Unified Theoretical Description of Physical Adsorption from Gaseous and Liquid Phases on Heterogeneous Solid Surfaces and its Application for Predicting Multicomponent Adsorption Equilibria

A. W. Marczewski, A. Derylo-Marczewska

Institute of Chemistry, M. Curie-Sklodowska University, 20031 Lublin, Poland

and M. Jaroniec†

Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada L8S 4M1

Abstract

A unified theoretical description of physical adsorption occurring at gas/solid and liquid/solid interfaces with energetically heterogeneous surfaces is presented. It is based on a qualitative similarity of the adsorption interactions of all mixture components with an adsorbent surface. This idea is applied to predict adsorption equilibria in multicomponent systems by using parameters characterizing single-component adsorption data. Theoretical considerations are illustrated by suitable model calculations. The usefulness of the description is confirmed by satisfactory results obtained to predict adsorption equilibria in the selected gas/solid and liquid/solid systems.

Introduction

The integral form of the overall adsorption isotherm is most often used in the theory of physical adsorption on heterogeneous solid surfaces. For adsorption of the ith pure gas on a heterogeneous solid surface this integral may be written as follows [1, 2]:

$$\Theta_{i,t}(p_i) = \int_{\Delta_i} \Theta_{i,l}(p_i, \epsilon_i) \chi_i(\epsilon_i) \, d\epsilon_i \qquad (1)‡$$

where $\Theta_{i,t}$ and $\Theta_{i,l}$ are the overall and local surface coverages, respectively; p_i is the equilibrium pressure of the ith pure gas; $\chi_i(\epsilon_i)$ is the distribution function of the adsorption energy ϵ_i; Δ_i is the integration region. Equation (1) may be easily extended to solute adsorption from dilute liquid solutions by replacing the pressure p_i by a solute concentration c_i. Moreover, we should remember that in the case of solute adsorption ϵ_i denotes the adsorption energy of the ith solute expressed with respect to the solvent adsorption energy [3, 4]. Equation (1) may also be transformed to a slightly different form describing adsorption from binary liquid mixtures

containing the ith and jth components over the whole concentration region; then, we have [1, 4, 5]

$$x_{i,t}^s(x_{ij}^l) = \int_{\Delta_i^*} x_{i,l}^s(x_{ij}^l, \epsilon_{ij}) \chi_i^*(\epsilon_{ij}) \, d\epsilon_{ij} \qquad (2)$$

To obtain equation (2) from equation (1), the overall and local surface coverages $\Theta_{i,t}$ and $\Theta_{i,l}$ should be replaced by the mol fractions of the ith component in the surface phase, $x_{i,t}^s$ and $x_{i,l}^s$, respectively; the pressure p_i should be replaced by the ratio of the mol fractions of the ith and jth components in the bulk phase

$$x_{ij}^l = x_i^l/x_j^l \quad (\text{where } x_i^l + x_j^l = 1)$$

the adsorption energy ϵ_i should be replaced by the difference in the adsorption energies of both components $\epsilon_{ij} = \epsilon_i - \epsilon_j$. Since in equation (2) the distribution function depends on the variable ϵ_{ij}, which is the difference between adsorption energies ϵ_i and ϵ_j, we added the asterisk at the symbol χ_i to distinguish this distribution from that appearing in equation (1), which depends on the adsorption energy ϵ_i only. Similarly, we distinguished the integration regions appearing in equations (1) and (2).

In the case of adsorption from n-component gas mixtures on heterogeneous surfaces (or similarly in the case of n-solute adsorption from dilute solutions) the overall adsorption isotherm is expressed as follows [1, 6].

$$\Theta_{i(n)t} = \int_{\Delta_n} \cdots \int \Theta_{i(n)l}(\boldsymbol{p}, \boldsymbol{\varepsilon}) \chi(\boldsymbol{\varepsilon}) \, d\boldsymbol{\varepsilon} \quad \text{for } i = 1, 2, \ldots, n \qquad (3)$$

where $\Theta_{i(n)t}$ and $\Theta_{i(n)l}$ are the relative overall and local adsorptions of the ith component from an n-component mixture; $\boldsymbol{p} = (p_1, p_2, \ldots, p_n)$, $\boldsymbol{\varepsilon} = (\varepsilon \epsilon_1, \epsilon_2, \ldots, \epsilon_n)$ and $\boldsymbol{n} = (1,$

† Permanent address: Institute of Chemistry, M. Curie-Sklodowska University, 20031 Lublin, Poland.

‡ For nomenclature used in this paper see p. 183.

$2, ..., n$) are the n-dimensional vectors; $\Delta_n = \Delta_1 \times \Delta_2 \times, ..., \times$ Δ_n is the n-dimensional integration region; and $\chi(\varepsilon)$ is the n-dimensional distribution function of ε. An analogous equation for equation (3) may be written for adsorption from n-component liquid mixtures of non-electrolytes [1, 4, 6]:

$$x^s_{i(n)t} = \int_{\Delta^*_n} ... \int x^s_{i(n)l}(x^l_n, \varepsilon_n)\, \chi^*(\varepsilon_n)\, \mathrm{d}\varepsilon_n \qquad (4)$$

where $x^s_{i(n)t}$ and $x^s_{i(n)l}$ are the overall and local mol fractions of the ith component in the n-component surface phase; $x^l_n = (x^l_{1n}, x^l_{2n}, ..., x^l_{n-1, n})$ and $\varepsilon_n = (\varepsilon_{1n}, \varepsilon_{2n}, ..., \varepsilon_{n-1, n})$ are $(n-1)$-dimensional vectors, in which $x^l_{in} = x^l_i/x^l_n$ and $\varepsilon_{in} = \varepsilon_i - \varepsilon_n$ (thus the nth component has been chosen as a reference component); $\chi^*(\varepsilon_n)$ and Δ^*_n denote the $(n-1)$-dimensional distribution function and integration region, respectively.

Equations (3) and (4) were solved analytically only for some specific assumptions concerning the form of the energy distribution function. Roginsky and Todes [7, 8] considered binary gas mixture adsorption assuming different dependences between the adsorption energies of both components. First, they discussed a case of the linear dependence between adsorption energies ε_1 and ε_2, i.e. $\varepsilon_2 = a \cdot \varepsilon_1 + b$ (a, b are constants). Then, the integral equation takes the following simplified form [1]:

$$\Theta_{i(2)t} = \int_{\Delta_1} \Theta_{i(2)l}[\varepsilon_1, \varepsilon_2(\varepsilon_1), p]\, \chi_1(\varepsilon_1)\, \mathrm{d}\varepsilon_1 \quad \text{for} \quad i = 1, 2 \qquad (5)$$

They also studied the case of a lack of correlation between the adsorption energies

$$\Theta_{i(2)t} = \int_{\Delta_1} \int_{\Delta_2} \Theta_{i(2)l}(\varepsilon, p)\, \chi_1(\varepsilon_1)\, \chi_2(\varepsilon_2)\, \mathrm{d}\varepsilon_1\, \mathrm{d}\varepsilon_2 \qquad (6)$$

Both equations were solved using the condensation approximation method [7, 8]. Glueckauf [9] investigated the linear dependence between adsorption energies of both components assuming Freundlich (exponential) distribution function with minimum energy equal to zero. He compared exact numerical solutions with some analytical isotherm approximations. A similar approach to the above one was presented by Tompkins and Young [10] and Young and Crowell [11] for the Freundlich-type distribution functions with equal exponents.

Jaroniec, in a series of papers summarized in the review [6], proposed some analytical solutions of equations (3) and (4) after assuming the constancy of the differences of adsorption energies ε_i and ε_n, i.e. $\partial(\varepsilon_i - \varepsilon_n)/\partial\varepsilon_i = 0$ ($i = 1, ..., n-1$) over the whole surface.

All the above approaches showed the possibility of prediction of multicomponent adsorption equilibria by using suitable single-component adsorption data. In the adsorption literature [12–17], other semiempirical or thermodynamical methods of adsorption prediction were also proposed. These approaches do not practically distinguish the energetic heterogeneity as a separate effect playing an important role in the adsorption process.

In the present paper, a new method of description of multicomponent adsorption systems involving energetic heterogeneity effects is proposed. It is based on the assumption that the differences in the adsorption energies of components vary in an ordered way. It demonstrates the possibility of expressing the integral equations (3) and (4) in

the form of a single integral which may be easily solved analytically or numerically. It also enables prediction of the multicomponent adsorption equilibria by using only the parameters characterizing suitable simpler adsorption systems, e.g. single-gas adsorption (single-solute adsorption) systems. The theoretical discussion is illustrated by several model calculations. Moreover, the adsorption data of two binary gas mixtures and two binary liquid mixtures were predicted by means of the single gas and vapour adsorption parameters, respectively. Additionally, simple relationships between Henry's constant and the energy distribution function are discussed including the temperature dependence of the heterogeneity parameters characterizing this distribution.

