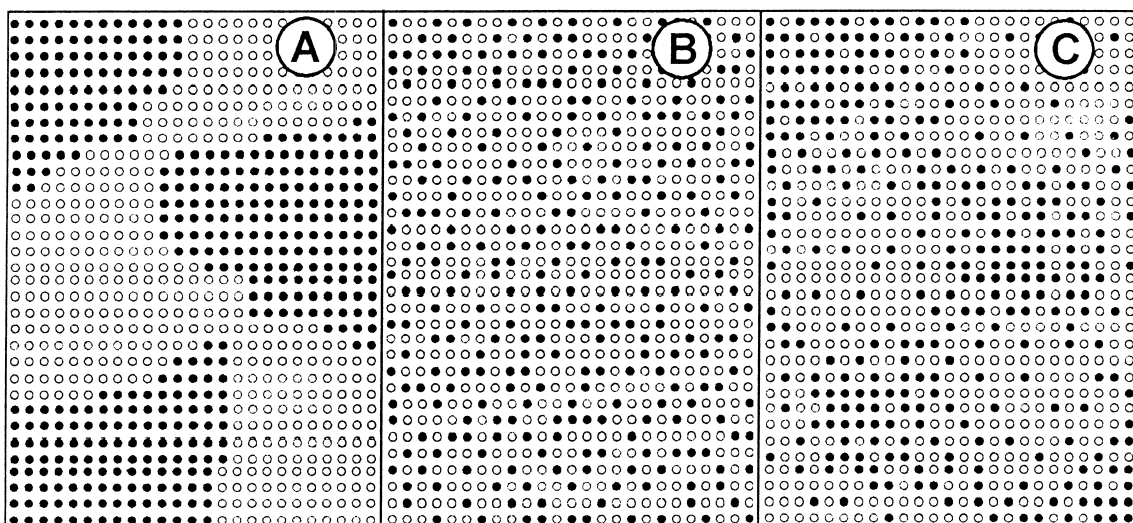


Fig. 3. (A) Diagram of the “patch-wise” type surface. (B) Diagram of the “random” type surface. (C) Diagram of the “intermediate” type surface. Two types of adsorption centres are marked with filled and blank circles.

there exists the correlation between the energies of the adsorption of the closed neighbours or even the neighbours of the closed adsorption sites. The diagram of such a topography is presented in Fig. 3C. When the correlation radius tends to infinity, the patch-wise topography is obtained [1]. If this correlation length falls to zero, then the system is characterised by the “random” topography. It can be assumed that in the case of well formed crystals with a few crystallographic planes, using the “patch-wise” model is more justified. Amorphous samples correspond better to the “random” model. But the problem is not quite explicit. Even in the case of well formed crystals that is the samples of the high extent of “bulk” arrangement, the surface can have poor arrangement of surface atoms. The problem of adsorption modelling on the surfaces characterised by the intermediate topography is very complicated. Some attempts of theoretical description are presented in Ref. [1].

#### 4. Adsorption integral isotherm

The experimental adsorption isotherm (the global one)  $\vartheta(T,p)$  (in the units of relative coverage) represents the average over all values of the adsorption energies  $\epsilon$ :

$$\vartheta(T,p) = \int_{\Omega} \theta(\epsilon,T,p) \chi(\epsilon) d\epsilon \quad (3)$$

where  $\theta(\epsilon,T,p)$  is a relative coating of adsorption centres of the adsorption energy  $\epsilon$  for a given temperature and pressure and  $\Omega$  is the physical domain of the adsorption energy. Eq. (3) is known in the literature as the integral form of the adsorption isotherm [25].

From a purely physical point of view, the distribution of adsorption energy  $\chi(\epsilon)$  could be expressed through the discrete distribution of the adsorption energy, however, the adsorption spectrum is so dense that  $\chi(\epsilon)$  can be approximated by the continuous function.

The result of Eq. (3) integration depends on the surface topography (that is on the distribution of adsorption sites having various values on the solid surface) only when interactions between adsorbed molecules take place. In the case of the adsorbed ideal phase (e.g., Langmuir model) the kind of topography does not affect thermodynamic properties of the system.

Taking into account the lateral interactions between adsorbing molecules and two boundary topographies of the surface, for the “patch-wise” type surface, the function  $\theta(\epsilon,T,p)$  in Eq. (3) has an analytical form, the same as for the homogeneous

surface but various patches have different adsorption energy. The assumption of such surface topography was the first one and therefore the function  $\theta(\epsilon, T, p)$  is traditionally called the local adsorption isotherm – the adsorption isotherm on the homogeneous patch of the surface.

In the case of the “random” type, the microscopic composition of the adsorbed phase in the surrounding of any centre is the same and identical to the average composition of the phase on the whole solid surface  $\vartheta(T, p)$ . It means that all potentials of interactions are the function of the averaged adsorption  $\vartheta(T, p)$ . So, in Eq. (3) the subintegral function  $\theta(\epsilon, T, p)$  will have the same form as for the homogeneous surface model, except for  $\theta(\epsilon, T, p)$  occurring in the terms of interactions. There,  $\theta(\epsilon, T, p)$  should be replaced by  $\vartheta(T, p)$ .

Many analytical expressions determining the adsorption energy distribution approximately were suggested for description of the gas–solid heterogeneous surface adsorption systems [1]. Besides the above mentioned quasi-Gaussian distribution (Eq. (2)) the exponential and Gaussian distributions were also used [1].

## 5. Methods to determine the shape of adsorption energy distribution function

So far the dependence of adsorption isotherm on the assigned form of adsorption energy distribution has been presented using integral Eq. (3). Here the reverse process that is determination of the distribution function shape from the experimentally obtained adsorption isotherms is discussed.

To obtain the functions of adsorption energy distribution, integral Eq. (3) can be solved by means of analytical or numerical methods, using certain assumptions, rather drastic in most cases.

### 5.1. Analytical methods

Two main methods can be distinguished among the analytical ones. The first one was proposed by Sips [23,24] as well as by Todes and Bondareva [27] at the same time. It consists in using the Stieltjes transform. However, this method has very serious limitations. It can be applied only in the case of local

isotherm representation through the Langmuir equation. Using this method, it is possible to determine the analytical functions of adsorption energy distribution corresponding to the assigned global adsorption isotherms and described by the Freundlich [23,24,28,29] and Dubinin–Radushkevich [28] equations.

