

Jan T. Duda · Mirosław Kwiatkowski  
Janina Milewska-Duda

## Computer modeling and analysis of heterogeneous structures of microporous carbonaceous materials

Received: 15 January 2005 / Accepted: 2 March 2005 / Published online: 9 July 2005  
© Springer-Verlag 2005

**Abstract** The aim of this work was to study the problems connected with computer modeling and analysis of heterogeneous structures of microporous carbonaceous materials. The research was focused on the numerical properties of original mathematical models for heterogeneous multilayer adsorption on microporous carbonaceous materials presented in our earlier papers and their applicability to examination of real microporous materials. These models are aimed at drawing information on pore structure and capacity on the basis of adsorption isotherms of small molecule adsorbates. They easily fit typical adsorption data in wide relative pressure ranges. In the theory presented, adsorption of small nearly spherical molecules in irregular pores of molecular size has been considered and side adsorbate–adsorbate interactions are neglected. The molecules mentioned are located in pores by forming aggregates, the size of which is limited by the geometry of the pores. The set of adsorbate molecules, which were adsorbed mainly due to adhesive interactions with the adsorbent matter, is treated as the first layer adsorption. Joining further molecules is viewed as the second, third,... layer adsorption. The main idea of the approach to modeling microporous structure presented, consists of introducing of realistic relationships between geometrical properties of pores and adsorption energy. Special attention was focused on the analysis of the influence of the number of model parameters on identification reliability and evaluation

errors of porous structure parameters. This paper gives more information on properties of the identification technique presented in our earlier papers. The five-parameter and six-parameter identification reliability is analyzed in more detail, for different values of the system parameters. In this context, the efficiency of simultaneous examination of two isotherms is also studied.

**Keywords** Adsorption · Heterogeneous · Microporous · Isotherms · Optimization

### Introduction and theoretical basis

Modeling of adsorption processes on solid surfaces is of vital interest in surface science and chemical technology. Microporous activated carbons are widely used as adsorbents, catalysts, and supports [1, 2]. Generally, the use of such materials in various fields of technology and science requires their characterization, which comprises determination of chemical composition, description of porosity, surface texture and energetic heterogeneity.

Many theories of adsorption processes have been described [3, 4]. Together with the development of computer techniques, more advanced methods of pore-structure description have been used. They use high-tech numerical tools, e.g. optimization algorithms [5–7], advanced molecular simulations [8–10] and approaches based on fractal geometry [11–14].

In microporous carbonaceous adsorbents (such as active carbons, molecular sieves and carbon fibers), the adsorption process is much more intensive in micropores, which have a high-adsorption potential, than in larger pores. Hence, the adsorption capacity and energy distribution are linked with geometrical properties of the pores. To exploit this fact in examination of such materials, a mathematical description of the heterogeneous adsorption process was developed that involves

J. T. Duda  
Faculty of Management, AGH-University of Science  
and Technology, Al. Mickiewicza 30,  
30-059 Kraków, Poland  
E-mail: jdu@ia.agh.edu.pl

M. Kwiatkowski · J. Milewska-Duda (✉)  
Faculty of Fuels and Energy, AGH-University of Science  
and Technology, Al. Mickiewicza 30,  
30-059 Kraków, Poland  
E-mail: kwiatkow@agh.edu.pl  
E-mail: milewska@agh.edu.pl  
Tel.: +48-12-6172117

explicitly parameters characterizing the geometrical structure of pores and appropriate geometry–energy relationships [15].

The models for heterogeneous adsorption on microporous carbonaceous materials described briefly in this paper are based on general thermodynamics, expressing changes of internal energy  $\Delta H$  and configurational entropy  $\Delta S$  due to the process [15–20]. A wider discussion, thermodynamic derivation and theoretical basis were presented in our earlier papers [15–20]. Adsorption of small nearly spherical molecules in irregular pores of molecular size is considered. The molecules are located in pores by forming aggregates, the size of which is limited by the geometry of the pores. In our approach the set of adsorbate molecules, which are adsorbed mainly due to adhesive interactions with the adsorbent matter, is treated as the first layer adsorption. Joining further molecules is viewed as the second, third,... layer adsorption [15–20]. The aggregates are formally constructed by adding consecutive layers in equilibrium with the volatile phase. A set of pore geometry–adsorption energy relationships was proposed and checked by multivariant fitting of the model to adsorption data.

The approach is addressed to the examination of adsorbents of random porous structure. It may be viewed as an alternative to classical techniques based on the BET or DR equations and on the other hand, to more complicated DFT-based techniques [5–7].

The paper presents a study of the numerical properties of the proposed adsorption models from the system-parameter identification perspective. Factors affecting the model parameter evaluation uncertainty are analyzed, and a technique for the identification reliability assessment is proposed.

### The *uniLET* model

The adsorption process in submicroporous and microporous materials may be considered as consisting of a number of sub-processes each of them involving  $m_{pa}$  moles of adsorbate molecules with the same energy. At a temperature  $T$  and pressure  $P$ , the sorption equilibrium in the  $a$ th subprocess can be described generally with the following formula [16]:

$$RT \ln(\pi) = \frac{\partial \Delta H}{\partial m_{pa}} - T \frac{\partial \Delta S}{\partial m_{pa}} \quad (1)$$

where  $m_{pa}$  is the amount of adsorbate in  $a$ th subsystem (mol/g),  $R$  is the gas constant,  $\pi = f/f_s$  stands for the relative fugacity of sorbate at  $(P, T)$ ,  $\Delta H$  and  $\Delta S$  are the total enthalpy and entropy change, respectively, due to the process,  $a$  is the  $a$ th adsorption subsystem.

The general *uniLBET* model describing the local adsorption isotherm on a  $k$ th type primary site is given in the form of the following algebraic equations written for the layers  $n = 1, \dots, k$  [19]:

$$-\Pi_{\kappa n}^* + (\Pi_{\kappa n}^* + 1) \cdot \theta_{\kappa n} - \theta_{\kappa n} \cdot \theta_{\kappa n+1} = 0, \quad \theta_{\kappa k+1} \equiv 0 \quad (2)$$

$$\Pi_{\kappa n}^* \stackrel{\text{def}}{=} \frac{\pi}{B_{\kappa n} (1 - \theta_{\kappa n+1})^{\beta_{\kappa n+1}-1}}, \quad \pi - \text{relative pressure} \quad (3)$$

where  $k$  is the maximum number of layers,  $\kappa$  counts different energy profiles across the layers  $n = 1, \dots, k$  of  $k$ th type agglomerates,  $\theta_{\kappa n}$  is the coverage ratio of  $(n - 1)$ th layer in agglomerates of  $\kappa$ th class:  $\theta_{\kappa n} = (m_{p\kappa n})/(\beta_{\kappa n} \cdot m_{p\kappa n-1})$ ,  $\beta_{\kappa n}$  is the pore shape factor ( $\beta_{\kappa n} = 1$  for stack-like agglomerates  $\beta_{\kappa n} > 1$  for branched ones),  $B_{\kappa n}$  is the energetic parameter of  $(\kappa n)$ th subsystem:  $B_{\kappa n} = \exp(Q_{\kappa n}/RT)$ ,  $Q_{\kappa n}$  is the molar energy contributed to the system by placing an adsorbate molecule at  $(\kappa, n)$ th subsystem, and  $\Pi_{\kappa n}^*$  is the transformed relative pressure. The coverage ratios  $\theta_{\kappa n}$  can be calculated recursively, starting from the top ( $k$ )th layer [19]:

$$\theta_{\kappa k} = \frac{\pi}{\pi + B_{\kappa k}}, \quad \theta_{\kappa n} = \frac{\Pi_{\kappa n}^*}{1 + \Pi_{\kappa n}^* - \theta_{\kappa n+1}}, \quad (4)$$

for  $n = k - 1, \dots, 1, \quad \theta_{\kappa k+1} \equiv 0$

To make the *uniLBET* model useful in examination of real adsorption systems, it is necessary to reduce the number of independent parameters. To this aim, additional relationships linking geometrical parameters and adsorption energy with adsorbent structure were proposed [19]. This leads to the *uLBET* model.

### The *uLBET* model

The following assumptions concerning the energy distribution were made:

- (a) The layers  $n = 2, k$  are homogeneous and  $B_{\kappa n} = B_C = \text{const.}$  for  $k = 1, \dots, K, n = 2, k - 1$

$$B_C \stackrel{\text{def}}{=} \exp(Q_C/RT), \quad Q_C \stackrel{\text{def}}{=} U_p(1 - 2 \cdot Z_{pp}) - Z_C \cdot Q_{cp} \quad (5)$$

where  $Q_{cp}$  is the molar adhesion energy in ideal adsorbent–adsorbate contacts,  $U_p$  is the molar cohesion energy of adsorbate, and  $Z_{pp}$  and  $Z_C$  are the correcting factors.

- (b) For  $n = k$ :  $B_{\kappa k} < B_C$  such that  $\theta_{\kappa k} = \Pi_{\kappa n}^*$  (1st type top layer adsorption) or  $B_{\kappa k} = B_C$  (2nd type top layer adsorption—see Ref. [19]).