Theory

(A) *General considerations dealing with the integral equation for gas and liquid adsorption*

Let us assume that an n-component ideal gas mixture (all molecules have identical molecular sizes; molecular interactions are neglected in the case of gas phase and are identical in the case of liquid phase) is in contact with an energetically heterogeneous solid and any two molecules of the ith and jth components ($i, j = 1, 2, ..., n$) adsorb on any surface site '*' with the energies ε_i^* and ε_j^* which are related in the following way:

$$F^* = \int_{E_{i, min}}^{E_i^*} \chi_i(E_i)\, \mathrm{d}E_i = \int_{E_{j, min}}^{E_j^*} \chi_j(E_j)\, \mathrm{d}E_j; \quad E = \varepsilon/RT;$$

$$F \in \langle 0, 1 \rangle \qquad (7)$$

In the above, E is the reduced adsorption energy (introduced for simplicity of further formulas) and F is the integral (cumulative) distribution function in a simple way connected with the differential distribution χ:

$$\frac{\mathrm{d}F}{\mathrm{d}E} = \chi(E) \qquad (8)$$

To simplify mathematical notation we use the same symbol χ for denoting the functions $\chi(\varepsilon)$ and $\chi(E)$. $F(E)$ represents the fraction of adsorption sites with energies lower than E. In the case of strongly heterogeneous gas/solid systems, when the condensation approximation method may be used to calculate the energy distribution [7, 8] and the pressure p satisfies the following relationship $\Theta_t(E, p) = 0.5$, the quantity $[1 - F(E)]$ is equal to the global surface coverage $\Theta_t(p)$. The function F shows a possibility for calculating the relationship between the adsorption energies of different components referring to the same solid surface:

$$E_i = E_i(F); \quad E_j = E_j(F) \quad \text{and} \quad E_j = E_j[F(E_i)]; \quad i, j = 1,$$
$$2, ..., n; \ i \neq j \qquad (9)$$

Thus, we may obtain the analogues of the integral equations for gas adsorption [equations (1) and (3)]:

$$\Theta_{i, t} = \int_0^1 \Theta_{i, l}[p_i, E_i(F)]\, \mathrm{d}F \qquad (10a)$$

and

$$\Theta_{i(n)t} = \int_0^1 \Theta_{i(n)l}[p, E(F)]\, \mathrm{d}F \qquad (10b)$$

where $E = (E_1, E_2, ..., E_n)$ and $E_i(F) = \epsilon_i/RT$ for $i = 1, 2, ... n$. In this way we simplified the multidimensional integral [equation (3)] to a single-dimensional integral [equation (10b)] which is fully described by a local isotherm $\Theta_{i(n)l}$, e.g. the multi-Langmuir equation

$$\Theta_{i(n)l} = \frac{K_{0i} \exp(\epsilon_i/RT)p_i}{1 + \sum\limits_{j=1}^{n} K_{0j} \exp(\epsilon_j/RT)p_j} = \frac{K_{0i} \exp(E_i)p_i}{1 + \sum\limits_{j=1}^{n} K_{0j} \exp(E_j)p_j} \quad (11)$$

and n functions $E_i(F)$ identical with these for single gas adsorption. In equation (10), K_{0j} for $j = 1, 2, ..., n$ are the entropy factors [6]. Each energy distribution function is characterized by two fundamental parameters: the mean energy $\bar{E} = \bar{\epsilon}/RT$ and energy dispersion $\sigma = \sigma_\epsilon/RT$, relating to the inhomogeneity of the adsorption system. They are defined as follows:

$$\bar{E} = \int_\Delta E \cdot \chi(E)\,dE = \int_0^\infty E(F)\,dF \quad (12a)$$

and

$$\sigma^2 = \int_\Delta (E - \bar{E})^2 \chi(E)\,dE = \int_0^1 [E(F) - \bar{E}]^2\,dF \quad (12b)$$

After introduction of a new variable $z = E(F) - \bar{E}$ and local Langmuir equation (11) in the integral equation (10b), we obtain

$$\Theta_{i(n)t} = \int_0^1 \frac{\bar{K}_i p_i \exp[z_i(F)]}{1 + \sum\limits_{j=1}^{n} \bar{K}_j p_j \exp[z_j(F)]}\,dF; \quad z_i(F) = E_i(F) - \bar{E}_i \quad (13)$$

where $\bar{K}_i$ is the equilibrium constant connected with the mean adsorption energy $\bar{E}$:

$$\bar{K}_j = K_{0j} \exp(\bar{E}) = K_{0j} \exp(\bar{\epsilon}/RT) \quad (14)$$

In Table I, the analytical forms of the functions $F(z)$ and $z(F)$ are shown for several known energy distribution functions. The expressions for energy dispersion σ presented in the same table are exact formulas, only in the case of Tóth and generalized Freundlich equations [6] these formulas are approximate ones. To show the differences and resemblances between the differential (χ) and integral (F) forms of the energy distribution, both these forms are shown for the symmetrical LF-type energy distribution function [18] (Table I) vs. $z = E - \bar{E}$ (Fig. 1A, C). Moreover, the dependences of the local surface coverage for single gas adsorption [equation (11)] vs. z (Fig. 1B) and vs. $F = F(E)$ (Fig. 1D) are plotted. The dashed areas in Fig. 1A, D refer to the global surface coverage Θ_t. However, the dependences σ vs. $(m^{-2} - 1)^{\frac{1}{2}}$ (Fig. 2A) and σ^2 vs. $(m^{-2} - 1)$ (Fig. 2B) for LF, T and GF energy distributions (see Table I) are drawn. In the case of LF function, their plots are linear; on the other hand, for T and GF distributions the linear approximations are also satisfying.

The above considerations can be extended to the case of adsorption of an n-component liquid mixture. For the local isotherm equation of the Everett type [14]

$$x_{i(n)l}^s = \frac{K_i x_i^l}{\sum\limits_{j=1}^{n} K_j x_j^l} = \frac{K_{in} x_{in}^l}{1 + \sum\limits_{j=1}^{n-1} K_{jn} x_{jn}^l}; \quad i = 1, ..., n \quad (15a)$$

where

$$K_{jn} = K_j/K_n = (K_{0j}/K_{0n}) \exp(E_j - E_n); \quad x_{jn}^l = x_j^l/x_n^l \quad (15b)$$

Table I. *Differential energy distribution functions $\chi(E)$ and corresponding functions $F(z)$, $z(F)$ and dispersion values*

Code	Distribution function χ	$F(z)$	$z(F)$	σ
G	$\dfrac{1}{\sqrt{(2\pi\sigma)}}\exp[-z^2/(2\sigma^2)]$	$\left[1 + \text{sign}(z)\,\text{erf}\left(\left\|\dfrac{z}{\sqrt{2}\sigma}\right\|\right)\right]\Big/2$	—	σ
R	$m \cdot \exp(mz)/[\exp(mz) + 1]^2$	$\exp(mz)/[\exp(mz) + 1]$	$\ln[F/(1-F)]/m$	$\dfrac{\pi}{\sqrt{3}}\dfrac{1}{m}$
Sq	$(1/\Delta E); \ z \in (-\Delta E/2, \Delta E/2)$	$[z/\Delta E + \tfrac{1}{2}]$	$\Delta E \cdot (F - \tfrac{1}{2})$	$\Delta E/(2\sqrt{3})$
k	$P_i = 1/k; \quad z_i = \Delta E\left(\dfrac{i-1}{k-1} - \dfrac{1}{2}\right)$	$F_i \in \left(\dfrac{i-1}{k}, \dfrac{i}{k}\right)$ for	$\Delta E\left(\dfrac{i-1}{k-1} - \dfrac{1}{2}\right)$ for	$\dfrac{\Delta E}{2\sqrt{3}}\sqrt{\dfrac{k+1}{k-1}}$
	$i = 1, 2, ..., k$	$z_i = \Delta E\left(\dfrac{i-1}{k-1} - \dfrac{1}{2}\right)$	$F_i \in [(i-1)/k; i/k]$	
F	$m\exp(-mz - 1); \ z \in (-1/m, \infty)$	$[1 - \exp(-mz - 1)]$	$[-\ln(1-F) - 1]/m$	$(1/m)$
LF	$(1/\pi)\sin(\pi m)\exp(mz)/W(m, z)$	$\dfrac{1}{m\pi}\tan^{-1}\left[\dfrac{\sin(\pi m)}{\exp(-mz) + \cos(m\pi)}\right]$	$\dfrac{1}{m}\ln\left\{\dfrac{\sin(\pi m F)}{\sin[\pi m(1-F)]}\right\}$	$\dfrac{\pi}{\sqrt{3}}\dfrac{\sqrt{(1 - m^2)}}{m}$
GF	$(1/\pi)\sin(\pi m)/[\exp(E') - 1]^m$	—	—	$\sim \dfrac{\sqrt{(1 - m^2)}}{m}$
	$E' = E - E_{min} > 0$			
T	$(1/\pi)\sin(\gamma/m)/[W(m, E')]^{1/(2m)}$	—	—	$\simeq 1.3\dfrac{\sqrt{(1 - m^2)}}{m}$
	$\gamma = \cos^{-1}\left\{\dfrac{\cos(\pi m)\exp(mE') + 1}{[W(m, E')]^{\frac{1}{2}}}\right\}$ $E' = E - E_0$			

Distribution function codes: G, Gaussian; R, Rudziński's [19]; Sq, continuous square-shaped; k, k-centred square-shaped; F, Freundlich (exponential); LF, Langmuir–Freundlich [18]; GF, Generalized Freundlich [18]; T, Tóth [18].