The other analytical method of Eq. (3) solution, called the condensation approximation (CA) method [1] is very simple and gives good results. In this case, the adsorption local isotherm is approximated by so called the condensation isotherm:

$$\theta_c(p, \epsilon) = \begin{cases} 0, & p < p_c(T, \epsilon) \\ 1, & p > p_c(T, \epsilon) \end{cases} \quad (4)$$

where  $p_c(\epsilon)$  is the so-called condensation pressure, assuming that the coverage of the surface on the patch possessing the adsorption energy  $\epsilon$  changes rapidly from zero to unity. As the values of the condensation pressure  $p_c(\epsilon)$  decrease monotonically with the increasing values  $\epsilon$ , Eq. (4) can be written in the following form:

$$\theta_c(p, \epsilon) = \begin{cases} 0, & \epsilon < \epsilon_c(T, p) \\ 1, & \epsilon > \epsilon_c(T, p) \end{cases} \quad (5)$$

When  $\theta(p, \epsilon)$  is replaced by  $\theta_c(p, \epsilon)$ , integral Eq. (3) assumes the following form:

$$\vartheta(p) = \int_0^{\infty} (\epsilon, p) \chi(\epsilon) d\epsilon \quad (6)$$

or using Eq. (5) it can be presented as follows:

$$\vartheta(p) = \int_{\epsilon_c(T, p)}^{\infty} \chi(\epsilon) d\epsilon \quad (7)$$

It is assumed for the mathematical convenience that the adsorption energy  $\epsilon$  in Eqs. (6) and (7) changes forms zero into infinity.

Differentiating Eq. (7) with respect to  $p$ , we obtain:

$$\left( \frac{\partial \vartheta}{\partial p} \right)_T = -\chi(\epsilon_c) \cdot \left( \frac{\partial \epsilon_c}{\partial p} \right)_T \quad (8)$$

Using the inverse dependence  $p_c(T, \epsilon)$  we obtain:

$$\chi(\epsilon) = - \left( \frac{\partial \vartheta}{\partial p} \right)_{p=p_c} \cdot \left( \frac{\partial p}{\partial \epsilon} \right)_{p=p_c} \quad (9)$$

The derivative  $(\partial \vartheta / \partial p)$  is known because  $\vartheta(p)$  is known in the form of the assigned analytical approximation (such as e.g., the Freundlich, Dubinin–Radushkevich, Toth isotherms or others) or the experimental set of the pairs of value  $(\vartheta, p)$ . The only difference results from the fact that differentiation in the last case must be carried out graphically or numerically.

Calculation of the second of the derivatives  $(\partial p / \partial \epsilon)$  requires knowledge of the function  $p = p_c(\epsilon)$ . In the literature there are two methods used to determine the condensation pressure  $p_c$  at which the surface patch possessing the adsorption energy is filled: the methods of Harris [30,31] and Cerofolini [32]. For example for the Langmuir local isotherm both of them give identical results:

$$\theta_c(p_c, \epsilon, T) = \frac{1}{2} \quad (10)$$

as a result the following form of the function  $p_c(\epsilon)$  is obtained:

$$p_c(\epsilon) = K^L \exp \left( - \frac{\epsilon}{kT} \right) \quad (11)$$

where  $K^L$  is the Langmuir constant.

The range of CA method applicability should also be discussed. The approximation is better when the adsorption temperature is lower and it becomes an accurate method when  $T \rightarrow 0$ . A minor error occurs when as a result of calculations, vast distributions of adsorption energy corresponding to high surface heterogeneity are obtained. The evaluation of the method error is presented in the papers by Harris [30,31] and discussed in Ref. [1].

Other methods of Eq. (3) solution are based on development of subintegral functions into series with respect to orthonormal functions or assuming the exponential polynomial for the function  $\chi(\epsilon)$  [1].

### 5.2. Numerical methods

Stable and reliable solution of Eq. (3) can be obtained only when we have an accurate experimental adsorption isotherm covering a large range of pressures – four- or five-orders of magnitude. As all

experimental points are exposed to some error, the experimental data must be smoothed out before they are subjected to the numerical analysis. Neglecting it can result in formation of unreal peaks on the function of adsorption energy distribution. Smoothing out of the experimental data can be made through  $n$ -point (odd  $n$ ) fitting by the least-squares quadratic fit or by the spline fitting technique [1].

However, smoothing out must be made carefully. The unsmoothed out data lead to unreal multiple peaks on the energy distribution but “oversmoothing” can lead to the loss of important information. Some smoothing out methods like “spline fitting” can introduce non-existing detailed structures into the energy distribution curve [33]. There is a need to determine a reliable condition to obtain the optimum of smoothing out but so far has been common for the authors to use subjective criteria whether to continue further smoothing out [1].

The methods of calculating the energy distribution function can be divided into two groups: those in which the general analytical form of distribution function is postulated and the parameters describing it are calculated from the experimental data and those in which the shape of this function is not assumed in advance [1]. A new alternative approach to the solution of the described problem is the direct use of the retention data to calculate the adsorption energy distribution [34].

## 6. Studies of solid surfaces by means of chromatographic methods

Though statistical measurements of adsorption are more precise, the dynamic ones by means of gas chromatography (GC) become more and more common and useful methods to study adsorption phenomena. These quick and simple measurements become more and more precise. Widely spread application of various kinds of GC to study adsorption phenomena, diffusion and reaction kinetics dates from the early 1970s. This type of physicochemical studies gave rise to a great variety of sensitive and innovatory experimental methods based on chromatography. Experimental and theoretical studies led to great development of knowledge about chromatographic processes.

The monograph by Conder and Young [35] includes a detailed discussion of these experiments together with their theoretical description being a standard reference for those interested in chromatographic physicochemical studies. Chromatographic physicochemical methods were widely used to determine various thermodynamic and kinetic properties of single and multicomponent adsorbate systems. Advantages of the above mentioned methods are a result of quick measurements and easy control of the temperature.

Despite these obvious advantages, the chromatographic methods used for physicochemical measurements have not been common until recently. The situation changed when the researchers of various materials and their surface properties came to the conclusion that various techniques of gas chromatography are advantageous for determination of chemical character of organic and inorganic material surfaces. In many new materials a kind of interface bond formed between the continuous phase and the environment surrounding it is of significant importance.

Application and improvement of new materials caused a rapid development of both theoretical and experimental studies concerning the material surfaces and various interfaces. This increase in the research intensity was simultaneous with application of new types of surface spectroscopy, particularly X-ray photoemission spectroscopy as well as secondary ion mass spectroscopy (SIMS), as follows from review papers [36,37] proved to be very useful to study polymer surface chemistry. However, these techniques do not provide thermodynamic information about the material surface. The data of this type are usually obtained by means of calorimetric methods or those based on determination of adsorption isotherms but their application can cause some difficulties and is time consuming.

Using chromatographic methods, it is possible to determine the functions of adsorption energy distribution. There can be distinguished two ways to determine them: by the studies of temperature and pressure dependencies of the retention data.

At first the physicochemical studies of adsorption by means of GC referred only to the low-pressure area (Henry's area) at which adsorption occurred. The description by means of virial formalism could

be applied in this area [38]. Therefore most measurements aimed at determination of the second and third virial gas–solid coefficients. Moreover, most experiments were carried out on the adsorbents with homogeneous surfaces, e.g., graphitised carbon black. The Henry's area for such systems allowed to obtain real values of virial coefficients. Their temperature dependencies can be used as the information about heterogeneity of such surfaces.