- (c) The first layer adsorption energy is expressed in the following form:

$$Q_{A\kappa} = U_p - Z_{A\kappa} \cdot Q_{cp}, \quad Q_A \stackrel{\text{def}}{=} U_p - Z_A \cdot Q_{cp} = \min_{k=1} (Q_{A\kappa}) \quad (6)$$

and the factor  $Z_{A\kappa}$  is uniformly distributed over a range depending on  $k$ :

$$Z_{Ak} \in \langle Z_A(1 - \zeta_{Ak}), Z_A(1 - \zeta_{fk}) \rangle, \zeta_{Ak} \geq \zeta_{Ak+1}, \zeta_{fk} \geq \zeta_{fk+1}, 0 \leq \zeta_{fk} \leq \zeta_{Ak}, \zeta_{A1} \equiv 1.$$

The distribution function related to the energetic parameter  $B_{A\kappa} \in (B_{Ak}, B_{fk})$  is

$$B_{Ak} \stackrel{\text{def}}{=} B_A \cdot (B_{cp})^{Z_A(1-\zeta_{Ak})}, \quad B_{fk} \stackrel{\text{def}}{=} B_A \cdot (B_{cp})^{Z_A(1-\zeta_{fk})},$$

$$f_k(B_{A\kappa}) = \frac{m_{hAk}}{\ln(B_{fk}/B_{Ak})} \frac{1}{B_{A\kappa}} \quad (7)$$

where  $m_{hA\kappa}$  is the amount of  $\kappa$  type primary sites (mmol/g), and

$$B_A \stackrel{\text{def}}{=} \exp(Q_A/RT), \quad B_{cp} \stackrel{\text{def}}{=} \exp(Q_{cp}/RT) \quad (8)$$

Moreover, we assume that

(a) an averaged pore shape factor  $\beta$  may be used to describe possible branching of agglomerates adequately

$$\beta_{kn} = \beta \quad \text{for } k > 1, \quad n = 2, \dots, k \quad (9)$$

(b) the number of primary adsorption sites capable of retaining agglomerates limited to  $k$ -layers is expressed by the exponential function [16, 19]:

$$m_{hAk} = m_{hA}(1 - \alpha)\alpha^{k-1}, \quad \alpha \in (0, 1) \quad (10)$$

The *uniBET* model (4) containing the above assumptions takes the following form (11) referred to as the *uLBET* formula [19]:

$$m_p = m_{hA}(1 - \alpha) \left\{ 1 - \frac{1}{\ln(B_A/B_{f1})} \ln \left( \frac{B_A + \pi}{B_{f1} + \pi} \right) \right\}$$

$$+ m_{hA}(1 - \alpha) \sum_{k=2}^K \alpha^{k-1} \left( 1 + \sum_{n=2}^k \prod_{j=2}^n (\beta \theta_{kj}) \right)$$

$$\times \left\{ 1 - \frac{1}{\ln(B_{Ak}/B_{fk})} \ln \left( \frac{B_{Ak}(1 - \theta_{k2})^\beta + \pi}{B_{fk}(1 - \theta_{k2})^\beta + \pi} \right) \right\} \quad (11)$$

where  $m_{hA}$  is the total number of the primary sites.

Two top-layer adsorption types are considered, corresponding to the different nature of restrictions for the adsorbate agglomerate size represented by  $k$ . If the restrictions are of formal nature (a competitive adsorption in larger pores) the generalized Henry's law is applicable (1st adsorption type). Thus for  $k > 1, j > 1$ :  $\theta_{kj} = \theta = \Pi_\infty^*$ , where  $\Pi_\infty^* \in (0, 1/\beta)$  is the lower root of the following equation:

$$B_C \Pi_\infty^* = \pi(1 - \Pi_\infty^*)^{1-\beta} \quad (12)$$

If the restrictions are of geometrical/energetic nature (2nd adsorption type) the ratio  $\theta_{kj}$  is expressed by Eq. 4, i.e. starts from the *Langmuir* model at the  $k$ th layer and tends to  $\Pi_\infty^*$ .

To make model (11) useful for practical examination of adsorbent structures, we should ensure its identifiability. This means that the model parameters should be reliably determinable by fitting the model to empirical adsorption data. Let  $N$  denote the number of empirical data  $\{m_{pn}, n = 1, \dots, N\}$ , and  $f(\pi_n, A)$  stand for an isotherm formula, involving a vector  $A$  of unknown parameters  $A = \{a_i, i = 1, \dots, M\}$ , and producing theoretical values of adsorption for particular  $\pi_n$ , when values  $A_o$  of the vector  $A$  are taken. Let  $J$  denote the  $N \times M$  Jacobian matrix:

$$J = \begin{bmatrix} \frac{\partial f(\pi_1, A_o)}{\partial a_1} & \dots & \frac{\partial f(\pi_1, A_o)}{\partial a_M} \\ \vdots & \dots & \vdots \\ \frac{\partial f(\pi_N, A_o)}{\partial a_1} & \dots & \frac{\partial f(\pi_N, A_o)}{\partial a_M} \end{bmatrix} \quad (13)$$

The model  $f(\pi, A)$  is well identifiable, if  $\text{rank}(J) = M$  and the matrix  $J$  is well conditioned. Otherwise, the model is overparametrized, i.e. there is a subset of parameters, that are undeterminable at all (if  $\text{rank}(J) < M$ ) or their values are much too sensitive to empirical and numerical errors. This is because effects of the particular excessive parameters to the sequence  $f(\pi_n, A)$  are poorly diversified. In effect, a fitting quality index (e.g. mean squared error) applied in identification procedures is too insensitive to changes of the parameters within an area, providing no preferences for accurate enough values. If enlarging the data range (by employing more measurements or taking a greater  $\max(\pi)$ ) does not solve the problem, it is necessary to put additional relationships linking some parameters or set the poorly determinable parameters arbitrarily, thus making evaluation of the remaining ones more reliable.

In microporous materials, a surface fraction of high  $Q_{A\kappa}$  is usually of weak effect on the isotherm shape, even if  $\max(\pi) \approx 1$ . This makes essential formal obstacles for reliable empirical evaluation of the right hand side profile of the energy distribution function. In turn, the fraction of smallest agglomerates ( $k = 1-3$ ) is often highly dominant. Hence, the parameters  $Z_A, \zeta_{A2}, \zeta_{A3}$  and  $\zeta_{f1}, \zeta_{f2}$  may be of significant effect, mainly to an initial section of isotherms. Hence, we proposed to avoid the energy distribution over parameterizations in the following way:

1.  $Z_A$  is treated as the key parameter to be evaluated by the model-fitting procedure.
2. The step points of the distribution function (values for  $Q_{Ak}$  and  $B_{Ak}$ ) are fixed arbitrarily by setting the coefficients  $\zeta_{f1}, \zeta_{Ak}$  and  $\zeta_{fk}$  for  $k = 2, \dots, K$ :
  - (a) Adsorption of single molecules is always treated separately by using the Langmuir formula with the individual parameter  $\zeta_{f1}$  producing  $B_{f1}$ .
  - (b) The isotherm for  $k = 2$  is treated optionally: either as a separate model with individual parameters  $\zeta_{A2}$  and  $\zeta_{f2}$  (option  $d = 1$ ) or together with remaining agglomerates  $k > 2$  (option  $d = 0$ ) with the same

**Table 1** Settings of the energy distribution function parameters  $\zeta_{A2}$ ,  $\zeta_{Ak}$ ,  $\zeta_{f1}$ ,  $\zeta_{f2}$  and  $\zeta_{fk}$  for particular surface heterogeneity variants  $\{h, d, \eta\}$  [19, 20]

	$h = 0$	$h = 1$	$h = 2$	$h = 3, 4, \dots, 9$		
$\zeta_{A2}$	1	1	1	$1 - (h - 3)/120$		
$\zeta_{Ak}, k > 2$	1	1	1	$d = 0$	$D = 1$	
$\zeta_{f1}$	1	$\zeta_{f\infty}$	1	$1 - (h - 3)/120$	$1 - (h - 3)/48$	
$\zeta_{f2}$	1	$\zeta_{f\infty}$	$\zeta_{f\infty}$	$1 - (1 - \zeta_{f\infty})(h - 3)/24$	$\eta = 0$	$\eta = 1$
$\zeta_{fk}, k > 2$	1	$\zeta_{f\infty}$	$\zeta_{f\infty}$	$((\zeta_0 - \zeta_{f\infty})/(2))$ $+ \zeta_{f\infty}, \zeta_0 = \{1, \zeta_{A2}\}$	$1 - 11 \cdot (1 - \zeta_{f\infty})(h - 3)/120$ $(\zeta_0 - \zeta_{f\infty})((3/4) - ((h - 3)/(24)))$ $+ \zeta_{f\infty}, \zeta_0 = \{1, \zeta_{A2}\}$	$1 - (1 - \zeta_{f\infty})(h - 3)/8$ $(\zeta_0 - \zeta_{f\infty})((7/8) - ((h - 3)/(48)))$ $+ \zeta_{f\infty}, \zeta_0 = \{1, \zeta_{A2}\}$
				$((\zeta_0 - \zeta_{f\infty})/(k))$ $+ \zeta_{f\infty}, \zeta_0 = \{1, \zeta_{A2}\}$	$((\zeta_0 - \zeta_{f\infty})/(k))$ $+ \zeta_{f\infty}, \zeta_0 = \{1, \zeta_{A3}\}$	$((\zeta_0 - \zeta_{f\infty})/(k - 1))$ $+ \zeta_{f\infty}, \zeta_0 = \{1, \zeta_{A3}\}$

$\zeta_{Ak} = \zeta_{A2}$  and  $\zeta_{fk}$  calculated in the same manner as for  $k > 2$ .