P_i, probability; σ, m, ΔE, heterogeneity parameters; $\Delta E = E_{max} - E_{min}$; E_0 – characteristic energy; $W(m, x) = [\exp(2mx) + 2 \exp(mx)\cos(m\pi) + 1]$; erf – probability integral.
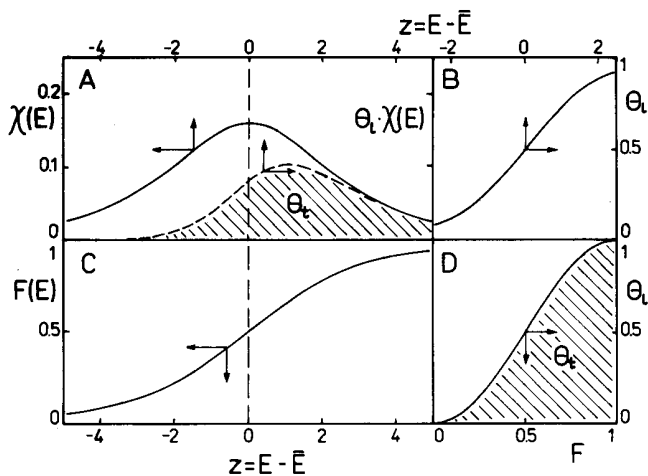
Fig. 1. Model curves for the Langmuir–Freundlich energy distribution function calculated according to eqns. (1), (7), (8) and (11) for $\bar{K}p = 1$ and heterogeneity parameter $m = 0.5$. (A) Distribution function $\chi(z = E - \bar{E})$ (———) and $\chi(z) \cdot \Theta_t(p,z)$ vs. z (– – – – –). (B) Dependence $\Theta_t(p,z)$ vs. z. (C) Integral distribution F vs. z (———). (D) Dependence of the local coverage Θ_t vs. F (———). The dashed areas in (A) and (D) refer to the global coverage Θ_t.
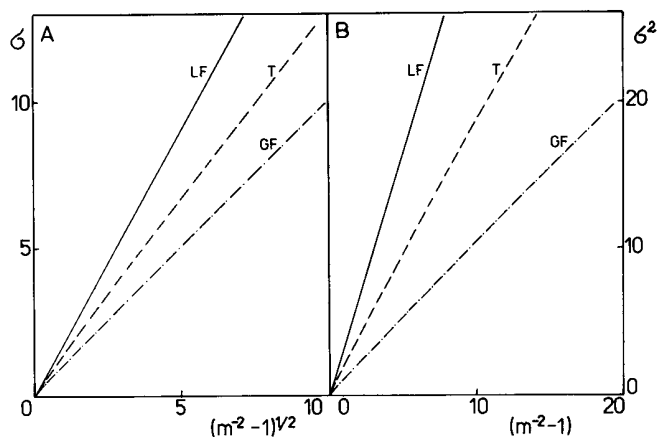
Fig. 2. Energy distribution dispersion. (A) σ vs. $(m^{-2}-1)^{\frac{1}{2}}$; (B) σ^2 vs. $(m^{-2}-1)$; for LF (———), Tóth (– – – –) and GF (–.–.–.–) distribution functions (see Table I); m is a heterogeneity parameter.

we obtain

$$x^s_{i(n)\,t} = \int_0^1 \frac{\bar{K}_i \exp[z_i(F)]\,x^l_i}{\sum\limits_{j=1}^n \bar{K}_j \exp[z_j(F)]\,x^l_j}\,dF$$

$$= \int_0^1 \frac{\bar{K}_{in} \exp[z_{in}(F)]\,x^l_{in}}{1 + \sum\limits_1^{n-1} \bar{K}_{jn} \exp[z_{jn}(F)]\,x^l_{jn}}\,dF \tag{16a}$$

where

$$\bar{K}_j = K_{0j}\exp(\bar{E}_j); \quad \bar{K}_{jn} = \bar{K}_j/\bar{K}_n; \quad z_{jn}(F) = z_j(F) - z_n(F);$$
$$z_{nn}(F) = 0 \tag{16b}$$

The overall isotherm (equation (16a)] is expressed by the parameters $\bar{K}_j$ and functions $z_j(F)$ characteristic for adsorption of single components (gas or vapour) or by suitable quantities for adsorption of the binary solution '$j+n$'.

(B) Prediction of adsorption equilibria in multicomponent systems

The new isotherm [equations (13) and (16a)] describing adsorption from n-component mixtures are fully characterized by mean energy constants $\bar{K}_j$ and characteristic functions $z_i(F) = E_i - \bar{E}_i$ obtained from single adsorption data. It gives the basis for using equations (10), (13) and (16) for simple prediction of mixture adsorption from the suitable experimental single gas or vapour adsorption data. Additionally, the adsorption from a multicomponent liquid mixture over the whole concentration range can be predicted by using the suitable binary liquid adsorption data [equation (16)]. However, this method requires the correct choice of the reference component 'n'. It should have the highest or the lowest value of energy dispersion σ_n. In this case, all parameters of the binary liquid mixture '$j+n$', $j = 1,...,n-1$, can be directly used in equation (16). However, the problem of special selection of the reference component 'n' should be discussed more extensively. Prediction of adsorption by means of the single gas or vapour adsorption data does not need the choice of a reference component, but its exactness, especially in the case of adsorption from multicomponent liquid mixtures, is not good enough. The results are loaded with errors of subtraction of two similar high energy values $E_i - E_j$ and change of the bulk phase physical state (the heterogeneity parameters can be found exactly enough). Thus, even a single point measured experimentally in a multicomponent mixture can be helpful in $\bar{K}_{ij}$ constants correction.

Equation (16) may be easily adapted to describe and predict multisolute adsorption from dilute solutions, especially if the solutes are organic and water is a solvent; then, water is a reference substance: 'w' = '$n+1$'. The mol fraction of water may be assumed to be constant ($x^l_w \simeq 1$), and the mol concentration of the solute 'j' in aqueous solution is

$$c_j = x^l_j c_w \tag{17}$$

where c_w is the mol concentration of water. Thus we obtain

$$\Theta_{i(n)\,t} = \int_0^1 \frac{c_i\,\bar{K}_{i(w)} \exp[z_{i(w)}(F)]}{1 + \sum\limits_{j=1}^n c_j\,\bar{K}_{j(w)} \exp[z_{j(w)}(F)]}\,dF \tag{18}$$

where the constants $\bar{K}_{j(w)} = \bar{K}_{jw}/c_w$ and function $z_{j(w)}(F) = z_{jw}$ (F) are characteristic for single solute adsorption:

$$\theta_{i,t} = \int_0^1 \frac{\bar{K}_{i(w)}\,c_i \exp[z_{i(w)}(F)]}{1 + \bar{K}_{i(w)}\,c_i \exp[z_{i(w)}(F)]}\,dF \tag{19}$$

Let us now consider the specific case of adsorption from an n-component gas mixture in which k components have very similar adsorptive properties [their distributions $z_i(F)$ are identical and equal to $z(F)$, whereas their mean energies $\bar{E}_i$ are different] and the other components adsorb with constant energies [$z(F) = 0$]. Thus single gas adsorption isotherms may be written as follows:

$$\Theta_{i,t} = G_z(\bar{K}_i p_i); \quad i \leq k \text{ and } G_z \text{ denotes a function of } \bar{K}_i p_i \tag{20}$$

$$\Theta_{i,t} = \bar{K}_i p_i/[1 + \bar{K}_i p_i]; \quad n \geq i \geq k+1; \quad \bar{K}_i = K_i$$

and a multicomponent adsorption isotherm is expressed by means of the parameters characteristic for single gas adsorption:

$$\Theta_{i(n)t} = \frac{\bar{K}_i p_i}{\sum\limits_{j=1}^{k} \bar{K}_j p_j} G_z \left[\sum\limits_{j=1}^{k} \bar{K}_j p_j \Big/ \left(1 + \sum\limits_{j=k+1}^{n} \bar{K}_j p_j\right) \right]; \quad i \leqslant k$$

$$\tag{21}$$

$$\Theta_{i(n)t} = \frac{\bar{K}_i p_i}{1 + \sum\limits_{j=k+1}^{n} \bar{K}_j p_j} \left[1 - G_z \left(\frac{\sum\limits_{j=1}^{k} \bar{K}_j p_j}{1 + \sum\limits_{j=k+1}^{n} \bar{K}_j p_j} \right) \right]; \quad i \geqslant k+1 \geqslant n$$

Analogous results were obtained by Jaroniec [20] and Jaroniec *et al.* [21] These considerations can be easily generalized to adsorption from multicomponent liquid mixtures and dilute solutions.