In the case of strongly heterogeneous surfaces only apparent values of virial coefficients can be obtained because the Henry's area occurs only at very low pressures, below accessibility of gas chromatography for adsorption measurements. In such cases the virial description becomes useless. Then pressure dependencies of the retention data must be analysed [1].

Characteristics of solid surfaces is generally determined by adsorption of gases and vapours in a wide range of pressures (from low to high relative pressures, in many cases to  $p/p_0=1$ ). Mean values of pore radii and surface energies can be obtained from such measurements. In many cases it is very useful. However, researchers are often made to study the characteristics of adsorbent surfaces from the data obtained at very low pressures of adsorbates at so called the zero coverage of the surface. Then the adsorbed amount depends on the vapour pressure linearly (Henry's law area).

Application of the GC methods to study physicochemical processes requires fundamental knowledge of chromatographic processes. In analytical chromatography identification and quantitative determination of an unknown substance is made by comparison of retention properties of an unknown adsorbate introduced into the mobile phase with the properties of a known adsorbate for the standard stationary phase (reference phase). However, the physicochemical GC studies allow one to make accurate and absolute measurements of adsorbate retention properties for any stationary phase. The net retention volume  $V_N$  associated directly with the partition of the adsorbate between the mobile phase and the stationary phase is a basic measured quantity. The retention volume is a basic physicochemical parameter determining chromatographic properties of vapours (solute) on a given stationary phase and is a function of adsorbate temperature, pressure and



concentration. Character of the retention data obtained by the GC method allows one to directly study the stationary solid phases. Relatively great simplicity of packing solid phases into columns used in gas chromatography aroused a great interest in the application of physicochemical GC methods for determining specific properties of solid surfaces.

A comprehensive description using the gas/solid adsorption chromatography was presented by Jaroniec and co-workers [34,39–41]. A special emphasis was placed on the use of retention data to characterise surface properties of porous solids, as well as to calculate adsorption isotherms and heats of adsorption from the temperature and pressure retention dependencies.

With the evolution of chromatographic techniques, inverse gas chromatography (IGC) has become quite common. It is an accurate, reliable and quick method used for determination of physicochemical properties of various kinds of adsorbents: polymers, fibres, modified silica, surfactants, etc. [42]. The word “inverse” indicates that the adsorbent placed in the chromatographic column is studied using the test adsorbates. It means that, contrary to the traditional analytical gas chromatography, known vapours or liquids are washed out from the stationary phase which allows to acquire elementary knowledge about chemical character of the surface of the solid placed in the chromatographic column. Specially selected test adsorbates are batched into the carrier gas stream and transported over the surface of the material in the column. Retention times and shapes of elution profiles of the standard adsorbate peaks (affected by the interactions between the adsorbate and the stationary phase) are used to determine these interactions.

The increase of interest in IGC application for determination of stationary phase surface properties resulted in many publications in this field. Papers [39,41] include an equation for the corrected specific retention volume of an infinitely dilute solute on an energetically heterogeneous surface, as well as a general integral equation to describe the distribution function of adsorption energy. According to Schreiber and Lloyd [43] a number of publications has increased significantly during the last 10 years. The evidence for which is the first IGC Symposium organised by the American Chemical Society in

1988. The increase of interest was partially caused by the demand for methods to study surface properties of packing fibrous materials, particularly those highly processed. Studies of fibres and packings by the IGC method are presented in the monograph by Williams [44].

A new IGC methodology (based on the reversed-flow gas chromatography technique) [45–47] has been introduced to measure local adsorption energies, local monolayer capacities and adsorption isotherms for probe gases on heterogeneous solid surfaces in the presence of nitrogen as the carrier gas. The method does not depend on analytical solutions of the classical integral equation comprising the adsorption energy distribution function as unknown, nor on numerical solutions and estimations from this equation, using powerful computers. It simply uses a time function on the chromatographic peaks obtained by short flow-reversals of the carrier gas, combined with the local isotherm model of Jovanovic. All three adsorption quantities and those mentioned above can be calculated as a function of the experimental time and refer to the instantaneous equilibrium of the probe gases with the heterogeneous surface, with different kinds of active sites being involved at different times [45–47].

## 7. Adsorption studies using inverse gas chromatography

So far surface properties of adsorbents have been studied using traditional methods of gas and vapour adsorption. These methods are still used including physical and chemical adsorption of vapours of organic substances or inert gases on the solid surface. The amount of the adsorbate on the adsorbent surface is determined by a graphical or volumetric method in the function of adsorbate concentration. The isotherms allow one to obtain information about substrate surface chemistry, adsorbent specific surface area, porosity as well as thermodynamics and kinetics of adsorption [48]. One of the main factors limiting application of these techniques is a long time needed to obtain a complete adsorption isotherm – for some materials the time is even a few days.

The IGC method allows one to study adsorption of

gases on solids in a wide range of temperatures, pressures and specific surface areas which refers to both physical and chemical adsorption. The pioneers in this field were Greene and Pust [49] who used this method to determine adsorption heats. Recently many papers have appeared in which the subject of IGC is widely discussed. Russian authors were the first to use this method to study inorganic powders. The results of their investigations of behaviour of the catalyst surface during chemisorption are presented in the monograph by Kiselev and Jashin [50]. The results of the studies on surface and volumetric characteristics of these materials carried out by means of the IGC method are presented in the paper by Schreiber and Lloyd [43]. Compared with the traditional adsorption techniques, the IGC method has many advantages of which the most important are [51]: (1) it is not necessary to pump out preliminarily the sample under vacuum, (2) it is easy to study temperature effects, (3) measurements are accurate at low surface concentrations, (4) both physical adsorption and chemisorption can be studied, (5) it is possible to make measurements using commercially available gas chromatographs.

In many cases commercial gas chromatographs can be modified to be applied for the IGC measurements. Such modifications are made to improve the monitoring of carrier gas flow-rate and its measurement, column temperature as well the effectiveness of measurements, pressure drop along the column [35,44].

Application of IGC for studying adsorption processes is based on the assumption that the solute equilibrium conditions are achieved between the mobile and stationary phases. Such a condition is satisfied at the zero coverage of the surface and precise elaboration of experimental conditions. Moreover, a chromatogram must be symmetric and the maximum of the chromatographic peak must be independent of the amount of the batched adsorbate. Moreover, the batched amount is very small, the concentration of the adsorbate in the gases phase is minimal so the adsorption process is conditioned by the real adsorbate–adsorbent interactions. Therefore under such conditions the adsorbate can be considered as ideal gas both in the gaseous phase and on the adsorbent surface. The retention time  $t_R$  of the adsorbates interacting with the surface makes it

possible to determine the net retention volume  $V_N$ . The quantity is obtained from the following equation [51]:

$$V_N = jF_c(t_R - t_M) \quad (12)$$

in which  $j$  is the compressibility correction factor:

$$j = \frac{3}{2} \cdot \frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1} \quad (13)$$

where  $p_i$  and  $p_o$  indicate the column inlet and outlet pressures, respectively,  $t_M$  is the dead time and  $F_c$  is the carrier gas flow-rate. The net retention volume  $V_N$  is the quantity from which all thermodynamical equilibrium quantities can be calculated.