- (c) For all clusters of  $k \geq 2 + d$ , the distribution function starts at the same point  $\zeta_{Ak} = \zeta_{A2+d}$ . The right hand side limits of the distribution  $\zeta_{fk}$  for  $k \geq 2 + d$  are expressed as a simple function of  $k$ , enabling fast calculations of the model with large  $K$ .
- 3. The identification of the model is proposed to be performed for a number of properly diversified variants of the energy distribution function, each of them having fixed values of  $\zeta_{f1}$ ,  $\zeta_{Ak}$  and  $\zeta_{fk}$  for  $k > 1$ .
- 4. A variant is generated by taking a combination of three integer parameters, i.e. the heterogeneity type  $h = 0, \dots, 9$ , the doublets treatment binary option  $d = 0, 1$  and a binary option  $\eta = 0, 1, \eta \leq d$ .
- 5. A couple of well-fitted variants (e.g. 3) may be used to assess the reliability of the identification results. If there is a variant giving an acceptable fitting quality much better than others, or model parameters and energy distribution shape are close for all variants in the couple, the best one may be accepted as showing reliably the system properties examined. Otherwise, we can only say that the system is poorly identifiable, and the acceptable variants may be viewed as alternative representations of its properties, or identification using more measurement.

The formulae proposed to calculate the parameters  $\zeta_{f1}$ ,  $\zeta_{Ak}$  and  $\zeta_{fk}$  for particular sets  $\{h, d, \eta\}$  are gathered in Table 1. The parameter  $\zeta_{f\infty}$  (a minimum value for  $\zeta_{fk}$ ) determines the smallest contact surface area that enables a place on a pore surface to be the primary adsorption site. One may assume that primary and secondary sites on the surface are strictly separated, i.e.  $\zeta_{f\infty} = Z_C/Z_A$  (see Eq. 5). This reduces the number of the model parameters. However, in general, the parameter  $\zeta_{f\infty}$  should be treated as independent (in fact,  $\zeta_{f\infty} > Z_C/Z_A$  is rather likely). Thus, the *uLBET* model involves five or six parameters:  $m_{hA}$ ,  $Z_A$ ,  $\alpha$ ,  $\beta$ ,  $B_C$  and optionally  $\zeta_{f\infty}$ , to be adjusted by fitting the model to empirical adsorption data, with a chosen variant  $\{h, d, \eta\}$  of the surface energy distribution function [19–24].

**The models of *LBET* type**

Examination of adsorption systems of random microporous structures needs a large number  $K$  in Eq. 11 to be taken (often  $K > 100$ ). It makes the identification procedures time consuming (isotherms have to be calculated thousands of times). Thus, to speed up the calculations, analytical formulae approximating the *uLBET* model were determined (referred to as the models of *LBET* type).

For heterogeneous adsorption the *uLBET* model can be brought into an analytical form, providing that: (a) the energetic parameters  $B_{Ak}$  and  $B_{fk}$  do not depend on  $k$  for  $k > 1 + d$ ; (b) the coverage ratios  $\theta_{kn}$  are the same ( $\theta_{kn} = \theta$ ) for all  $k > 1 + d, n > 1 + d$ . For  $k > 1 + d$  we have  $B_{Ak} = B_{A2+d}$ . Effect of  $k > 1 + d$  on  $B_{fk}$  has to be eliminated, but  $B_{fk}$  may be dependent on  $\theta$ . Thus we have to find  $B_{f\theta} \equiv B_{fk}$ .

The resultant heterogeneous adsorption model of *LBET* type has the following form:

$$\begin{aligned} \frac{m_p}{m_{hA}} = & (1 - \alpha) \left\{ 1 - \frac{1}{\ln(B_A/B_{f1})} \cdot \ln \left( \frac{B_A + \pi}{B_{f1} + \pi} \right) \right\} \\ & + d \cdot \alpha(1 - \alpha)(1 + \beta\theta_2) \\ & \times \left\{ 1 - \frac{1}{\ln(B_{A2}/B_{f2})} \ln \left( \frac{B_{A2}(1 - \theta_2)^\beta + \pi}{B_{f2}(1 - \theta_2)^\beta + \pi} \right) \right\} \\ & + \alpha^{d+1} \left[ d + (\beta\theta)^d \left( 1 + \frac{\beta\theta}{1 - \alpha\beta\theta} \right) \right] \\ & \times \left\{ 1 - \frac{1}{\ln(B_{A2+d}/B_{f\theta})} \ln \left( \frac{B_{A2+d}(1 - \theta)^\beta + \pi}{B_{f\theta}(1 - \theta)^\beta + \pi} \right) \right\} \end{aligned} \tag{14}$$

We define a quantity  $\Pi^*$ :

$$\Pi^* \stackrel{\text{def}}{=} \frac{\pi}{B_C(1 - \theta)^{\beta-1}} \tag{15}$$

For the 1st type adsorption  $\theta = \Pi^* = \Pi_\infty^*$ . Thus no simplifications are needed.

For the 2nd type, the following averaging formula was found to be appropriate:

**Table 2** Options generating the variants of the surface energy distribution used in calculations

Options	Variants of <i>LBET</i> model used to fit data ( $h_{\text{fit}}, \zeta_0 = \zeta_{A2+d}$ ) and of <i>LBET</i> or <i>uLBET</i> model producing data ( $h_{\text{dat}}, \zeta_0 = 1$ )																													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
$h_{\text{fit}}$	0	1	2	3	3	3	5	5	5	7	7	7	9	9	9	0	1	2	3	3	3	5	5	5	7	7	7	9	9	9
$h_{\text{dat}}$	0	1	2	3	3	3	4	4	4	6	6	6	8	8	8	0	1	2	3	3	3	4	4	4	6	6	6	8	8	8
$d$	0	0	0	0	1	1	0	1	1	0	1	1	0	1	1	1	0	0	0	1	1	0	1	1	0	1	1	0	1	1
$\eta$	-	-	-	0	1	0	0	1	0	0	1	0	0	1	0	-	-	-	0	1	0	0	1	0	0	1	0	0	1	0
Type	Top layer adsorption of 1st type															Top layer adsorption of 2nd type														

$$\theta = \Pi^* \left( \frac{1 + w_H \Pi^*}{1 + \Pi^*} \right), \quad w_H = \frac{\alpha(1 + \alpha - \alpha^2)}{2 - \alpha} \text{ for } d = 0, \\ w_H = \frac{2 + \alpha}{3(2 - \alpha)} \text{ for } d = 1 \quad (16)$$

$$Z_{f0}(\alpha, \beta\theta) = \frac{Z_{A2+d} - Z_{f\infty}}{1 - \frac{\ln(1-\alpha) - (\beta\theta)^{1+\eta} \ln(1-\alpha\beta\theta) + (d-\eta)\alpha(1-(\beta\theta)^{2+\eta})}{\alpha^{1+d-\eta} \frac{1-\beta\theta}{1-\alpha} [d + (\beta\theta)^d (1 + \frac{\beta\theta}{1-\alpha\beta\theta})]}} + Z_{f\infty} \quad (18)$$

The model (11) is directly applicable to the energy distribution of  $h = 1$  and 2. For  $h > 2$ , the following simplified formulae were determined to get  $B_{fk} = B_f \theta$  [19]:

$$B_{f\theta} \stackrel{\text{def}}{=} B_A \exp((Q_{cp}/RT) \cdot (Z_{f\theta} - Z_{f\infty})), \\ B_A \stackrel{\text{def}}{=} \exp(Q_A/RT) \quad (17)$$

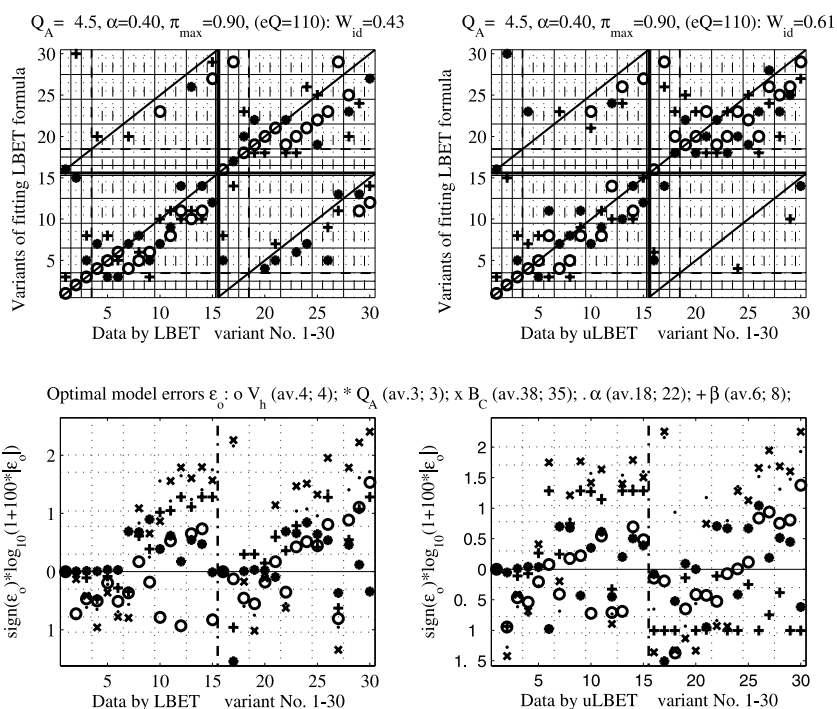
where  $Q_{cp}$  is the molar adhesion energy in ideal adsorbent-adsorbate contacts [1],  $Q_A$  is the first layer adsorption energy,  $R$  is the gas constant,  $T$  is the temperature,  $Z_{f\theta}$  denotes an averaged value of the upper bounds  $Z_{fk}$  (Eq. 2) calculated with the formula [21]:

The *LBET* models have five or six adjustable parameters (the same as in *uLBET*:  $m_{hA}, Q_A, \alpha, \beta, B_C$  and optionally  $\zeta_{f\infty}$ ). The five parameter identification assumes  $\zeta_{f\infty} = Z_C/Z_A$ , which considerably improves the numerical properties of the task. The energy distribution is attributed by setting the options  $\{h, d, \eta\}$  (see Table 1 and Eq. 15).