(C) *Special relations for adsorption from binary mixtures*

The case of adsorption from binary liquid mixtures and adsorption of two-component gas mixtures under conditions of almost full surface coverage is especially interesting ($\Theta_{1(2)t} + \Theta_{2(2)t} \simeq 1$). The equilibrium in such systems is fully described in terms of adsorption energy differences [equation (16a) for $n = 2$ and equation (13) for $\bar{K}p_1$, $\bar{K}p_2 \gg 1$ and $n = 2$]. Thus we can find dispersion σ_{12} of the adsorption energy difference $E_{12} = E_1 - E_2$ ($z_{12} = z_1 - z_2$):

$$\sigma_{12}^2 = \int_0^1 z_{12}^2(F)\, \mathrm{d}F = (\sigma_1 - \sigma_2)^2 + 2(1 - r_{12})\sigma_1\sigma_2 \tag{22a}$$

$$r_{12} = \int_0^1 \left[\frac{z_1(F)}{\sigma_1}\right]\left[\frac{z_2(F)}{\sigma_2}\right] \mathrm{d}F \tag{22b}$$

where r_{12} is the correlation coefficient of the distributions χ_1 and χ_2. If a linear dependence between the energies E_1 and E_2 exists, we obtain

$$z_1(F) = z_2(F)\sigma_1/\sigma_2; \quad r_{12} = 1; \quad \sigma_{12} = |\sigma_1 - \sigma_2| \tag{23}$$

As it results from equations (22) and (23), the dispersion (or width) of the adsorption energy differences distribution function is equal to a positive value obtained by subtracting dispersions of linearly correlated energies E_1 and E_2. In Fig. 3, the model discrete (Fig. 3A) and continuous (Fig. 3B)
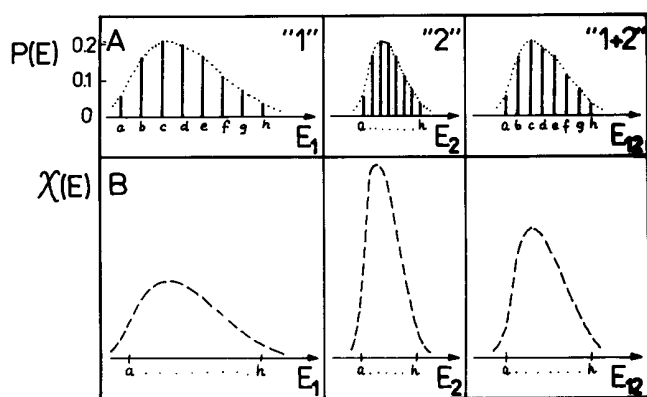
Fig. 3. Model energy distributions for single-component adsorption ('1' and '2') with corresponding distributions of adsorption energy differences E_{12} for binary mixture '1+2'; correlation coefficient $r_{12} = 1$. (A) Discrete energy distributions $P(E)$ (P = probability). (B) Continuous energy distributions $\chi(E)$. Small letters a, b, ..., h denote types of adsorption sites.

energy distributions are drawn for the single components '1' and '2'. These distributions produce the suitable distribution functions of the differences of the energies $E_1 - E_2 = E_{12}$, which are also presented. The last functions describe properties of the adsorption system with the binary mixture '1+2' and refer to the positive correlation of the adsorption energies E_1 and E_2 [$z_1(F)$ and $z_2(F)$]. According to many authors [6, 7, 10, 11, 20] the situation when $\sigma_1 = \sigma_2$ and $r_{12} = 1$ (i.e. heterogeneity parameters are the same) is very frequent. Thus, $\sigma_{12} = 0$ ($z_{12} = 0$) and the competitive monolayer adsorption may be described in terms of the mean differences only:

$$x_{1(2)t}^s / x_{2(2)t}^s = \bar{K}_{12}\, x_{12}^l \tag{24a}$$

or

$$\Theta_{1(2)t} / \Theta_{2(2)t} = \bar{K}_{12}\, p_1/p_2 \tag{24b}$$

In the case of gas adsorption, even if a monolayer is not filled up, the simple relation [equation 24b)] is still kept (of course for $\sigma_{12} = 0$) and individual global coverages can be described by equations (20) and (21). However, when we consider adsorbates of extreme opposite properties (for example, acidic and basic or the like,) it may happen that an opposite correlation of $z_1(F)$ and $z_2(F)$ is valid:

$$z_1(F) = -z_2(F)\sigma_1/\sigma_2; \quad r_{12} = -1; \quad \sigma_{12} = \sigma_1 + \sigma_2 \tag{25}$$

The knowledge of heterogeneity parameters of single gas (or vapour) adsorption data make the calculation of heterogeneity parameters for mixed adsorption possible. When both mixture components are of the same type, for example, adsorption of these components is characterized by the Freundlich energy distribution functions with heterogeneity parameters m_1 and m_2, we have (see Table I)

$$r_{12} = 1; \quad \sigma_{12} = |\sigma_1 - \sigma_2| \tag{26a}$$

$$1/m_{12} = |1/m_1 - 1/m_2| \tag{26b}$$

or for LF, Tóth or GF distributions ($r_{12} \simeq 1$)

$$\sigma_{12} \simeq |\sigma_1 - \sigma_2| \tag{27a}$$

$$(m_{12}^{-2} - 1)^{\frac{1}{2}} \simeq |(m_1^{-2} - 1)^{\frac{1}{2}} - (m_2^{-2} - 1)^{\frac{1}{2}}| \tag{27b}$$

The above equations give simple relations between heterogeneity parameters of single and mixed adsorption data. However, for adsorption of two substances of chemically dissimilar nature it may be necessary to describe them by different-type distribution functions, for example the Freundlich and Rudziński's distributions. Thus, a correlation coefficient is not equal to unity and $\sigma_{12} \neq |\sigma_1 - \sigma_2|$. In this case, the formulas analogous to equations (26b) and (27b) are only crude approximations because the resulting distribution $\chi_1^*(E_{12})$ [equations (8) and (16b)] is of an intermediate character between the functions $\chi_1(E_1)$ and $\chi_2(E_2)$.

The values of the correlation coefficient r_{12} for some theoretical distribution functions are shown in Table II. However, in Fig. 4 the values of r_{12} for LF and R (solid line) and LF and G distributions (dashed line) are drawn *vs.* the heterogeneity parameter m. It is evident from Table II and Fig. 4 that the quasi-Gaussian distributions R and LF are very similar to the Gaussian (G) one (especially in the case of small m values referring to great heterogeneities). Besides, the other symmetrical distributions, like continuous square-
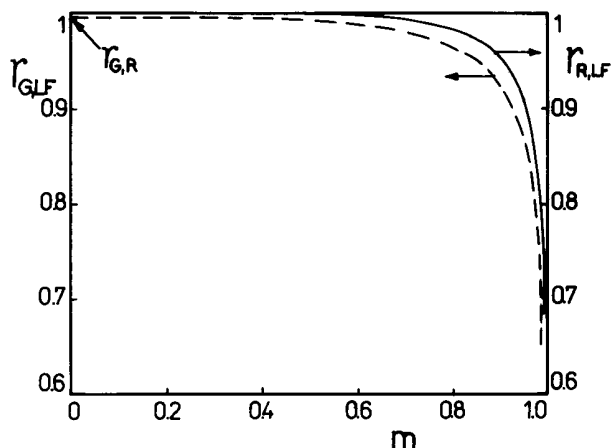
Fig. 4. Correlation coefficient r [equation ($22b$)] drawn for LF and G (------) and LF and R (——) distributions *vs.* heterogeneity parameter of LF distribution (m). Correlation coefficient for R and G distributions $r_{G,R}$ is indicated.

Table II. *Correlation coefficients r_{12} [equation ($22b$)] for some chosen distribution functions (codes are the same as in Table I)*

Code	F	R	G	Sq	k
F	1	$\pi\sqrt{3}/6 \simeq 0.89$	—	$\sqrt{3}/2 \simeq 0.86$	—
G	—	~ 0.996	1	—	—
Sq	$\sqrt{3}/2 \simeq 0.86$	$3/\pi \simeq 0.955$	—	1	$\sqrt{\left(1-\dfrac{1}{k^2}\right)}$

shaped or k-centred square-shaped ones, can be used to approximate the quasi-Gaussian distributions. For example, when we have adsorption data in a narrow range of surface coverages, there is no distinct difference between the global coverages for different kinds of symmetrical distributions with the same mean energy and dispersion.

(D) *Some remarks on prediction of adsorption for mixtures of components showing certain non-correlation of adsorption energies*

The previous considerations concerned a model mixture after assuming a functional dependence for the adsorption energies $E_j = f(E_i)$ defined by equations (7)–(9); however, the factual dependence for the experimental system may be more or less of the probability character. In the case of a complete lack of energies correlation, the multivariate distribution in equations (3) and (4) will be defined as a product of independent functions:

$$\chi(\varepsilon) = \chi_1(\varepsilon_1)\,\chi_2(\varepsilon_2)\cdots\chi_n(\varepsilon_n) \tag{28}$$

and equation ($10b$) will take the form

$$\Theta_{i(n)t} = \int_0^1 \cdots \int_0^1 \Theta_{i(n)l}\,[p, E_1(F_1)\ldots E_m(F_n)]\,\mathrm{d}F_1\ldots\mathrm{d}F_n \tag{29}$$

Equations analogous to equations (3) and (4) with the distribution function 28 were discussed for binary gas mixtures by Roginski and Todes in terms of condensation approximation [8] and by Jaroniec for adsorption from an n-component gas mixture with local Jovanović behaviour and Guassian distributions $\chi_i(\epsilon_i)$ [22]. The case of two-component dilute solution and bivariate Gaussian energy distribution

function with the correlation coefficient $r\in(0, 1)$ was investigated and tested experimentally by Mueller *et al.* [23, 24]. They found a positive correlation (r close to unity) in most cases studied, concluding also that their model gives distinctively better prediction than IAS theory [13, 16].