The quantities  $V_N$  and the slope of adsorption isotherms are connected by Eq. (14) for which the solute concentration is sufficiently small for the isotherm to have a linear shape. Such a range of concentrations is called an area of “infinite dilution”:

$$V_N = K_s S = \frac{q}{c} \cdot S \quad (14)$$

where  $K_s$  means the inclination of the isotherm at infinitely great dilution and is equal to the coefficient of partition or distribution of the adsorbate between the mobile and the stationary phases. The quantity  $S$  is the specific surface area of the studied material,  $c$  is the concentration of the adsorbate in the gaseous phase and  $q$  is its concentration in the stationary phase. For higher concentrations of the solute, for which the isotherm is not linear, a more general equation is employed in which  $y_0$  denotes the molar fraction of the adsorbate in the gaseous phase [51]:

$$V_N = S(1 - jy_0) \cdot \frac{dq}{dc} \quad (15)$$

This area of higher concentrations is called the finite concentration area. From Eq. (15) it is possible to determine the relation between the chromatographic peak shape and the adsorption isotherm slope. Fig. 4 presents graphically a general relation between the chromatographic peak shape and the adsorption isotherm shape. At batching such amounts of the sample for which the isotherm shape is linear (Fig. 4A) Eq. (14) suggest that  $V_N$  should be independent of the batched sample amount. This

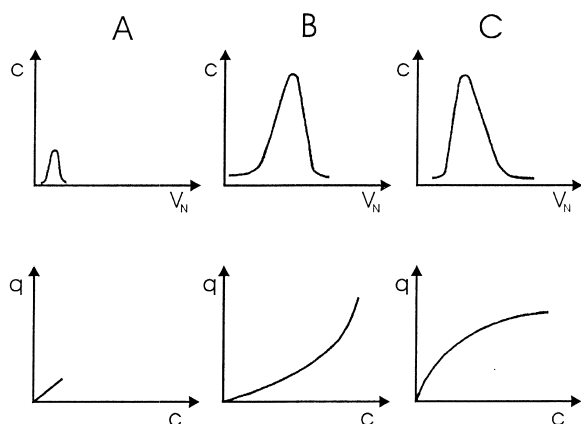


Fig. 4. Relation between the adsorption isotherm shape and the chromatographic peak shape. (A) refers to the linear isotherm which follows from the Gaussian shape of the peak. (B) and (C) refer to the non-linear adsorption isotherms resulting from the tailing chromatographic peaks.

suggestion was confirmed experimentally. With the increase of the batched sample amount, non-linearity of the isotherm causes asymmetry of the peaks on chromatograms (Fig. 4B and C) and slight dependence of  $V_N$  on the batched sample amount as follows from Eq. (15). A more complex shape of peaks is observed when adsorption is characterised by an occurrence of an inflexion point, though the curves of this type can be also analysed.

Dorris and Gray [52] proposed the IGC method as an alternative one to study surface properties of silica powders and cellulose fibres. Using the IGC method, it is possible to estimate in a quantitative way adsorption properties and thermodynamic quantities such as enthalpy, free energy as well as adsorption entropy at different temperatures and relative humidities which can be adjusted introducing different amounts of water into the carrier gas stream [53]. By means of the IGC method, it is possible to estimate the acidic–basic character of soil in a qualitative way [54]. In 1985 Munk and co-workers [55–57] began the studies on the effect of the batched sample amount, adsorbate diffusion in the mobile phase, changes of carrier gas flow-rate, kind of packing and temperature on the effectiveness of the IGC method. The parameters affect linearity and ideality of adsorption of the IGC columns. The effect of these parameters on the sorption processes during

chromatographic process was described by many authors [35,50,58–60]. The peak profiles possess various asymmetric and non-Gaussian shapes which indicate different reasons for disturbance of these peaks. However, the linear and ideal isothermal adsorption does not need to be characterised by the symmetric or Gaussian shape of the peak [35]. In the case of cellulose fibres [52,53] at a given temperature and at a constant rate of carrier gas flow a moderately asymmetric peaks can be obtained due to the increase of the batched sample amount. In the case when the peaks are very asymmetric and non-Gaussian it is difficult to estimate the retention time at infinitely great dilution of the mobile phase by the maximum peak method because then the peak is assumed to be perfectly symmetric and Gaussian.

To overcome this difficulty some methods were proposed, described in the monograph by Conder and Young [35]. One of these methods is based on the mathematical model but the others are empirical. As a result of theoretical assumptions and difficulties with modelling various shapes of peaks, the mathematical models are very rarely used [58]. Out of the empirical methods, those most frequently used to estimate the retention time are [35,59,61,62]: (1) the peak maximum (PM) method, (2) the Conder and Young (CY) method, (3) the first-order moment method.

In the first-order moment method the retention time is the average time of the sample dwell in the column. It is defined as the first statistical moment or as the centre of dwell time distribution from the beginning of the peak to the complete washing out of the sample from the packed column. This method allows to determine the retention time for the asymmetric and non-Gaussian peaks [59]. Application of this method produces some difficulties: zero line drift, differentiation of the signal intensity and noise intensity ratio, dead volume and peak tailing caused by the apparatus as well as those associated with determination of the moment of complete washing out of the sample. These difficulties can cause change of retention time measurement conditions.

The CY method is good approximation for measurement of retention time as the midpoint of peak weight [35] from which thermodynamic functions for moderately asymmetric peaks can be determined.

After drawing a tangent to the beginning and end of the peak tail, it is possible to minimise the effects of strong peak tailing produced by noise or the detector.

In the case of perfectly symmetrical and Gaussian peaks the peak maximum method, PM, is the simplest and most common. The time corresponding to the peak maximum is assumed to be the retention time  $t_R$ . The peak maximum method is also useful for the peaks, showing slight tailing in the leading or trailing part. The “skewness ratio”, defined as the ratio of tangent slope to the peak leading part and tangent slope to the peak trailing part whereas both tangents are drawn in the inflexion points, is a very useful parameter, Conder et al. [58] stated that the peak maximum method is useful for determination of retention time if the skewness ratio is 0.7 to 1.3. Slight asymmetry of the pack is attributed to an insufficient number of shelves in the column but not to the nonlinearity of the adsorption isotherm [58]. For the peak strongly tailing in the tailing part the skewness ratio is smaller than 0.6 but for that tailing in the leading part it is greater than 1.3. The retention time of the tailing peak of the skewness ratio smaller than 0.6 is underestimated but for the peak tailing in the leading part and characterised by the skewness ratio greater than 1.3 the retention time is overestimated when determined by the peak maximum method. In such a case the first-order moment method or the Conder and Young method [58,59] is recommended. The retention time  $t_R$  is calculated from the following equations [61]:

(1) for the peak maximum method:

$$t_R = t_{\max}$$

(2) for the first-order moment method:

$$t_R = \int_0^{\infty} tc(t)dt / \int_0^{\infty} c(t)dt$$

(3) for the Conder and Young method:

$$t_R = (t_L + t_T)/2$$

where:  $t_{\max}$  is the time corresponding to the peak maximum;  $c(t)$  is the concentration at the time  $t$ ;  $t_L$  and  $t_T$  are the times at which the tangents drawn to the peak leading and trailing parts in their inflexion points intersect the zero line (Fig. 5).