**Computer analysis of the new mathematical models**

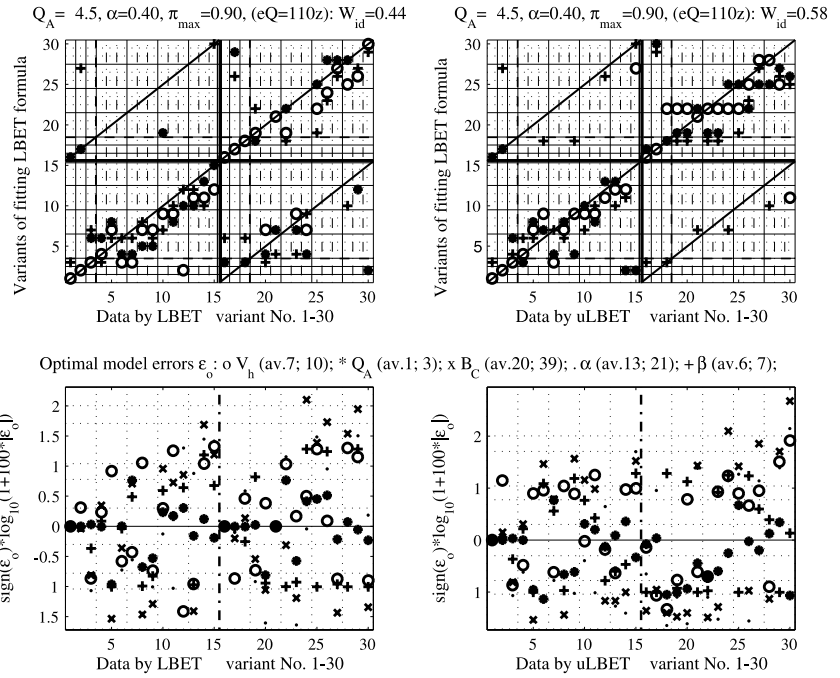
Before applying any model to examination of real adsorption systems, it is necessary to assess the identifiability of the model itself, i.e. to outline an uncertainty

**Fig. 1** The recognition correctness of adsorption type and of energy distribution not perfectly mapped in the *LBET* models—a five parameters case ( $Q_A/RT = -4.5, \alpha = 0.4, \pi_{\text{max}} = 0.9$ )





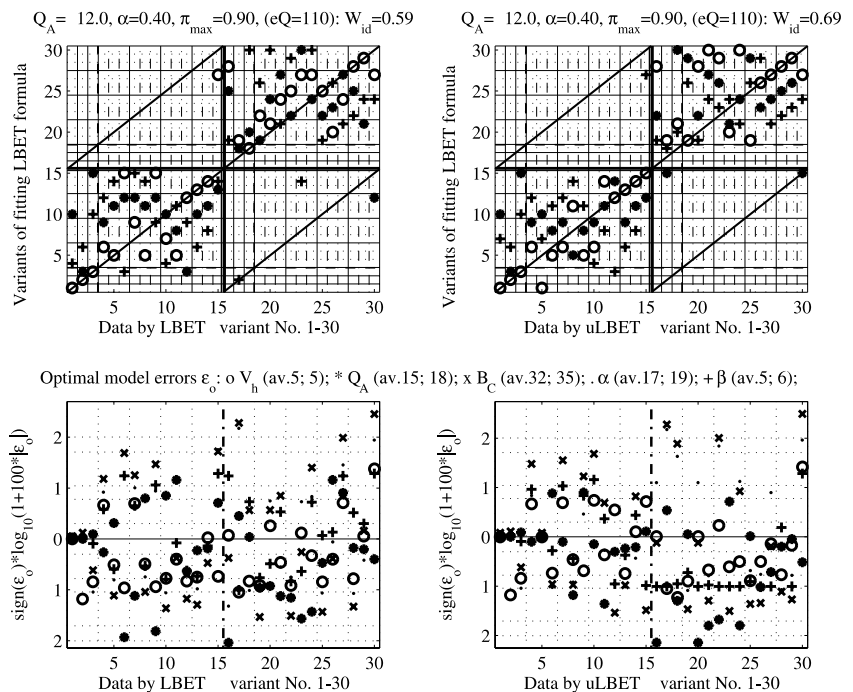
**Fig. 2** The recognition correctness of adsorption type and of energy distribution not perfectly mapped in the *LBET* models—a six parameters case ( $Q_A/RT = -4.5, \alpha = 0.4, \pi_{\max} = 0.9$ )



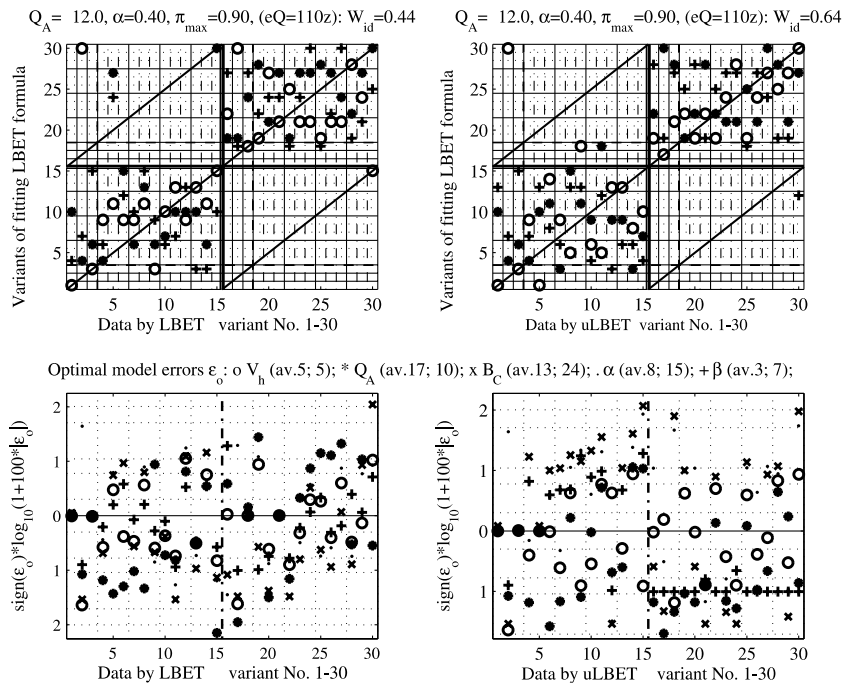
area of its parameters evaluated by fitting the model to data produced with the same or a similar model. In our approach the simplified *LBET* formula is proposed to be used directly as the identified (fitting) model, assuming that the parameters found in this way may be treated as the *uLBET* model parameters (*uLBET* is to be an adequate description of an adsorption system). Thus, the first question is how far *uLBET*–*LBET* discrepancies worsen the identification results, i.e. are they really negligible. Next, the main factors affecting a numerical conditioning of the *LBET* model must be characterized.

The applicability and reliability of the *LBET*-based identification method is generally discussed in Refs. [18–21]. In particular, it was shown that the five-parameter *LBET* formula is perfectly identifiable, but for practical use fitting of both, the six-parameter and five-parameter models are recommended. The main porous-structure parameters evaluated in this way are more reliable than those gained with classical adsorption model. This paper gives more information on the properties of the proposed identification technique. The five-parameter and six-parameter identification reli-

**Fig. 3** The recognition correctness of adsorption type and of energy distribution not perfectly mapped in the *LBET* models—a five parameters case ( $Q_A/RT = -12.0, \alpha = 0.4, \pi_{\max} = 0.9$ )



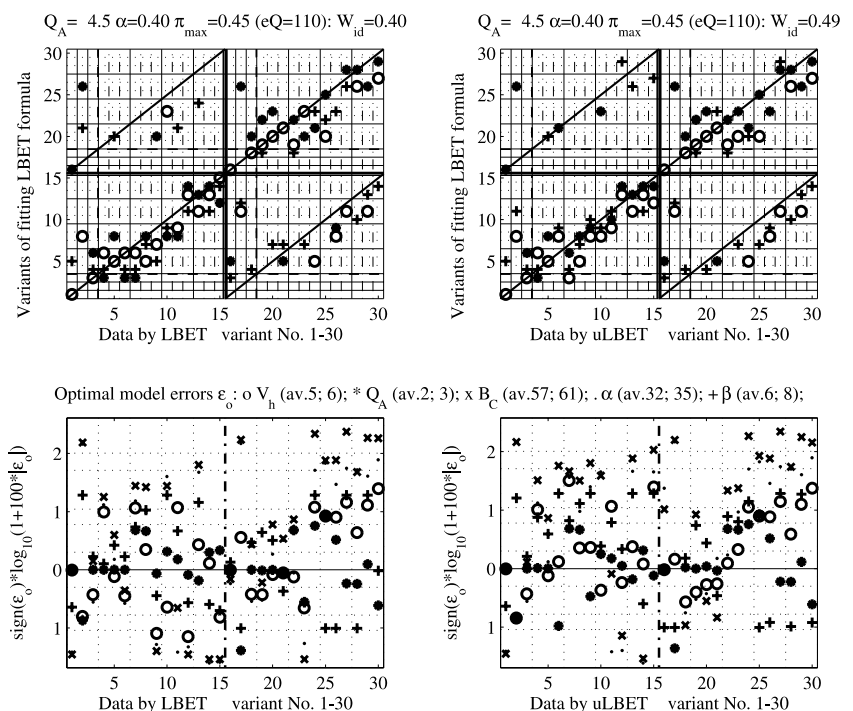
**Fig. 4** The recognition correctness of adsorption type and of energy distribution not perfectly mapped in the *LBET* models—a six parameters case ( $Q_A/RT = -12.0$ ,  $\alpha = 0.4$ ,  $\pi_{\max} = 0.9$ )