We must underline here that values $r = \mathrm{cov}\,(x, y)/(\sigma_x\sigma_y)$ less than unity do not require the probabilistic character of relation between two physical quantities. For mixed adsorption it can also mean that the obtained distribution functions, isotherm equations or data used are approximate or the dependence $E_2(E_1)$ is curvilinear. Additionally, a certain non-correlation can be a result of other approximations and assumptions made. However, in most cases, energy distributions are well correlated [many papers [6, 7, 10, 11, 20, 23, 24] deal with the data and theoretical equations fulfilling equations (20) and (21) or (24)]. The effect of energy distribution functions non-correlation can be examined by investigating adsorption data of binary gas and liquid mixtures [equations (22)–(27)]. If single-component distribution functions have very similar heterogeneity parameters (and dispersions σ_1, σ_2), then the dispersion σ_{12} should be very sensitive to changes of the correlation coefficient r_{12}:

$$\sigma_{12} = [(\sigma_1-\sigma_2)^2+2(1-r_{12})\,\sigma_1\sigma_2]^{\frac{1}{2}} \simeq [2(1-r_{12})\,\sigma_1\sigma_2]^{\frac{1}{2}} \tag{30}$$

Comparing the heterogeneity parameters predicted and found from the mixed data, we can determine whether the adsorption energies are actually correlated or not.

In Fig. 5, the problem of the adsorption energies correlation is shown for a competitive adsorption model for a binary mixture. Fig. 5A represents $z_1(F_1)$ (solid line) and $z_2(F_2)$ (dashed line) observed in single-component systems, whereas Fig. 5B shows $z_{12}(F)$ (solid line) calculated according to the assumption that $F_1 = F_2 = F$ for each site on the surface (the complete correlation of adsorption energies of components '1' and '2'). However, in Fig. 5C the single component energies are plotted *vs.* joint scale $F = F_2\,(F_1 = F_2)$ for a model
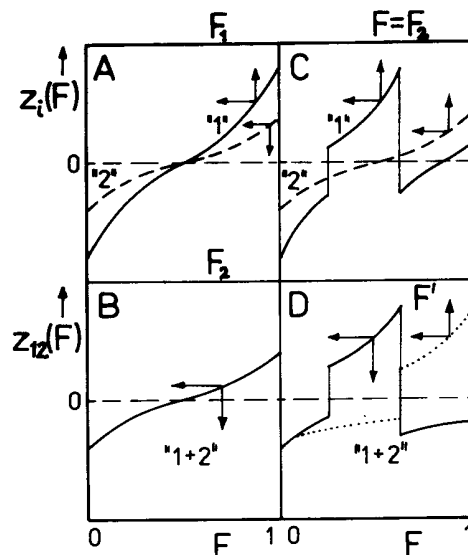

Fig. 5. Model energy characteristic curves $z(F)$ for adsorption of single components '1' and '2' and competitive adsorption of mixture '1+2'. (A) Fully correlated $z_1(F_1)$ (——) and $z_2(F_2)$ (- - - -). (B) Energy difference characteristic curve $z_{12}(F)$ for the case of correlated single component distributions. (C) Partially correlated $z_2(F = F_2)$ (- - - -) and $z_1(F = F_2)$ (——) with actually the same distribution $F_1(z_1)$ as for $z_1(F_1)$ (5A). (D) Curve $z_{12}(F = F_2)$ (——) for partially correlated adsorption energies (5C) and observed in the mixture '1+2'; $z_{12}(F')$ *vs.* rearranged F' scale ($\cdots$).

non-correlation, whereas in Fig. 5D the resulting curve z_{12} $(F) = z_1(F) - z_2(F)$ (solid line) is drawn. In Fig. 5D the function $z_{12}(F')$ (dotted line) is plotted vs. the rearranged F' scale (to give a monotonous course of z_{12}). It must be emphasized that single-component distributions $z_1(F_1)$ and $z_1(F = F_2)$ are observed experimentally as actually identical. Moreover, a lack of correlation between energies E_1 and E_2 observed in Fig. 5C and D is a specific feature of the model system.

Summing up the theoretical discussion, it ought to be remarked that the new theoretical description of adsorption and its application for predicting the multicomponent adsorption equilibria has a universal character. We will use the following abbreviation for this method: 'Subtraction of adsorption energy dispersions' – SAED. In comparison with other approaches dealing with energetic heterogeneity, it does not restrict types of energy distribution functions for single components which may be used in multicomponent adsorption prediction. The general relationships proposed are rather simple in usage. This method also creates the possibility of simplifying these equations for some special cases. However, its inconvenience lies in the assumption of ideality of the bulk phase and differences in molecular sizes. It may be expected that taking both effects into account would distinctly improve prediction quality. Additionally, the method makes it possible to explain the Henry constant relation to energy distribution function and to discuss temperature dependences of heterogeneity parameters (see Appendices A and B). It is also possible to check the quality of approximation of the continuous distribution of adsorption energy by a discrete function (see Appendix C).

Results and discussion

To show the advantages and disadvantages of the proposed prediction method, we analysed adsorption of binary gas mixtures and two binary liquid mixtures on heterogeneous solids by using the single gas and vapour adsorption data, respectively.

The data on ethane, ethylene, propane and propylene (pure gases) adsorption on Nuxit Al charcoal [25–27] ($T = 293$ K) were analyzed by using the semi-graphical methods developed in a series of papers [18, 28–30]. The Langmuir–Freundlich isotherm equation [6] was found to be the best approximation of the data

$$a_i = a_{m,i}\{(\bar{K}_i p_i)^{m_i}/[1 + (\bar{K}_i p_i)^{m_i}]\} \qquad (31)$$

where a_i and $a_{m,i}$ are the adsorption amount and monolayer capacity of the ith gas, respectively, whereas m_i is the heterogeneity parameter [see Table I and equation $(27b)$]. The results of optimization are presented in the first part of Table III and in Fig. 6A. It is obvious from Table III that ethane and ethylene as well as propane and propylene have very similar monolayer capacities and heterogeneity parameters. In Fig. 6A, the linear plots of the Langmuir–Freundlich [equation (31)]

$$a_i = a_{m,i} - a_i/(\bar{K}_i p_i)^{m_i} \qquad (32)$$

are presented for ethane (black triangles and a solid line), ethylene (white triangles and a solid line), propane (black points and a dashed line) and propylene (white points and a dashed line). Though the linear plot predicted by equation

(32) is very sensitive to every change in the theoretical equation (31), a very good linear correlation is obtained. Similarity of $a_{m,i}$ and m_i values made it possible to use the mean values of $\bar{a}_m = 0.5$ $(a_{m,i} + a_{m,2})$, $\bar{m} = 0.5$ $(m_1 + m_2)$ and $\bar{K}_{21} = \bar{K}_2/\bar{K}_1$ in mixture adsorption prediction. Moreover, the values m_{12} obtained from the parameters m_i by using equations $(27a)$ and $(27b)$ are very close to unity (Table III); it confirms the possibility of applying one common distribution with $\bar{m}$ for both mixture components [see equations (20), (21)] instead of the full form of integral equation (13) with slightly different $z_1(F)$ and $z_2(F)$ functions. Thus, the multi-Langmuir–Freundlich equation in its linearized form was applied to the mixture data analysis (for simplicity we omitted the subscripts '(2) t' in a_i symbols):

$$a_1 + a_2 = \bar{a}_m - (a_1 + a_2)/[\bar{K}_1(p_1 + \bar{K}_{21} p_2)]^{\bar{m}} \qquad (33)$$

The results of prediction are shown in Fig. 6B. Theoretical lines are compared with the experimental points (triangles and a solid line for ethane (1) + ethylene (2) mixtures, circles and a dashed line for propane (1) + propylene (2) adsorption). A good agreement is observed, whereas the visible discrepancies seem to be caused by the difference in

Table III. *Parameters of the Langmuir–Freundlich isotherm [equation (31)] for single gas adsorption on Nuxit A1 (charcoal) at 293 K [20–22]*

The parameters for adsorption of gas mixtures predicted from single gas adsorption data and obtained from binary gas experimental data [equation (34)].

Adsorbate	LF equation (31) Single gases			LF equations (33) and $(27b)$ Predicted for mixtures				Equation (34)	
	$a_{m,i}$	m_i	$\ln \bar{K}_i$	$\bar{a}_m$	$\bar{m}$	$\ln \bar{K}_{21}$	m_{12}	$\ln \bar{K}_{21}$	m_{12}
Ethane (1)	152	0.62	−6.78	153	0.635	−0.30	0.995	−0.42	0.99
Ethylene (2)	154	0.65	−7.08						
Propane (1)	122	0.54	−4.26	125	0.56	−0.09	0.988	0.05	1.00
Propylene (2)	128	0.58	−4.35						

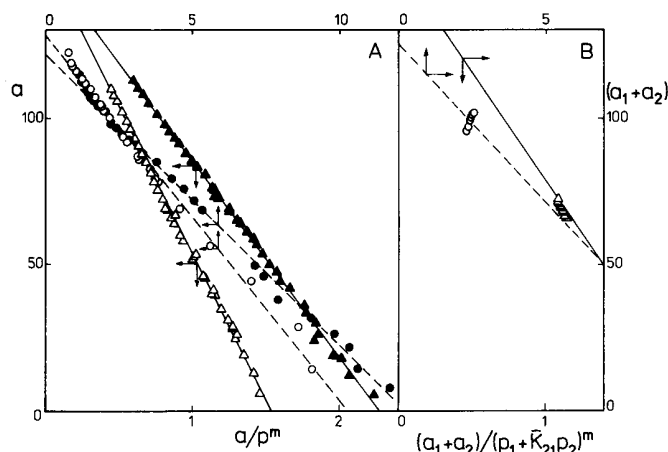$a(\text{cm}^3 \text{STP/g})$, p (Torr).