Comparison of the both above mentioned methods allows one to state [61] that in the case of the symmetric peak, the first-order moment methods, CY

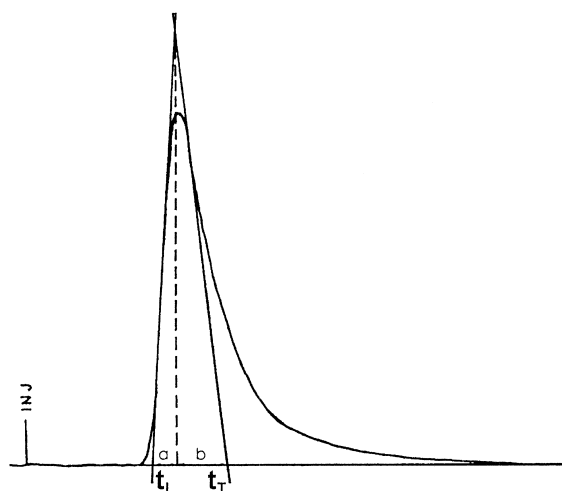


Fig. 5. Exemplary chromatogram presenting a graphic technique used in the Conder and Young method to calculate the skewness (here  $a/b=0.5$ ) and the obtained retention time  $t_R$  [61].

and PM, are equivalent and the retention times determined with their use are identical. In the case of asymmetric peaks, the use of the CY method allows to avoid problems connected with the zero line drift, the effect of noise on the signal intensity and the long tailing appearing while using the first-order moment method.

## 8. Estimation of solid surface energetic heterogeneity using the experimental data obtained by means of inverse gas chromatography

IGC is of significant importance to study the effects of the surface energetic heterogeneity because it allows one to calculate the energy distribution function from the chromatographic data. The retention data are used to solve the integral Eq. (3) by means of analytical and numerical methods (described in Section 5) to obtain the adsorption energy distribution function.

The general equation for the absolute retention volume is as follows:

$$V_N = \frac{kT}{j} \cdot \frac{\partial N_t}{\partial p} \quad (16)$$

where  $j$  is the James–Martin coefficient,  $k$  is the

Boltzman constant,  $T$  is the measurement temperature,  $N_t$  is the total adsorbed amount dependent on the pressure  $p$  of the adsorbate in the gaseous phase. Eq. (16) can be written in another form introducing the surface coverage where  $N_m$  is the amount adsorbed in the monolayer:

$$V_N = \frac{N_m kT}{j} \cdot \frac{\partial \theta}{\partial p} \quad (17)$$

The adsorption energy distribution function in the condensation approximation, CA can be obtained by simple differentiation of the experimental isotherm [1]:

$$\chi_{CA} = \frac{p}{kT} \cdot \frac{\partial \theta}{\partial p} \quad (18)$$

Combining Eqs. (17) and (18) we obtain:

$$\chi_{CA} = \frac{jp}{N_m (kT)^2} \cdot V_N \quad (19)$$

It means that the approximated distribution of CA can be obtained from recalculation of the experimental data. This indicates usefulness of the data obtained using the IGC method because differentiation of the isotherm  $N_t(p)$  obtained from the statistical adsorption measurements can be a source of serious errors in some cases.

The function  $\chi_{CA}$  is the approximation of the real function of the adsorption energy distribution  $\chi_\epsilon$ . A more accurate form of  $\chi_\epsilon$  can be obtained using the so-called asymptotically correct condensation approximation (ACCA). This method was worked out by Hobson [63,64] and developed later by Cerofolini [65,66]. Using this method one can obtain the following form of the distribution function  $\chi_{ACCA}$ :

$$\chi_{ACCA} = \frac{jp^2}{N_m (kT)^2} \cdot \frac{\partial V_N}{\partial p} \quad (20)$$

Owing to its simplicity, this equation is most commonly applied in the studies of surface heterogeneity by means of IGC [1].

A very effective analytical approximation to the experimentally measured functions  $V_N(p)$  was proposed by Gawdzik et al. [67]:

$$V_N = \exp \sum_{m=0}^s A_m p^m \quad (21)$$

where the coefficient  $A_m$  is obtained as the result of the best fit of Eq. (21) to the experimental data. Then the form of the function can be calculated from the equation:

$$\chi_{ACCA} = -\frac{y}{(kT)^2} \cdot \exp \sum_{m=1}^s A_m y^{m-1} \exp \sum_{m=0}^s A_m y^m \quad (22)$$

where

$$y = K \exp \left( -\frac{\epsilon}{kT} \right) \quad (22a)$$

and where  $K$  is the ratio of molecular distribution functions in the gaseous and surface phases.

Fig. 6 presents the example of calculations made by Leboda and Sokolowski [68] using Eq. (20) who studied energetic heterogeneity of silica during adsorption of cyclohexane at two temperatures.

Another approximation of solving integral Eq. (3) to determine the adsorption energy distribution in the experimentally measured isotherm was the Adamson method [69]. At first Adamson and co-workers used the equation of Langmuir or Fowler–Guggenheim isotherm [69] as the local one. Then the method was generalised so that the BET equation could be applied for the local isotherm [70].

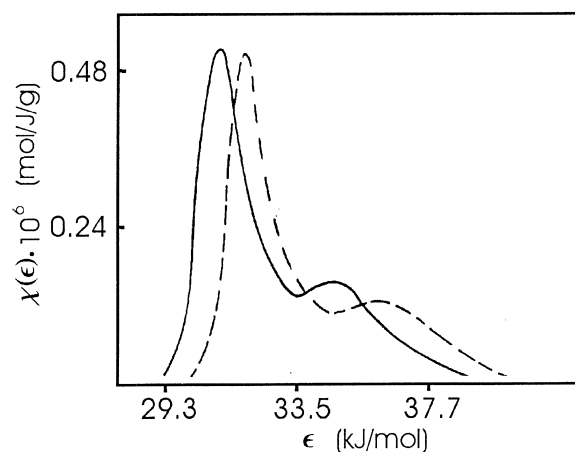


Fig. 6. Distribution of adsorption energy  $\chi_{ACCA}$  calculated by Leboda and Sokolowski [68] for the cyclohexane–silica system using Eqs. (20) and (21). Calculations were made for two temperatures: 409.3 K (continuous line) and 376.3 K (broken line).