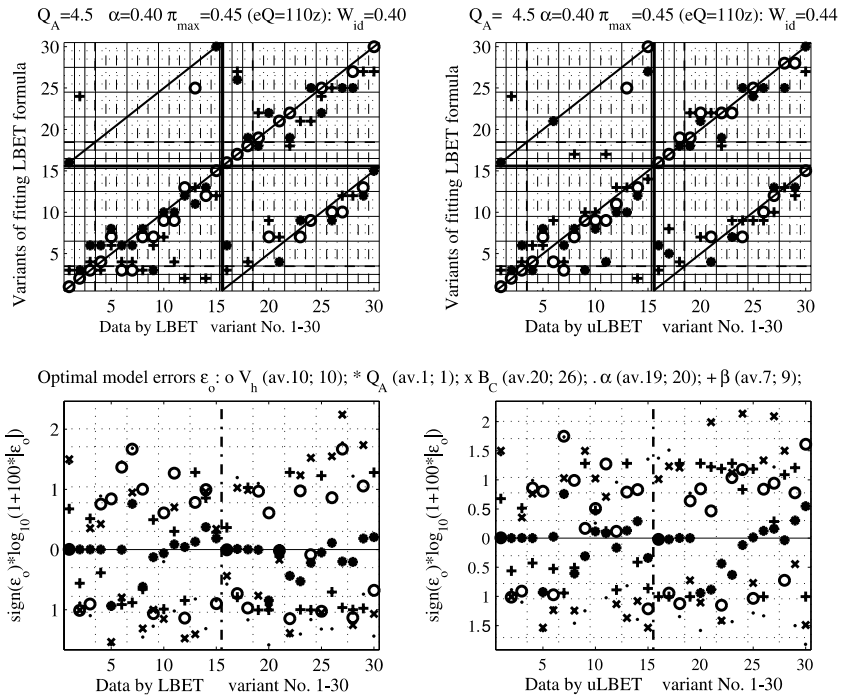
ability is analyzed in more detail for different values of the system parameters. In this context, the efficiency of the simultaneous examination of two isotherms is also studied. Calculations were performed for a simulated microporous adsorbent with the solubility parameter  $\delta_c = 30$ , which is typical for carbonaceous adsorbents [25]. The isotherms (data) have been generated for relative pressures  $\pi$  ranging to  $\pi_{\max} = 0.9$ , by employing *LBET* or *uLBET* models, and fitted with the *LBET* formula.

The fitting was done using a typical constrained optimization procedure (the *fmincon* function available in the *MATLAB* package) minimizing the fitting error dispersion  $\sigma_e$ . No arbitrary regularization techniques were used [26], as multivariant identification is proposed instead. The following parameters were adjusted:  $V_{hA} = m_{hA} V_s$ —volume of a first layer region ( $V_s$  is the molar volume of adsorbate molecule in liquid state),  $\alpha$  and  $\beta$  are the geometric parameters of the porous structure,  $Z_A$  and  $Z_C$  are the correction

**Fig. 5** The recognition correctness of adsorption type and of energy distribution not perfectly mapped in the *LBET* models—a five parameters case ( $Q_A/RT = -4.5$ ,  $\alpha = 0.4$ ,  $\pi_{\max} = 0.45$ )



**Fig. 6** The recognition correctness of adsorption type and of energy distribution not perfectly mapped in the *LBET* models—a six parameters case ( $Q_A/RT = -4.5$ ,  $\alpha = 0.4$ ,  $\pi_{\max} = 0.45$ )



factors used to calculate  $Q_A$ ,  $B_C$  (see Eq. 5) and optionally— $Z_f \infty$ . In simultaneous identification of multiple isotherms, the same values for  $V_{hA}$ ,  $\alpha$ ,  $\beta$  and  $\{h, d, \eta\}$  were assumed for all isotherms, but each of them involves two additional parameters  $Z_A$  ( $Q_A$ ) and  $Z_C$  ( $B_C$ ).

The following constraints were applied:

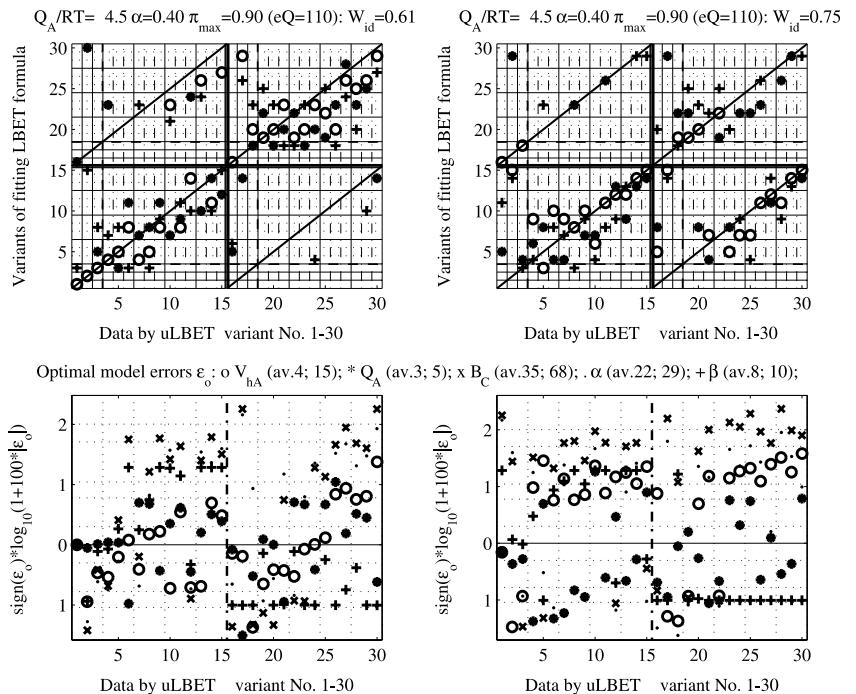
$$0 \leq \alpha \leq 1, \quad 1 \leq \beta \leq 1.3, \quad Z_{pc} \geq 1/12 \quad \text{and} \quad B_C \geq 1, \\ 0.6V_{hL} \leq V_{hA} \leq 10V_{hL}$$

$$0.5Z_{AN} \leq Z_A < 1, \quad Z_A \in (0.2, 1), \\ Z_C \in \langle 1/6, U_p(1 - 2Z_{pp})/Q_{cp} \rangle, \quad \pi_m(\beta, B_C) < p_{\max}$$

where  $Z_{AN}$  corresponds to a nominal value for  $Q_A$ , and  $V_{hL}$  is a value appointed according to linear *Langmuir* formula.

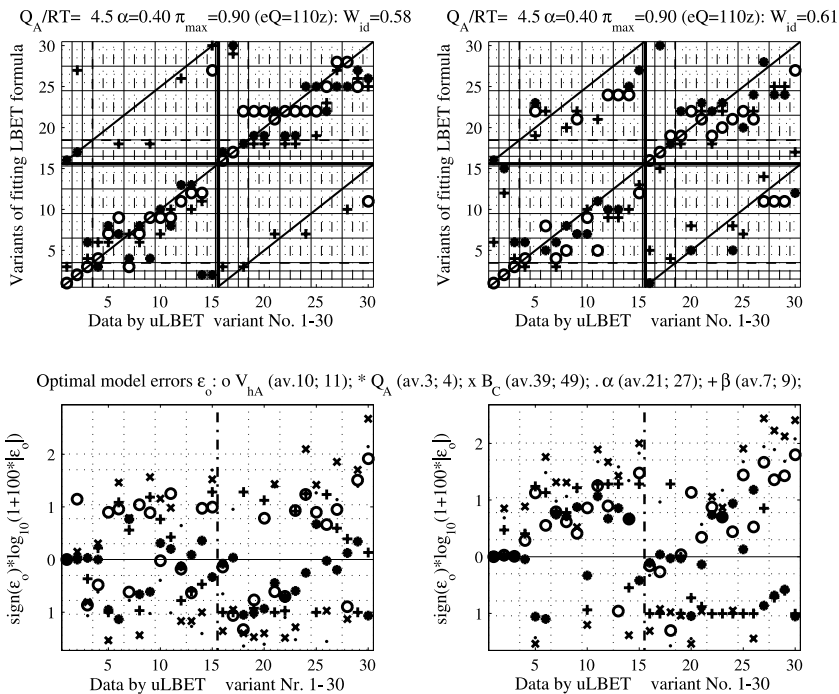
The research was focused on analysis of the identification uncertainty. Theoretical isotherms were generated employing the *uLBET* or *LBET* formulae, with fixed values of the system parameters and a selected

**Fig. 7** Comparison of exemplary results of calculations for single and double adsorption isotherms for data generated by *uLBET* models with five parameters in realistic case of the surface energy mapping ( $Q_A/RT = -4.5$ ,  $\alpha = 0.4$ ,  $\pi_{\max} = 0.9$ )





**Fig. 8** Comparison of exemplary results of calculations for single and double adsorption isotherms for data generated by *uLBET* models with six parameters in realistic case of the surface energy mapping ( $Q_A/RT = -4.5, \alpha = 0.4, \pi_{\max} = 0.9$ )