Fig. 6. Linear plots of Langmuir–Freundlich equations (32) and (33) for adsorption on Nuxit Al charcoal [25–27] at 293 K; $a(\text{cm}^3 \text{STP/g})$ and p (Torr). (A) Single gas adsorption of ethane (▲), ethylene (△) (———), propane (●) and propylene (○) (– – – –). (B) Mixed-gas adsorption of ethane (1)+ethylene (2) (△, ———) and propane (1)+propylene (2) (○, – – – –).

propane and propylene molecular sizes (see $a_{m,i}$ values in Table III). Additionally, to confirm the validity of assumption referring to the mixture components adsorption energy correlation [equations (7)–(9) (then $m_{12} \simeq 1$ and equation (27 a, b) are followed), we plotted the mixture data according to the linear form of equation (24 b), taking into account a certain dispersion of the energy difference distribution [31]:

$$\ln(a_1/a_2) = m_{12} \ln \bar{K}'_{12} + m_{12} \ln(p_1/p_2) \qquad (34)$$

The above equation is approximate; however, it is fully justified for the higher total coverages $[(a_1 + a_2)/\bar{a}_m]$, when only the competitive effects are important. The results presented in Fig. 7 and Table III fully confirm the validity of our assumptions, the values m_{12} are almost the same as predicted. The constants $\bar{K}'_{21} = 1/\bar{K}'_{12}$ for mixtures differ no more than 15% from the predicted values of $\bar{K}_{21} = \bar{K}_2/\bar{K}_1$. This difference may be caused by small differences in molecular sizes $(\bar{K}'_{12} \simeq \bar{K}_{12} a_{m,1}/a_{m,2})$ and by optimization errors.

In Fig. 8, the effect of the model non-correlation of adsorption energies for binary mixture components is presented for experimental binary data from Table III. It is evident that even small deviations from the full linear correlation $(r_{12} = 1)$ cause a strong decrease of the heterogeneity parameter m_{12}. For $r_{12} \ll 1$, a very strong heterogeneity can be observed, which confirms that for the experimental systems analysed the linear correlation is actual [see Table III, Fig. 7 and equation (34)].

Let us now analyse the single vapour and binary liquid mixture adsorption data of benzene and tetrachloromethane (CCL_4) on aerosil 303 K [32] and on macroporous silica gel KSK at 293 K [33]. First, we determined monolayer capacities for vapour and liquid mixture adsorption by using different methods. The results are presented in Table IV. In the case of systems with aerosil, we compared the $a_{m,i}$ values for BET equation [11] with the results obtained by using the slightly modified Lopez-Gonzales and Deitz (LGD) multilayer isotherm equation [11, 34]:

$$a_i = a_{m,i} \left[\frac{1 - (x_i)^{2/2}}{1 - x_i} \right] \cdot \left[\frac{K_{x,i} x_i/(1 - x_i)}{1 + K_{x,i} x_i/(1 - x_i)} \right]; \quad x_i = p_i/p_{s,i} \qquad (35)$$

where $p_{s,i}$ is the saturation pressure and $K_{x,i}$ is the constant connected with the usually used K_i constant $(K_{x,i} = K_i p_{s,i})$. Additionally, monolayer adsorption capacities found from the B-point method (for aerosil) and from the starting point of the capillary hysteresis loop [11, 35] (for silica gel) are given.

Figure 9 presents multilayer adsorption isotherms (black points) of benzene (solid lines) and tetrachloromethane

(dashed lines) on macroporous silica gel KSK [33] (Fig. 9A) and aerosil [32] (Fig. 9B). Desorption hysteresis loops are denoted by white points and dotted (for CCL_4) and dotted-dashed (benzene) curves. A starting point of the hysteresis loop (Fig. 9A) and B-point (Fig. 9B) for benzene are indicated by stretches. The corresponding values for carbon tetrachloride are calculated according to the ratio of adsorbate molar volumes (see Table IV). In further calculations, the mean values of LGD, BET and B-point methods (for aerosil) and the starting point of the hysteresis loop method value (for silica gel) were used (the BET values for macroporous silica gel were admitted to be too low in comparison with monolayer estimation for a suitable binary liquid mixture – see below; additionally, for the porous adsorbents, the BET method is not suitable [11, 35]).

Mean values for '1 + 2' systems are equivalent to the n^s monolayer capacity values (see Table IV) obtained for corresponding binary liquid mixtures using the Everett equation [36] in its linear form: $(x_1^t x_2^t/n_1^e)$ vs. x_1^t, where n_1^e is
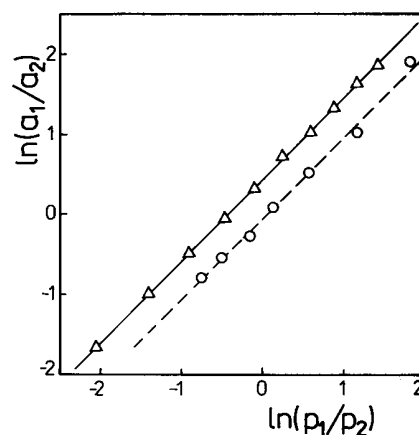

Fig. 7. Mixture gas adsorption data [27] plotted according to linear equation (34). Legend as in Fig. 6B.
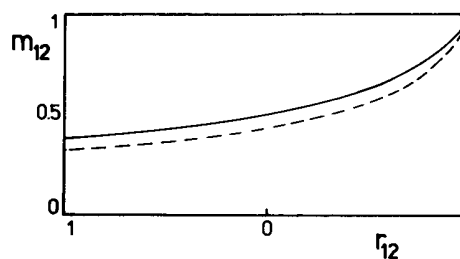

Fig. 8. Uncorrelation effect of adsorption energies of binary gas mixture components on the heterogeneity parameter m_{12} characterizing distribution function of E_{12}. Model curves are drawn vs. r_{12} [eqn. (30) and $\sigma(m)$ from Table I] for single gas parameters from Table III. Legend as in Fig. 6B.

Table IV. *Adsorption monolayer capacities $(mmol/g)$ for single vapours and binary liquid mixtures obtained by using various methods*

Adsorbent	Adsorbate	$a_{m,i}^{BET}$	$a_{m,i}^{LGD}$ [equation (35)]	$a_{m,i}{}^a$	$\overline{a_{m,i}}$	$\bar{a}_m$	n^s (Everett)
Aerosil [32]	Benzene (1)	0.599	0.601	0.60	0.600	0.567	0.55
(303 K)	CCl_4 (2)	0.511	0.578	0.52^b	0.536		
Silica gel KSK	Benzene (1)	1.08	—	1.38	1.38^c	1.33	1.33
(293 K) [33]	CCl_4 (2)	1.06	—	1.28^b	1.28^c		

^{a} Point B method [11] (aerosil) or method utilizing the beginning of hysteresis loop point [11, 35] (silica gel).
^{b} Calculated from the values for benzene adsorption according to the ratio of molar volumes of adsorbates.
^{c} BET results were not taken into consideration.

the surface excess. An analysis carried out according to the results of our previous papers [18, 28–30] led to the conclusion that the monolayer generalized-Freundlich equation [6, 18, 28–30] (see also Table I),

$$a'_i = a_{m,i}\{[\bar{K}_{x,i}\,x_i/(1-x_i)]/[1+\bar{K}_{x,i}\,x_i/(1-x_i)]\}^{m_i} \qquad (36)$$

$$x_i = p_i/p_{s,i}$$

with the multilayer LGD [equation (35)] or BET correction [6] were the best for single vapour adsorption data description. The parameters of equation (36) for single vapour adsorption are collected in Table V. In Figs. 10 and 11 the experimental single-vapour isotherms (black points) of benzene (1) and tetrachloromethane (2) on aerosil and silica gel KSK, respectively, are drawn in logarithmic coordinates ($\ln a$ vs. $\ln x$). White circles are drawn for the monolayer adsorption values calculated according to the LGD multilayer correction [equation (35)] [11, 34], i.e. $\ln a' = \ln [a(1-x)/(1-x^2/2)]$, whereas the dashed-dotted lines are drawn for the monolayer adsorption estimated according to the BET model [11] $\ln a' = \ln [a(1-x)]$ (both plotted against $\ln [x/(1-x)]$). Solid lines are the theoretical GF multilayer isotherms calculated according to equations (35) and (36) and para-
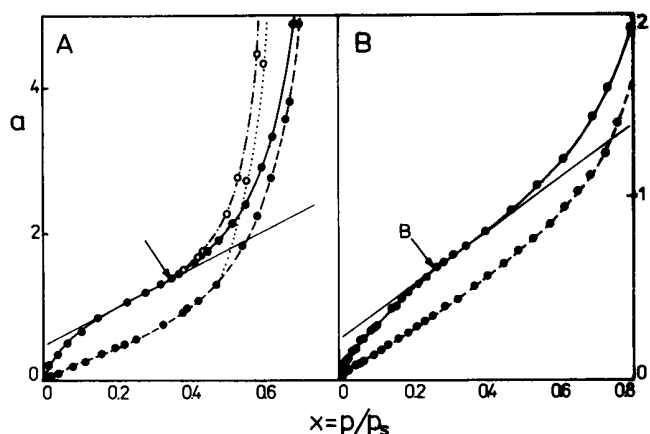
meters from Table V, whereas the dashed lines are the GF monolayer adsorption isotherms [equation (36)]. For all theoretical isotherms, a good correlation with the experimental data is observed (white points with dashed lines and black points with solid lines).