The Adamson method [69] employs the integral form of adsorption energy distribution:

$$X_A(\epsilon) = \int_{\epsilon}^{\infty} \chi d\epsilon \quad (23)$$

where  $X_A(\epsilon)$  describes a part of the surface of adsorption site energy equal or greater than  $\epsilon$ . Then the integral equation can assume the following form:

$$\vartheta(\epsilon) = \int_0^1 \theta(\epsilon, p) dX_A \quad (24)$$

where  $\theta(\epsilon, p)$  is the local isotherm.

The Adamson method is the basis for many other methods used for determination of adsorption energy distribution. Among others, the method HILDA worked out by House and Jaycock [71] is its modification.

Other methods used for determination of adsorption energy distribution are CAEDMON worked out by Ross and Morrison [72], those based on the Laplace and Stjeltjes transforms [73–77] as well as the Rudziński–Jagiello (RJ) method [78].

The latter has become very popular in literature. Rudziński and co-workers [78–80] showed new possibilities for solving integral Eq. (3) taking into account its physical domain. The RJ method is based on the condensation approximation, CA. As mentioned earlier in Section 5, this type of approximation gives the best results only when the measurement temperature is close to the absolute zero. This approximation is not quite correct in the conditions most frequently applied in IGC, i.e., at room temperature or at slightly higher temperatures. The Rudziński–Jagiello method enables more accurate calculation of the distribution function  $\chi_{RJ}$  based on the limited development of the even derivatives  $\chi_{CA}$  according to the equation:

$$\chi_{RJ}(\epsilon) = \sum_{j=0}^{\infty} kT^{(2j)} b_{2j} \chi_{CA}^{(2j)}(\epsilon) \quad (25)$$

using the values  $b_0 = 1$  and  $b_{2j} = (-1)^j \pi^{2j} / (2j + 1)!$ .

The above approximation is based on the fact that the product of the first derivative of the local isotherm  $\partial\theta/\partial\ln p$  and the distribution function  $\chi(\epsilon)$  tends to zero close to a certain characteristic value of

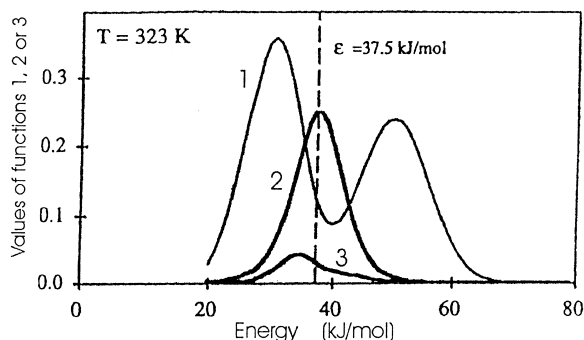


Fig. 7. Model presentation of the product of bi-Gaussian function of the adsorption energy distribution and local derivative of the Langmuir isotherm  $\partial\theta/\partial\ln p$  centred at the energy 37.5 kJ/mol [82]. 1=Thin continuous line: the bi-Gaussian distribution function; 2=thick continuous line: the Langmuir isotherm derivative; 3=thickest continuous line: the result of functions 1 and 2 above.

energy  $\epsilon_m$  corresponding to the pressure  $p_m$  due to a bell-like shape of this derivative as presented in Fig. 7.

A main difficulty which appears here is the necessity of multiple differentiation of the experimentally determined  $\chi_{CA}$  without intensification of the experimental disturbances. On the other hand, the main advantage of this method is the fact that it enables a precise check of the calculations comparing the values  $\chi_{RJ}$  of the higher and higher order. To carry out multiple differentiation Jagiello and Schwarz [81] applied the virial development enabling the fit of the obtained derivatives to the experimentally determined isotherms.

The examples of the distribution function determined using this method can be found in literature [1,81–83]. Great flexibility of this equation using a limited number of parameters involves the common problems concerning fitting by means of polynomials which consists in addition of the residual oscillations to the experimental data intensified due to multiple differentiation [83].

Therefore a correct production of experimental data [84] is of significant importance because intensification of incidental and systematic experimental errors can take place in the process of calculations. In order to carry out this type of analysis, it is necessary to take into consideration a few important factors concerning [82]: (1) choice of suitable experimental conditions enabling preparation of iso-

therms in a wide range of pressures, (2) choice of the adsorption model based on some physical assumptions and leading to the equation connecting the distribution function under consideration with the experimental isotherm, (3) choice of a suitable mathematical method to solve the equation which warrants a stable solution.

Balard [82] verified the above requirements for the adsorption isotherms determined experimentally using the IGC method and for the calculation of adsorption energy distribution function based on the Rudziński–Jagiello method as well as on the method of multiple differentiation of the function  $\chi_{CA}$  method using the Fourier discrete transforms.

A starting point of his studies was determination of the adsorption isotherm from a single chromatographic peak using the elution by the characteristic point method ECP [35]. Using this method it is easy to determine the first derivative of the adsorption isotherm taking into account the retention times  $t_R$  and the signal intensity corresponding to the characteristic points lying on the dropping diffusion part of the chromatogram. The method is based on the assumption that the diffusion fronts of chromatographic peaks corresponding to different volumes of the batched adsorbate overlap. The effect of batched substance vapours on the carrier gas flow-rate is insignificant and contribution of the batching “band” width and longitudinal diffusion processes on the column is insignificant (ideal chromatographic conditions) [82].

In Eq. (3) only one term is known – the left side of the equation that is the experimental isotherm. The local isotherm  $\theta$  was chosen according to the physical hypothesis describing interactions of the molecule with the adsorption centres and with the neighbouring adsorbed molecules. Therefore the character of the calculated distribution function  $\chi(\epsilon)$  depends on the choice of the local isotherm. The most frequently applied local isotherm equations are given in the review paper by Lum Van and White [85].

The Langmuir local isotherm equation assumes the existence of localised adsorption centres and lack of lateral interactions between the adsorbed molecules but the BET isotherm equation assumes possible monolayer adsorption. The Frumkin, Fowler and Guggenheim isotherm equations take into account

lateral interactions between the adsorbed molecules and assume possible static adsorption. Contrary to that the Volmer isotherm is used for calculation of mobile adsorption not taking into account the lateral interactions. The Hill and De Boer model assumes both mobile adsorption and possibility of lateral interactions.

To choose the lateral isotherm properly it is necessary to know real values of some parameters, e.g., interaction energy between two adsorbed molecules. This creates some difficulties because in the case of the Fowler–Guggenheim isotherm, this energy is approximated by evaporation heat of the substance being an adsorbate [71]. Thus a rough approximation is obtained because adsorption affects strongly the electron state of the adsorbed molecules and as a result ability for lateral interactions. As for mobile adsorption, the local isotherm equations take into account only mobility on the homogeneous part of the surface, but in the case of real heterogeneous surfaces mobility is anisotropic to a great extent and anisotropy degree depends on adsorption energy of neighbouring centres.