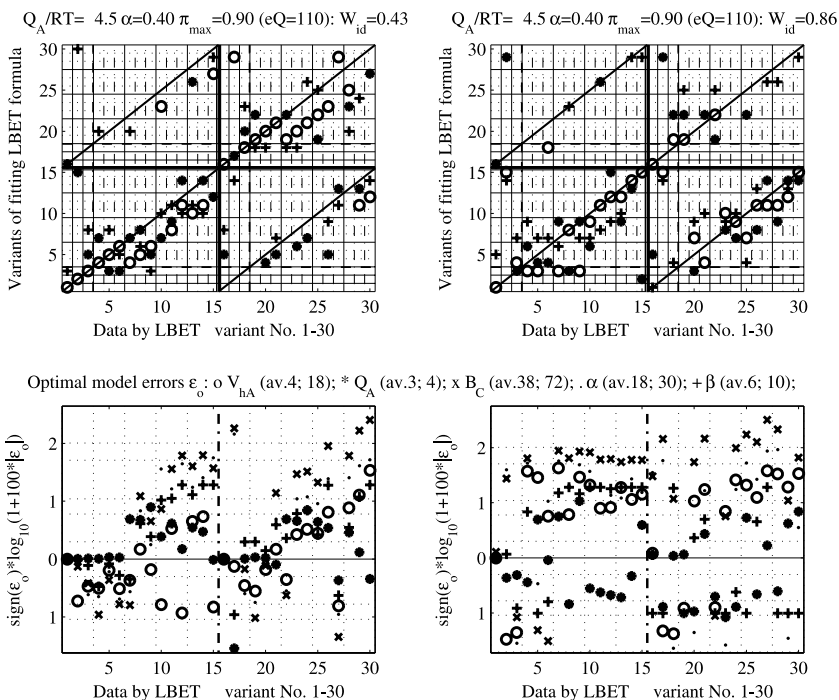


energy distribution variant. The 30 variants of different  $\{h_{dat}, d, \eta\}$  producing the distributions covering cases discussed in the literature were taken under study (see Table 2). Calculations with different values of the system parameters affecting the isotherm shape ( $Q_A/RT, B_C, \alpha, \beta$ ) were carried out. Each isotherm was fitted by the *LBET* formula in its 30 variants combining  $\{h_{fit}, d, \eta\}$  options, as specified in Table 2. Different  $h_{fit}/h_{dat}$  and  $\zeta_0$  values were taken in partic-

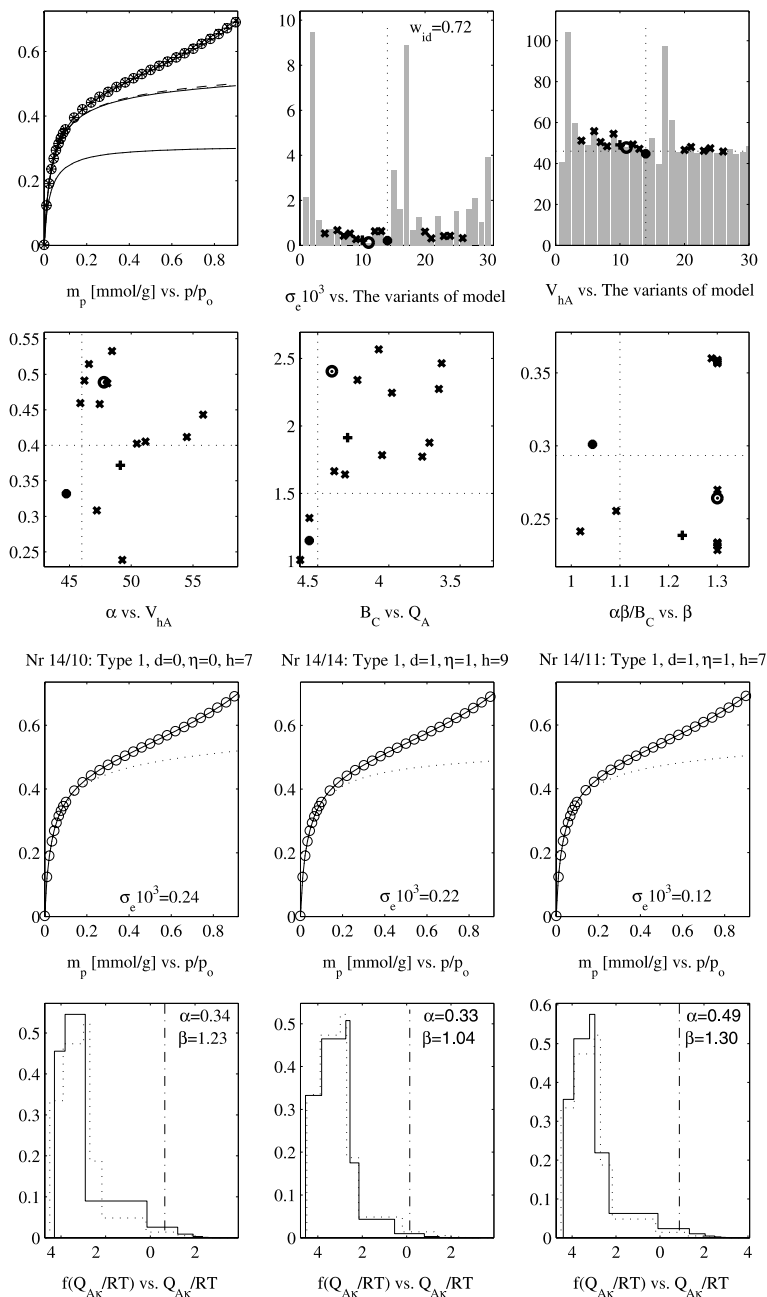
ular variants, to map realistic process-model mismatches.

The reliability of identification was assessed on the basis of the residual dispersion  $\sigma_e$  and relative errors of the parameters calculated for all 30 variants. To make possible a final choice of the best variant, the detailed results are shown for the three best fits. Moreover, ten well-fitted variants from 30 were treated as acceptable ones. In order to get a synthetic measure of the identi-

**Fig. 9** Comparison of exemplary results of calculations for single and double adsorption isotherms for data generated by *LBET* models with six parameters in realistic case of the surface energy mapping ( $Q_A/RT = -4.5, \alpha = 0.4, \pi_{\max} = 0.9$ )



**Fig. 10** The multivariant identification results for a single isotherm generated by *uLBET* models in realistic case of the surface energy mapping and fitted by *LET* formulas with five parameters (*Type 1*,  $h = 8$ ,  $Q_A/RT = -4.5$ ,  $\alpha = 0.4$ ,  $\pi_{\max} = 0.9$ )



fication uncertainty, we defined the following identification index  $w_{id}$  [20]:

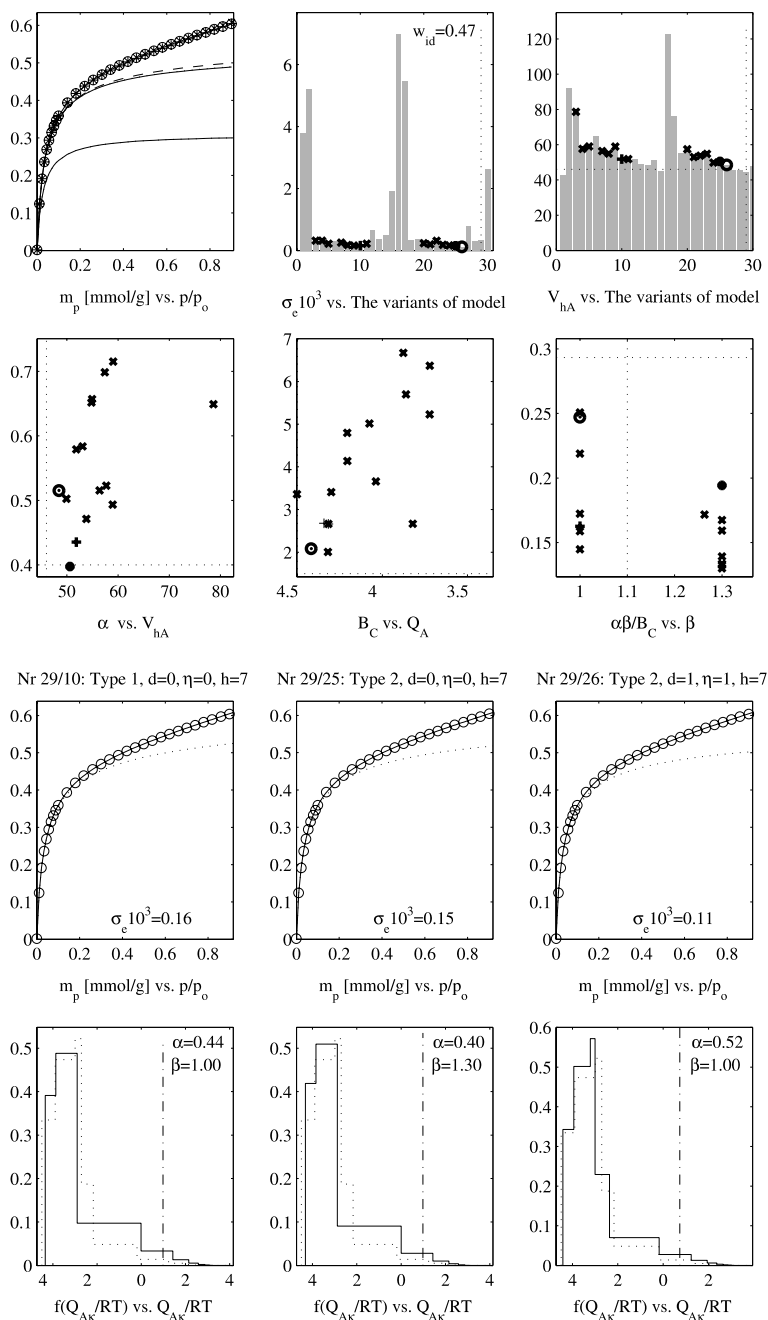
$$w_{id} = 1 - \frac{\sigma_{e \min}}{\frac{1}{10} \sum_{opt=1}^{10} \sigma_{e \text{ opt}}} \quad (19)$$

where  $\sigma_{e \min}$  and  $\sigma_{e \text{ opt}}$  express the error dispersion of the best fitting and the sequence of increasing dispersion error of the ten well fitted models.