Let us now discuss details of prediction of adsorption from binary liquid mixtures for systems under consideration. According to Myers and Sircar [37], constant K_{21} in adsorption from a binary liquid mixture on a homogeneous solid surface may be obtained from the suitable BET constants of single vapour adsorption data

$$K_{21} = K_{x,2}/K_{x,1} \qquad (37a)$$

However, in the case of adsorption on heterogeneous solids, we may write [6]

$$\bar{K}_{21} = \bar{K}_{x,2}/\bar{K}_{x,1} \qquad (37b)$$

Assuming that for two GF distributions $r_{12} \simeq 1$ we get the heterogeneity parameters m_{12} for the mixtures according to the relationship in equation ($27b$), whereas the surface phase capacity n^s is assumed to be equal to the average of the mixture component monolayer capacities measured for vapour adsorption (Table V). In Table VI the predicted parameters of binary liquid mixture adsorption are collected. The theoretically predicted isotherms were compared with the experimental data by using a suitable linear form of GF [equation (36)] for binary solutions:

$$\ln\{(x^s_{1,t})^{1/m_{12}}/[1-(x^s_{1,t})^{1/m_{12}}]\} = \ln \bar{K}_{12} + \ln x^l_{12} \qquad (38a)$$

where

$$x^s_{1,t} = n^e_1/n^s + x^l_1 \qquad (38b)$$

Fig. 9. Adsorption isotherms (●) of benzene (——) and carbon tetrachloride (– – – –) on (A) the wide porous silica gel KSK [33] and (B) aerosil [32]. Desorption capillary hysteresis loops are denoted by white points and dotted lines (CCL₄) and dotted-dashed lines (benzene). Characteristic points of the isotherms are indicated by stretches; a in (mmol/g).
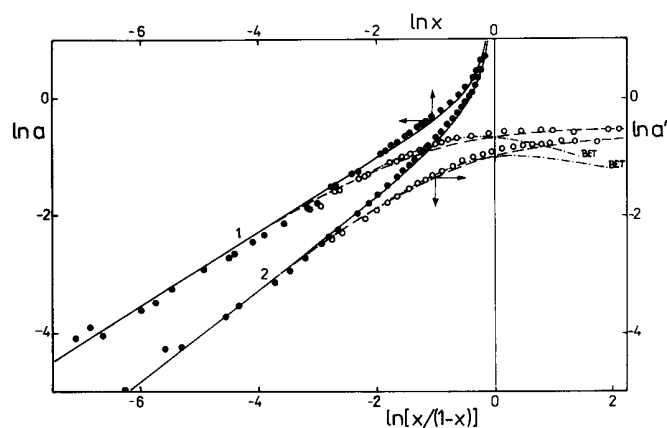

Fig. 10. Dependence $\ln a$ vs. $\ln x$ (——) for benzene (1) and carbon tetrachloride (2) vapour adsorption on aerosil at 303 K [32] (●). White points denote adsorption values calculated from the experimental points for LDG multilayer correction [eqn. (35)], however the dashed-dotted lines are drawn for the BET correction and the dashed ones are monolayer theoretical isotherms for GF equation (36) (parameters from Table V).
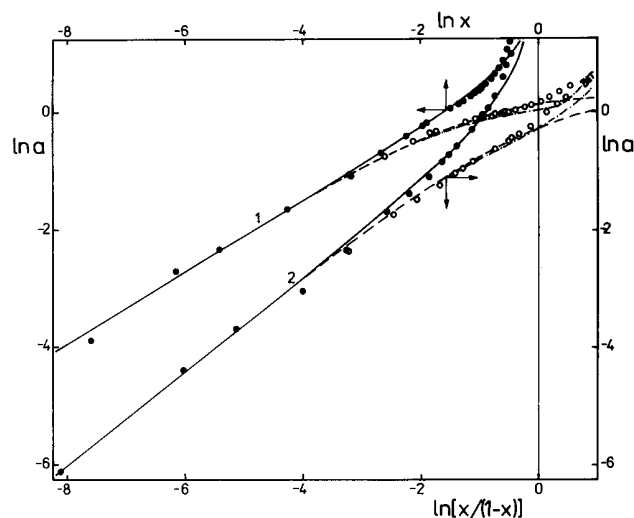

Fig. 11. Single vapour adsorption on wide porous silica gel at 293 K [33]. Legend as in Fig. 10.

Table V. *Parameters of* GF *equation* (36) *for benzene and* CCl₄ *single vapour adsorption on aerosil* [32] *and silica gel* KSK [33], ($\bar{a}_{m,i}$ *values are taken from Table IV*)

Adsorbent	Adsorbate	$\ln \bar{K}_{x,i}$	m_i	$\bar{a}_{m,i}$
Aerosil	Benzene	1.20	0.634	0.600
(303 K)	CCl₄	0.59	0.769	0.536
Silica gel KSK	Benzene	1.03	0.613	1.38
(293 K)	CCl₄	0.08	0.79	1.28

Table VI. *Comparison of parameters predicted from single vapour adsorption data and experimental parameters of* GF *equation* (38 a) *for the binary liquid mixture of benzene* (1) *and carbon tetrachloride* (2)

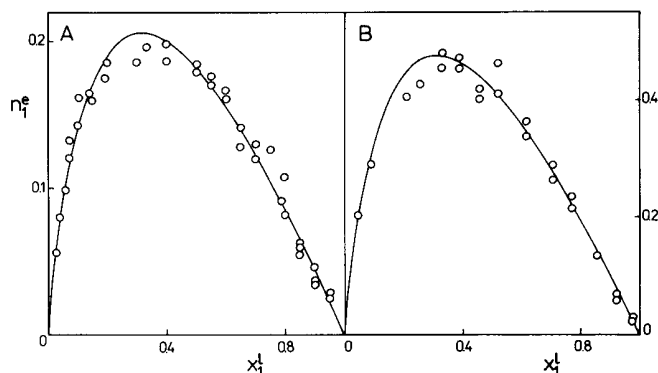| Adsorbent | Predicted from single vapour adsorption | | | exp [eqn. (38a)] |
	$\bar{n}^s = \bar{a}_m$	m_{12}	$\ln \bar{K}_{12}$	$\ln \bar{K}_{12}$
Aerosil [32]	0.567	0.938	0.61	1.45
Silica gel KSK [33]	1.33	0.89	0.95	1.35

Fig. 12. Benzene (1) + carbon tetrachloride (2) liquid mixture excess adsorption isotherms (O) on (A) aerosil [32] at 303 K; and (B) wide porous silica gel KSK [33] at 293 K. Solid lines are theoretical GF excess isotherms calculated according to the predicted $\bar{n}^s$, m_{12} values and experimental $\ln K_{12}$ values (see Table VI).

We found that the linearity was good and the slope close to unity, though the predicted and experimental values [i.e. from equation (38a)] of the equilibrium constants were distinctly different (see Table VI). In Fig. 12, the experimental excess isotherms for benzene (1)+carbon tetrachloride (2) liquid mixture on aerosil at 303 K [32] (Fig. 12A) and silica gel KSK at 293 K [33] (Fig. 12B) are compared with the theoretical GF isotherms with the predicted n^s, m_{12} values and $\ln \bar{K}_{12}$ values found from equation (38a) (Table VI). A good correlation is observed. Distinct discrepancy in the predicted and observed $\ln \bar{K}_{12}$ may be caused by optimization errors as well as by change of the bulk phase physical state (from vapour to liquid) or by neglecting the differences in molecular sizes [38]. However, as in the case of mixed-gas adsorption prediction, the heterogeneity parameters were predicted very well. Thus, the results obtained from analysis of adsorption data confirm the usefulness of the SAED method to predict the multicomponent adsorption equilibria on energetically heterogeneous solid surfaces.

Conclusions

A new form of the integral equation for multicomponent adsorption was proposed under the assumption of functional relations between adsorption energies of all components. In this way, the multiple integral was reduced to the single one which might be solved analytically or numerically. This equation enables simple prediction of adsorption from multicomponent mixtures by using parameters characterizing suitable single or binary systems. For some special cases, very simple (exact or approximate) relationships between the heterogeneity parameters of binary- and single-component

adsorption systems were obtained. The theory was checked by analysis of several experimental systems and theoretical prediction of adsorption was shown.

Appendix A. The Henry constant and its relation to adsorption energy distribution

Let us introduce the equilibrium constant written as [39].

$$K_G = \Theta_t/[p(1-\Theta_t)] \qquad (A\ 1)$$

Thus, the Henry constant K_H may be expressed as

$$K_H = \lim_{p \to 0} K_G \qquad (A\ 2)$$

From the integral equation (13) for single gas adsorption [(or equation (1)] we may easily obtain

$$K_H = \bar{K} \int_0^1 \exp[z(F)]\,dF = \bar{K} \cdot H(z) = K_0 \int_\Delta \exp(E)\chi(E)\,dE \qquad (A\ 3)$$

As it results from equation (A 3), the Henry constant K_H is not connected in a simple way with the maximal adsorption energy, but it is defined by the mean adsorption energy $\bar{E}$ and a function dependent on the energy distribution. An analogous function, let us call it the Langmuir constant, can be obtained for pressures tending to infinity:

$$K_L = \lim_{p \to \infty} K_G = \bar{K}/\int_0^1 \exp[-z(F)]\,dF = \bar{k}/H(-z) \qquad (A\ 4)$$

For the symmetrical distribution functions $\chi(E)$ we have $H(-z) = H(z)$; however, for asymmetrical we have $H(z) \neq H(-z)$. When the function $H(z)$ or $H(-z)$ tends to infinity, the corresponding isotherm equation does not obey Henry's law [equation (A 2)] or its analogue for high pressures [equation (A 4)]. For example, the Gaussian (G) distribution (see Table I) gives $H(z) = H(-z) = \exp(\sigma^2/2)$, when for LF distribution $H(-z) = H(-z) = +\infty$. The obtained values of K_H lie always between $\bar{K}$ and $K_0 \cdot \exp(E_{max})$ values. Taking this into account, the lateral interactions will affect only the K_L, but not the K_H, value.