Because of the above problems most authors use the simplest model of the local isotherm which is the Langmuir model [82]. This choice seems to be most rational because regardless of the kind of local isotherm, the energy characteristics of the adsorption centre  $\epsilon$  is connected directly with the pressure of the adsorption centre  $p_c$  at the value  $\theta=1/2$ . This relation is presented in Eq. (11). The Langmuir constant  $K^L$  in Eq. (11) can be given by [34]:

$$K = K^0(T) \exp(\epsilon/RT) \quad (26)$$

In the above  $K^0(T)$  is the pre-exponential factor, which is the ratio of the partition function of an isolated molecule in the gas and adsorbed phases and thus, it reflects changes in the rotational, vibrational and translational degrees of freedom during the adsorption of an isolated molecule.

The detailed expression for  $K^0$  is given in the monograph by Clark [86]. In the current calculations a low-temperature approximation for  $K^0$  was used which, according to Ross and Olivier [25], leads to the following equation:

$$K^0 = kT \cdot \left( \frac{2\pi m_a kT}{h^2} \right)^{3/2} \quad (26a)$$

where  $m_a$  is the molecule mass,  $k$  is the Boltzmann constant and  $h$  is Planck's constant.

The literature also presents other equations proposed by House and Jaycock [71] as well as by Jagiello et al. [87]. These equations lead to a similar scale of energy [1].

Most isotherms are II type isotherms according to the classification by Brunauer [88], so while using the Langmuir local isotherm or the Fowler–Guggenheim isotherm as a subintegral isotherm of Eq. (3), some corrections for multilayer adsorption should be introduced into the experimental isotherm. Comparing the BET equation with the Langmuir equation [85] it can be stated that the BET equation:

$$N = N_m \cdot \frac{Cx}{(1-x)(1-x+Cx)} \quad (27)$$

can be transformed into the Langmuir equation:

$$N(1-x) = N_m \cdot \frac{C \cdot \frac{x}{1-x}}{1 + C \cdot \frac{x}{1-x}} \quad (28)$$

Substituting the relative pressure  $x=p/p_0$  with the expression  $x'=1/(1-x)$ , and the amount of substance  $N$  with the expression  $N'=N(1-x)$  one can obtain the equation corrected for the multilayer adsorption:

$$N' = N_m \cdot \frac{Cx'}{1 + Cx'} \quad (29)$$

where  $N'$  and  $x'$ , are the values  $N$  and  $x$ , respectively corrected for the relative pressure of multilayer adsorption.

IGC enables determination of the first derivative of the isotherm. Integration and differentiation following if lead to the loss of some information. It is desirable to use the above mentioned correction for multilayer adsorption directly for the isotherm first derivative using the following equation [82]:

$$\frac{\partial N'}{\partial p'} = (1-x^2) \cdot \frac{\partial N}{\partial p} - (1-x^2) \cdot \frac{N}{p_0} \quad (30)$$

where  $N'$  and  $p'$  are the values  $N$  and  $p$  after corrections for multilayer adsorption.

Fig. 8A presents the experimental isotherms and those corrected for multilayer adsorption and Fig. 8B presents the first derivative of the isotherms after the

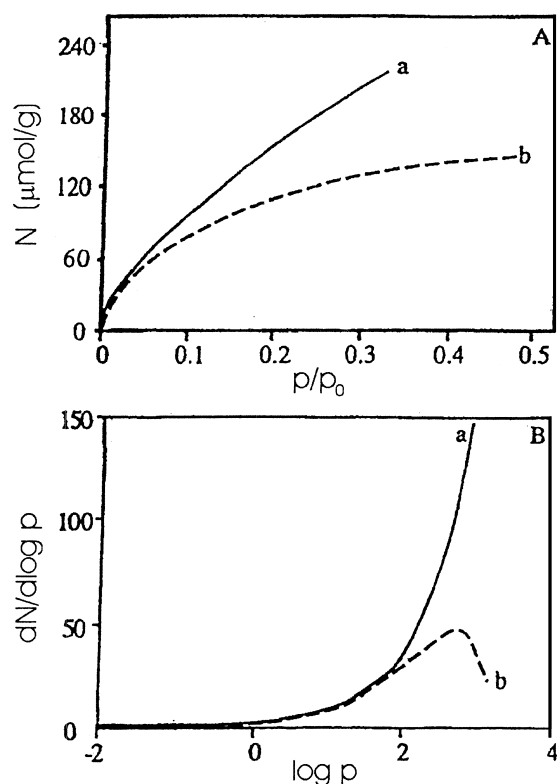


Fig. 8. (A) Correction for multilayer adsorption introduced into the experimental isotherm of octane adsorption on the crumbled mica [82]: a=the uncorrected isotherm; b=the corrected isotherm. (B) Correction for multilayer adsorption introduced into the adsorption isotherm  $\partial N/\partial \log p$  [82]: a=the uncorrected derivative; b=the corrected derivative.

pressure logarithm determined from the adsorption data for the mica samples crumbled by means of the IGC method [82].

As expected the corrected isotherms reach the plateau area but the first derivative passes through the maximum corresponding to the inflexion point of the corrected isotherm drawn in the function of pressure logarithm.

Another step in the analysis of the experimental data is calculation of the adsorption energy distribution function  $\chi_{CA}$  using Eq. (18). Fig. 9 presents as an example the adsorption energy distribution function determined by means of the IGC method for the crumbled mica [82].

Using the Rudziński and Jagiello method for calculation of the real function  $\chi(\epsilon)$  requires an



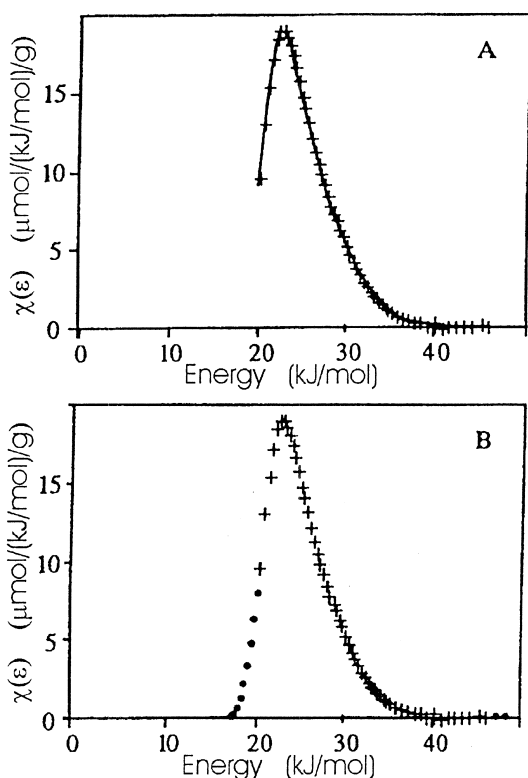


Fig. 9. (A) Function  $\chi_{CA}$  of *n*-octane adsorbed on the crumbled mica determined at 30°C using the IGC method. (B) Extrapolation of this function to zero on the low- and high-energetic sides [82].

effective method enabling multiple differentiation of the function  $\chi_{CA}$ . Taking into account the shape of the obtained function  $\chi_{CA}$ , it can be treated as a component of the periodical function. Balard [82] suggested fitting this function the Fourier series of the type:

$$\chi_{CA}(\epsilon) = A_0 + \sum_{k=1}^n A_k \sin(kw\epsilon) + B_k \cos(kw\epsilon) \quad (31)$$

where  $k$  is the harmonic order and  $w$  is the frequency corresponding to the period chosen on the energy scale. In this case, the even derivatives of the function  $\chi_{CA}$  in Eq. (25) can be easily calculated from the Fourier series differentiation according to the equation:

$$\chi_{CA}^{(2j)}(\epsilon) = \sum_{k=1}^n (kw)^{2j} [A_k \sin(kw\epsilon) + B_k \cos(kw\epsilon)] \quad (32)$$

where  $2j$  is the derivative order.