The three variants mentioned above for exemplary systems are shown in full detail, to show relations between the fitting-error dispersion and system-parameter evaluation uncertainty. The relative errors of the parameters determined for the best fitted variants are

compared to those obtained with other acceptable variants. The results of computer calculations are shown in Figs. 1, 2, 3, 4, 5, 6, 7, 8, 9. The upper diagrams are divided into quarters with bold solid lines separating model variants of the 1st type adsorption (the agglomerate size limited due to competitive adsorption), from variants of 2nd type adsorption (the limitations of agglomerate size are of geometrical nature). The lines separating the distributions of different  $h$  are shown (see Table 2). The first row and column of each quarter correspond to the homogenous system. The marks show positions of the three best fittings in two-dimensional space of the model variants studied. In every column the best-fitted isotherm is distinguished by “o”. The second

**Fig. 11** The multivariate identification results for a single isotherm generated by *uLBET* models in realistic case of the surface energy mapping and fitted by *LET* formulas with five parameters (*Type 2*,  $h = 8$ ,  $Q_A/RT = -4.5$ ,  $\alpha = 0.4$ ,  $\pi_{\max} = 0.9$ )

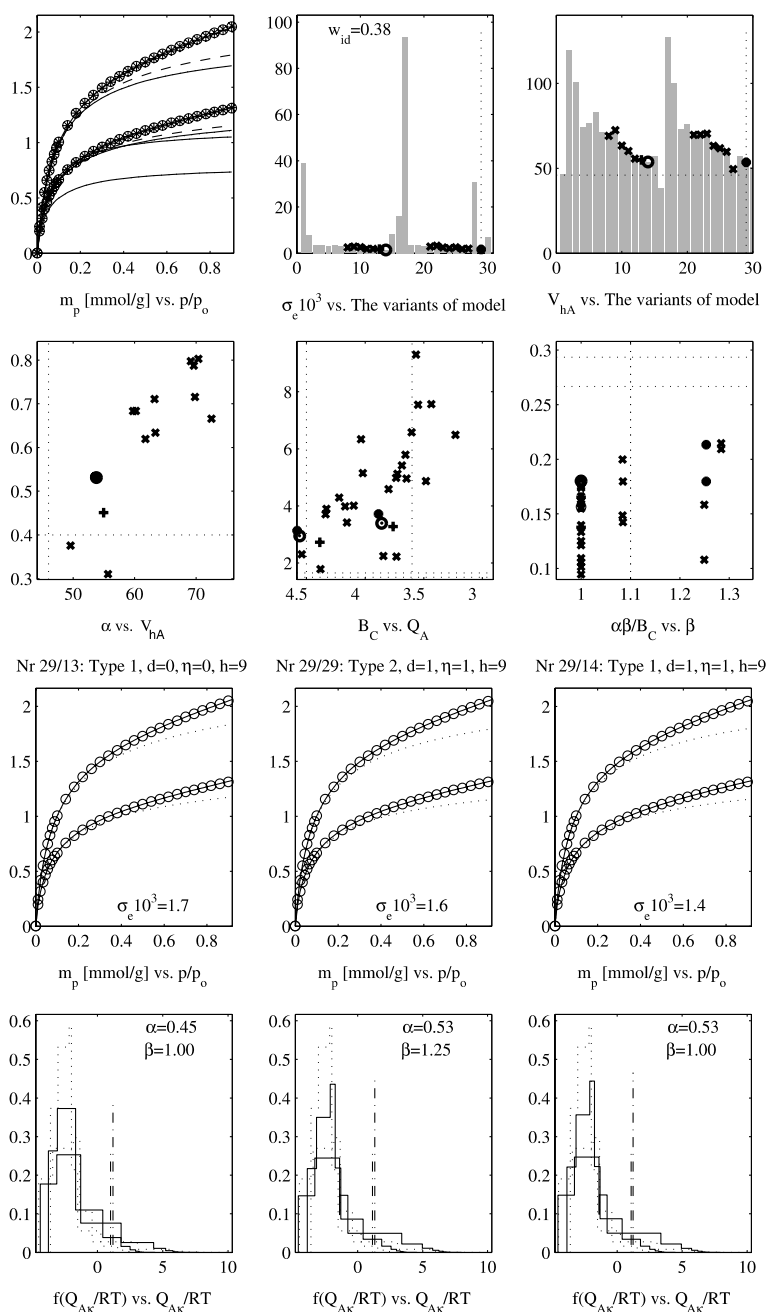


and third best fits are marked by “\*” and “+”. In the optimum case, all “o’s” should lay on the main diagonal of the diagram. Their position at the upper diagonal of the left quarter denotes correct recognition of energy distribution class with incorrect qualification of adsorption type. The position of marks on the bottom diagonal of the right quarter means an incorrect interpretation of adsorption 2nd type as adsorption 1st type. The bottom diagram in the figures shows the relative evaluation errors of the system parameters. Horizontal dotted line shows the levels of  $\pm 1$ ,  $\pm 5$ ,  $\pm 10$ ,  $\pm 50$  and  $\pm 100\%$ .

The detailed results of the analysis are shown in Figs. 10–13, showing fitting quality and optimal identification uncertainty for selected variants. The first column of the first row shows the fitted isotherm. Data are marked with circles “o”, a solid line “—” presents the theoretical isotherm calculated by the *uLBET* model with the parameters of the best-fitted *LBET* variant. Dotted lines mean theoretical cover of the first adsorption layer.

The second figure in this row contains bar diagrams of the dispersion error of the fitting with different *LBET* model variants. The bold “o” refers to the best-fitted

**Fig. 12** The multivariate identification results for a double isotherm generated by *uLBET* models in realistic case of the surface energy mapping and fitted by *LET* formulas with five parameters (*Type 2*,  $h = 8$ ,  $Q_A/RT = -4.5$ ,  $\alpha = 0.4$ ,  $\pi_{\max} = 0.9$ )



one. Next “+” and “\*” mean the second and third best fits. Also, the value of the identifiability factor  $w_{id}$  is shown. The more diversified the heights of individual bars and the bigger the differences between the lowest bar and the remaining ones, the better identifiability of the adsorption system (the factor  $w_{id}$  reaches a big value).

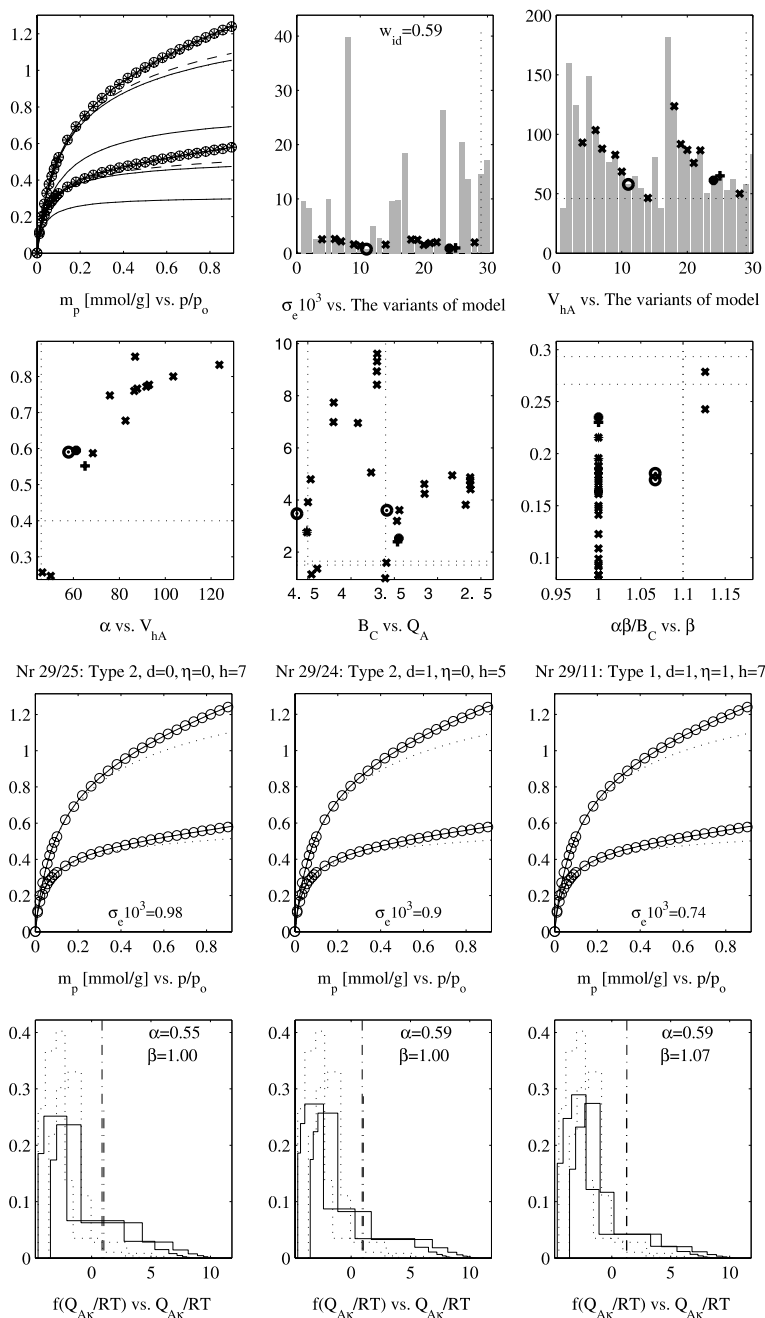
The third figure in the row discussed shows the values of the most important structure parameters, i.e. monolayer capacity  $V_{hA}$ , obtained in individual variants. Three best-fitted variants are marked in the same way as in the previous figure. The headline gives the name of the adsorption system i.e. adsorbate symbol, the carbonaceous adsorbent symbol, the binary options

$h$ ,  $d$ ,  $\eta$  and parameters  $\alpha$ ,  $\beta$  obtained with the best-fitted variant.