Appendix B. Temperature dependence of heterogeneity parameters

Let us assume that energy distribution defined in terms of the adsorption energy $\epsilon = ERT$. ($E =$ reduced energy) remains invariant with temperature changes. Then the energy dispersion σ_ϵ

$$\sigma_\epsilon^2 = \int_\Delta (\epsilon - \bar{\epsilon})^2 \chi(\epsilon)\,d\epsilon \qquad (A\ 5)$$

will be temperature independent quantity. Thus, the reduced energy dispersion σ [equation (12b)] will be expressed as follows:

$$\sigma(T_2) = \sigma_\epsilon/RT_2 = \sigma(T_1) \cdot T_1/T_2 \qquad (A\ 6)$$

Knowing the dependence of the heterogeneity parameter on the reduced energy dispersion (see Table I), we can write characteristic equations for different energy distribution

functions, for example for the Freundlich and Rudziński's distributions

$$m(T_2) = m(T_1) \cdot T_2/T_1 \tag{A 7}$$

whereas for LF, Tóth and GF equations

$$[m(T_2)]^{-2} = (T_1/T_2)^2 \{[m(T_1)]^{-2} - 1\} + 1 \tag{A 8}$$

For the Gaussian distribution, this dependence is defined directly by equation (A 6).

Appendix C. Quality of approximation of the energy distribution

In many cases, the experimental adsorption isotherms are described by different theoretical equations involving heterogeneity effects with almost the same accuracy. Moreover, even very advanced numerical methods of energy distribution evaluation give apparently different solutions [6]. Our method allows the possibility of estimation of these inaccuracies and simple evaluation of the differences in discrete and continuous distribution functions. Assuming that a continuous distribution, having maximum and minimum energies, is approximated by a discrete k-centred distribution with the same mean energy and dispersion $\sigma_{dis} = \sigma_{cont}$ and constant differences of centre energies $(E_{i+1} - E_i = (E_{max} - E_{min})/k$, $i = 1, ..., k-1)$, thus from equation $(22a, b)$ we have

$$\sigma_{dis, cont}/\sigma_{cont} = 1/k \tag{A 9}$$

Acknowledgement

Nomenclature

a	adsorption amount
a'	monolayer adsorption amount calculated from experimental value by using the BET or LGD [equation (35)] models
a_m	monolayer capacity for gas adsorption
c	mol concentration
E	reduced energy of adsorption
F	integral distribution function of adsorption energy
G_z	function defined by equation (20)
H	function defined by equation (A 3)
k	parameter of discrete square-shaped energy distribution function
K	equilibrium constant of Langmuir-type [equation (11)] and Everett [equation (15a)] local isotherms
k_0	entropy factor
m	heterogeneity parameter
n^e	adsorption excess
n^s	monolayer capacity for liquid adsorption
p	gas pressure
p_s	saturation pressure
r_{12}	correlation coefficient of energy distribution functions χ_1 and χ_2

R	gas constant
T	temperature
x	mol fraction; relative pressure
z	variable defined by equation (13)
ϵ	adsorption energy
ΔE	parameter of square-shaped energy distribution
Δ	energy integration region
Θ	surface coverage
χ	differential distribution function of adsorption energy
σ	reduced energy dispersion
σ_ϵ	energy dispersion

bold italic character denotes vector index (e.g. E, n, ε, etc.)

Superscripts

l	bulk phase
s	surface phase

overbar denotes mean value or its derivative (e.g. $\bar{E}$, $\bar{K}$, etc.)

Subscripts

G	index for quantity defined by equation A 1
H	index for Henry constant [equation (A 2)]
i, j, k, n	component index
l	local variable
L	index of constant defined by equation (A 4)
max	maximum value
min	minimum value
n	number of mixture components
(n)	index for n-component mixture
t	global variable
w	water index
(w)	index for water dilute solution
x	index for vapour equilibrium constant multiplied by saturation pressure value [equation (35)] (analogous to BET constant)

Composite subscripts

ij, in, jn	difference of single-component variables (ϵ, z, E)
ij	ratio of single-component variables (x, K)

References

1. Ross, S. and Olivier, J. P., *On Physical Adsorption*. Wiley, New York (1964).
2. Jaroniec, M., Patrykiejew, A. and Borowko, M., *Progress in Surface and Membrane Sci.* **14**, 1–68 (1981).
3. Derylo-Marczewska, A., Jaroniec, M., Gelbin, D. and Seidel, A., *Chem. Scr.* **24**, 239 (1984).
4. Borowko, M. and Jaroniec, M., *Advan. Colloid Interface Sci.* **19**, 137 (1983).
5. Jaroniec, M., Martire, D. E. and Borowko, M., *Advan. Colloid Interface Sci.* **22**, 177 (1985).
6. Jaroniec, M., *Advan. Colloid Interface Sci.* **18**, 147 (1983).
7. Roginsky, S. and Todes, O., *Acta Physicochim. URSS* **20**, 307 (1945).
8. Roginsky, S. and Todes, O., *Acta Physicochim. URSS* **20**, 695 (1945).
9. Glueckauf, E., *J. Chem. Soc., Faraday Trans.* **49**, 1066 (1953).
10. Tompkins, F. C. and Young, D. M., *J. Chem. Soc., Faraday Trans.* **47**, 88 (1951).
11. Young, D. M. and Crowell, A. D., *Physical Adsorption of Gases*. Butterworths, London (1962).
12. Cook, W. H. and Basmadjian, D., *Can. J. Chem. Eng.* **43**, 78 (1965).

13. Myers, A. L. and Prausnitz, J. M., *AIChE J.* **11**, 121 (1965).
14. Minka, C. and Myers, A. L., *AIChE J.* **19**, 453 (1973).
15. Radke, C. J. and Prausnitz, J. M., *AIChE J.* **18**, 761 (1972).
16. Jossens, L., Prausnitz, J. M., Fritz, W., Schluender, E. U. and Myers, A. L., *Chem. Eng. Sci.* **33**, 1097 (1978).
17. Rosene, M. R. and Manes, M., *J. Phys. Chem.* **80**, 953 (1976).
18. Jaroniec, M. and Marczewski, A. W., *Mh. Chem.* **115**, 997 (1984).
19. Rudziński, W., Narkiewicz-Michalek, J., Schöllner, R., Herden, H. and Einicke, W. D., *Acta Chim. Acad. Sci. Hung.* **113**, 207 (1983).
20. Jaroniec, M., *Colloid and Polymer Sci.* **255**, 32 (1977).
21. Jaroniec, M., Narkiewicz, J., and Rudziński, W., *J. Colloid Interface Sci.* **65**, 9 (1978).
22. Jaroniec, M., *J. Colloid Interface Sci.* **53**, 422 (1975).
23. Mueller, G., Radke, C. J. and Prausnitz, J. M., *J. Colloid Interface Sci.* **103**, 484 (1985).
24. Mueller, G., Radke, C. J. and Prausnitz, J. M., *J. Colloid Interface Sci.* **103**, 484 (1985).
25. Szepesy, L. and Illés, V., *Acta Chim. Acad. Sci. Hung.* **35**, 37 (1963).
26. Szepesy, L. and Illés, V., *Acta Chim. Acad. Sci. Hung.* **35**, 53 (1963).
27. Szepesy, L. and Illés, V., *Acta Chim. Acad. Sci. Hung.* **35**, 245 (1963).
28. Marczewski A. W. and Jaroniec, M., *Mh. Chem.* **114**, 711 (1983).
29. Jaroniec, M. and Marczewski, A. W., *Mh. Chem.* **115**, 997 (1984).
30. Marczewski, A. W., Derylo-Marczewska, A. and Jaroniec, M., *Przem. Chem.* (in the press).
31. Jaroniec, M. and Marczewski, A. W., *Thin Solid Films* **92**, 385 (1982).
32. Kurbanbeknov, E., *Kand. Diss.*, Moskva (1971).
33. Kazaryan, S. A., Larionov, O. G. and Chmutov, K. V., *Zh. Fiz. Khim.* **51**, 188 (1977).
34. Lopez-Gonzalez, J. deD. Deitz, V. R., *J. Research Nat. Nur. Standards* **48**, 325 (1952).
35. Avgul, N. N., Dzhigit, O. M., Dreving, V. P., Guriev, M. V., Kiselev, A. V. and Likhacheva, O. A., *Dokl. Aka. N. SSSR* **77**, 77 (1951).
36. Everett, D. H., in Colloid Science (ed. D. H. Everett), *Specialist Periodical Reports*, vol. 1. Chem. Soc., London (1973).
37. Myers, A. L. and Sircar, S., *J. Phys. Chem.* **76**, 3415 (1972).
38. Marczewski, A. W., Derylo-Marczewska, A. and Jaroniec, M., *J. Colloid Interface Sci.* **109**, 310 (1986).
39. Graham, D., *J. Phys. Chem.* **57**, 665 (1953).