The next stage of the Balard procedure [82] was collecting and averaging the distribution function determined from various chromatograms and computer treatment techniques of the function  $\chi_{CA}$ . Balard proposed collecting signals determined from the successive chromatographic experiments and subjecting the obtained averaged distribution function to simple smoothing out by means of the “spline” method. Its aim was to diminish intensity of residual noises of high frequency and of the period lower than 1 kJ/mol.

Before this method was applied to study real solids, Balard [82] checked its effectiveness and applicability constructing a numerical program enabling determination of theoretical chromatograms based on the theoretical distribution functions  $\chi(\epsilon)$ . Then he analysed the chromatogram introducing additionally a definite level of incidental noises or removing them in an incidental way. The exemplary results obtained by this method are presented in Fig. 10 where the bi-Gaussian distribution function was a starting point. As follows from Fig. 10 there is very good agreement between the theoretical function  $\chi(\epsilon)$  and the Rudziński–Jagiello approximation of the sixth order  $\chi_{RJ6}$  (sixth derivative  $\chi_{CA}$ ) in the case of the bi-Gaussian distribution.

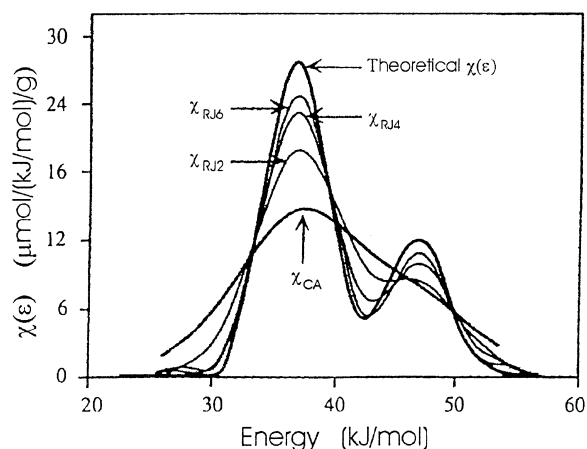


Fig. 10. Functions  $\chi_{CA}$ ,  $\chi_{RJ2}$ ,  $\chi_{RJ4}$  and  $\chi_{RJ6}$  obtained by means of the differential method based on the theoretically determined chromatogram [82], where the functions  $\chi_{RJi}$ ,  $i=2, 4, 6$  are the adsorption energy distribution functions calculated by means of the Rudziński–Jagiello method using the  $i$ th derivative of the function  $\chi_{CA}$ .

The method described by Balard [82] can be applied for various packings like micas and clays as well as silicas [89], talcs [89], alumina [89] and carbon [90]. However, apolar or weakly polar substances like pyridine or 2-propanol are applied as test substances. These applications are discussed in Ref. [91].

Pyda and Guiochon [92] described the way of determination of methanol and dichloromethane adsorption energy distribution on porous silica and silica samples modified by means of the reaction with octadecyldimethylchlorosilane. They carried out the numerical estimation of the distribution function using the expectation – maximisation (EM) method [93]. Primarily, this method was used by Shepp and Vardi [94] for illustrative reconstruction of the data of positron emission topography undergoing the Poisson distribution. Possibilities of general application of this method algorithm to estimate the integral Eq. (3) based on the data concerning noises were presented by Stanley and Guiochon [93]. Pyda and Guiochon [92] used open capillary columns with covered walls instead of classical packed columns. Using these columns improves accuracy and precision of the adsorption data enabling determination of heterogeneous properties of adsorbent surfaces. The evidence for it is overlapping of chromatograms obtained for various amounts of the batched sample. Shapes of the adsorption energy distribution curves indicate that there are at least two or even three kinds of adsorption centres on the surface of silica under consideration [92].

The experimental results also show that modification of silica surface consisting in binding alkyl  $C_{18}$  chains causes a significant decrease of its adsorption capacity and shift of highly energetic adsorption bands of the studied adsorbates towards lower values of energy. The temperature increase causes a decrease of adsorption capacity of both initial and modified silica surface.

Stanley and Guiochon [95] determined also surface energetic heterogeneity of various commercial silica (also modifying them) using the non-linear IGC. They used diethyl ether, methanol, ethanol, pyridine and heptane as adsorbates making measurements at different temperatures. The shapes of the obtained adsorption energy distributions were similar to those obtained in Ref. [92].

Stanley and Guiochon [95] studied the effect of the local isotherm model on adsorption energy distribution to find out if the above mentioned effects result only from low energy or from lateral interactions and those connected with multilayer adsorption. At low concentrations the results obtained using different models of local isotherm are similar but at higher concentrations there appear some divergences which allow to differentiate the models. However, one should bear in mind that the ECP technique is useful for low pressures but high pressures cannot be obtained. Therefore the studies of local isotherm model correctness using this chromatographic method are of small applicability.

Analysing reliability of the ways used for estimation of adsorption energy distribution from the IGC data, it can be stated that this reliability requires fulfilment of a few conditions [95]:

Adsorption energy distribution can be calculated precisely when the adsorption energy is by 10 kJ/mol higher than the evaporation heat. If adsorption energy is lower, the intermolecular interactions diminish accuracy of the obtained results. Then the values of molecular pressures indispensable for exact “examination” of suitable centres are too high. At such pressures, the retention times obtained on the capillary columns become very small and profiles of bands overlap slightly. Due to the maximum pressure increase, it is impossible to make any assumptions about the local isotherm model. To obtain high molecular pressures on the column outlet it is necessary to introduce extreme concentrations of the studied substances on the column inlet. This causes worsening of overlapping effectiveness of chromatographic bands formed due to successive batching of various adsorbate amounts.

Other experimental parameters also diminish the accuracy of measurements. These are, among others, detector ranges and resolving power. Standard chromatographic apparatus allows to obtain five-orders of signal intensity whereas the real surface heterogeneity is included in a much wider range.

As follows from the analysis of the quoted papers IGC is an excellent, quick and precise method for obtaining data to calculate the adsorption energy distribution function. Moreover, it allows to obtain these data both at low and high pressure of adsorbate vapours.

## Acknowledgements

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