The figures in the second row show the diversification of the model parameters, obtained in the ten good fits. The symbol “o” means the optimum fitting parameters, “\*”, “+”—these of the second and third fitting quality, “x” the seven remaining parameters. These are presented in pairs in rectangular coordinate systems.

The third row of figures shows the three best fits of the *LBET* models. In the headlines of the diagrams the symbol of the adsorption system and the number of the *LBET* model variant are separated by a slash. In the lower part of each diagram the value of the fitting

**Fig. 13** The multivariate identification results for a double isotherm generated by *uLBET* models in realistic case of the surface energy mapping and fitted by *LET* formulas with six parameters (*Type 2*,  $h = 8$ ,  $Q_A/RT = -4.5$ ,  $\alpha = 0.4$ ,  $\pi_{\max} = 0.9$ )



quality measure  $\sigma_e$  is located (the lower value of the factor, the better identification reliability).

In the fourth row the corresponding energy distributions are shown. Vertical lines show the value of the adsorption energy on the second and next layers.

Synthetic measures of the identification reliability are gathered in Tables 3, 4, 5.

## Conclusions

The study presented paper gives evidence that the simplified *LBET* formulae are accurate enough to be used effectively in the identification of adsorption systems,

instead of their rigorous counterparts—the *uLBET* models.

The *LBET* model may be well fitted to different adsorption data in a wide pressure range, providing relatively accurate information on the system parameters studied. Identification results obtained with low-pressure data and these reached by fitting isotherms in the full pressure range are of comparable quality.

Identification based on adjusting six parameters (including  $Z_f \infty$ ) gives more reliable results than gained using only five free parameters. This also applies to the simultaneous identification of two isotherms. Thus, the task-conditioning problem is not critical for the *LBET* formula.



**Table 3** Comparison of the results of the computer calculations

The analyzed problem	Parameters values of the simulated adsorption system				$w_{id\ BET}$	$w_{id\ uLBET}$
	$Q_A/RT$	$\alpha$	$\pi_{max}$	Number of parameters		
<i>LBET</i> versus <i>uLBET</i>	-4.5	0.4	0.9	5	0.43	0.61
				6	0.44	0.58
<i>LBET</i> versus <i>uLBET</i>	-4.5	0.8	0.9	5	0.57	0.63
				6	0.66	0.62
<i>LBET</i> versus <i>uLBET</i>	-12.0	0.4	0.9	5	0.59	0.69
				6	0.44	0.64
<i>LBET</i> versus <i>uLBET</i>	-4.5	0.4	0.45	5	0.40	0.49
				6	0.40	0.44
<i>ULBET</i> single versus double	-4.5	0.4	0.9	5	0.61	0.75
				6	0.58	0.61
<i>LBET</i> single versus double	-4.5	0.4	0.9	5	0.43	0.86
				6	0.44	0.47

**Table 4** Comparison detailed results of calculations for adsorption system (single isotherm) with following parameters assumed:  $Q_A/RT = -4.5$ ,  $\alpha = 0.4$ ,  $\pi_{max} = 0.9$ ,  $h = 8$ ,  $\beta = 1.10$ 

System	Number of the models parameters	Type of the top layer adsorption	$w_{id}$	Parameters of the best fitting variants	The best fitting variants		
					1st	2nd	3th
Single Isotherm	5	1st	0.72	$\sigma_e \cdot 10^3$	0.12	0.22	0.24
				$\alpha$	0.49	0.33	0.34
				$\beta$	1.30	1.04	1.23
	6	2nd	0.47	$\sigma_e \cdot 10^3$	0.11	0.15	0.16
				$\alpha$	0.52	0.40	0.44
				$\beta$	1.00	1.30	1.00
Double Isotherm	5	1st	0.91	$\sigma_e \cdot 10^3$	0.019	0.04	0.043
				$\alpha$	0.30	0.39	0.52
				$\beta$	1.08	1.07	1.29
	6	2nd	0.64	$\sigma_e \cdot 10^3$	0.053	0.077	0.079
				$\alpha$	0.49	0.51	0.63
				$\beta$	1.00	1.00	1.00

**Table 5** Comparison detailed results of calculations for adsorption system (double isotherm) with following parameters assumed:  $Q_A/RT = -4.5$ ,  $\alpha = 0.4$ ,  $\pi_{max} = 0.9$ ,  $h = 8$ ,  $\beta = 1.10$ 

System	Number of the models parameters	Type of adsorption	$w_{id}$	Parameters of the best fitting variants	The best fitting variants			
					1st	2nd	3th	
Double Isotherm	5	1st	0.39	$\sigma_e \cdot 10^3$	2.8	2.5	2.3	
				$\alpha$	0.50	0.37	0.49	
				$\beta$	1.30	1.15	1.30	
	6	2nd	0.38	$\sigma_e \cdot 10^3$	1.4	1.6	1.7	
				$\alpha$	0.53	0.53	0.45	
				$\beta$	1.00	1.25	1.00	
	Double Isotherm	5	1st	0.50	$\sigma_e \cdot 10^3$	1.1	1.2	1.2
					$\alpha$	0.48	0.48	0.46
					$\beta$	1.00	1.26	1.00
6		2nd	0.59	$\sigma_e \cdot 10^3$	0.74	0.9	0.98	
				$\alpha$	0.59	0.59	0.55	
				$\beta$	1.07	1.00	1.00	

## References

1. Rudzinski W, Everett DH (1992) Adsorption of gases on heterogeneous surfaces. Academic Press, London San Diego
2. Jankowska H, Świątkowski A, Choma J (1991) Active carbon. Ellis Horwood, Chichester
3. Ding LP, Bhatia Sk (2001) Carbon 39:2215–2229
4. Kruk M, Jaroniec M, Choma J (1998) Carbon 36:1447–1458

5. Kowalczyk P, Terzyk AP, Gauden PA (2001) *J Colloid Interface Sci* 243:300–305
6. Jagiełło J, Thommes M (2004) *Carbon* 42:1227–1232
7. Yin YF, Mcenaney B, Mays TJ (1998) *Carbon* 36:1425–1432
8. Nicholson D, Parsonage N (1982) *Computer simulation and the statistical mechanics of adsorption*. Academic Press, NY
9. Gauden PA, Terzyk AP, Rychlicki G, Kowalczyk P, Cwiertnia MS, Garbacz JK (2004) *J Colloid Interface Sci* 273:39–45
10. Kowalczyk P, Terzyk AP, Gauden PA, Gun'ko VM, Solarz L (2002) *J Colloid Interface Sci* 256:378–395
11. Jaroniec M, Kruk M, Olivier J (1995) *Surf Sci* 342:1127–1130
12. Terzyk AP, Wojsz R, Rychlicki G, Gauden PA (1997) *Colloids Surf* 126:67–73
13. Diduszko R, Swiatkowski A, Trznadel BJ (2000) *Carbon* 38:1153–1162
14. Terzyk AP, Gauden PA, Kowalczyk P (2003) *Arabian J Sci Eng* 28:133–167
15. Duda JT, Milewska-Duda J (2002) *Langmuir* 18:7503–7514
16. Milewska-Duda J, Duda J, Jodłowski G, Kwiatkowski M (2000) *Langmuir* 16:7294–7303
17. Milewska-Duda J, Duda JT (2002) *Colloids Surf* 208:71–81
18. Milewska-Duda J, Duda JT (2002) *Appl Surf Sci* 96:115–125
19. Duda JT, Milewska-Duda J (2005) *Langmuir* (in print)
20. Kwiatkowski M (2004) Numerical methods of microporous structure description of carbonaceous sorbents. PhD Dissertation, AGH-UST, Faculty of Fuels & Energy, Krakow (in polish)
21. Milewska-Duda J, Duda JT, Kwiatkowski M (2003) Chemistry of interfacial phenomena. Annals of the Polish Chemical Society, preliminary reports presented during XLVI Meeting of the Polish Chemical Society and the association of engineers & technicians of chemical industry, vol 2 (Part III). p 1130
22. Milewska-Duda J, Duda JT, Kwiatkowski M (2004) Proceedings of the fifth international symposium surface heterogeneity effects in adsorption and catalysis on solids, August–September 2004, Gdańsk, Poland, p 154
23. Duda JT, Kwiatkowski M, Milewska-Duda J (2004) *Polish J Appl Chem XLVII(3–4):93–104*
24. Duda JT, Milewska-Duda J, Kwiatkowski M (2004) Proceedings of the third international conference: new carbon and composite materials 2004. Progress in preparation, investigation and applications: Ustron–Zawodzie 9–12 May 2004, Poland. P. I. 10
25. Milewska-Duda J, Duda J, Nodzeński A, Lakatos J (2000) *Langmuir* 16:5458–5466
26. Puziy AM, Volkov VV, Poznayeva OI, Bogillo VI, Shkilev VP (1997) *Langmuir* 13:1303–1306. The research is done within the university grants 11.11.210.62