Adsorption (2008) 14: 37–53
DOI 10.1007/s10450-007-9044-2

Application of the LBET class models to describe the structure of microporous activated carbons on the basis of argon and benzene adsorption isotherms

Mirosław Kwiatkowski

Received: 18 January 2006 / Revised: 15 July 2007 / Accepted: 31 July 2007 / Published online: 22 September 2007

Abstract The reported research is concerned with the properties of the new LBET class models designed to describe the heterogeneous adsorption on microporous carbonaceous materials. In particular, the new adsorption models were applied to a computer analysis of the microporous structure of two active carbons on the basis of argon and benzene adsorption isotherms. This paper provides for more thorough information on the properties of the proposed models and identification technique presented in the earlier papers.

Keywords Adsorption · Modeling · Activated carbon · Micropores · Adsorption isotherms

Abbreviations

m_p	Amount of adsorbate
m_{hA}	Number of primary sites
θ_{kj}	Coverage ratio of jth layer at kth type clusters
θ	Coverage ratio of the layers above the first layer
π	Relative pressure
α	Geometrical parameter of the porous structure
β	Pore shape parameter
B_{Ak}, B_{fk}	Energy parameters
Q_{cp}	Molar adhesion energy in ideal adsorbent-adsorbate contacts
Q_A	First layer adsorption energy $Q_L = Q_A/RT$
R	Gas constant
T	Temperature
$Z_{f\theta}$	Averaged value of upper boundary parameter of the distribution function range
Z_{fk}	Distribution function range
V_{hA}	Volume of the first adsorption layer
Z_A, Z_C	Correction factors of energy
w_{id}	Identifiability index
$\sigma_{e\,\min}$ and $\sigma_{e\,\mathrm{opt}}$	Standard deviation error of the best fitting
$\sigma_{e\,\mathrm{opt}}$	Sequence of increasing deviation error of the ten well fitted models

1 Introduction and theoretical basis

Carbonaceous microporous materials are the adsorbents used most widely in a variety of industrial applications owing to their good adsorption capabilities for many vapors and gases. The use of carbonaceous materials requires their characterization, which includes, among others, description of microporosity and energetic heterogeneity (Rodrıguez-Reinosou and Molina-Sabio 1998). Many approaches to a description of the adsorption process have been proposed in the literature, and a number of techniques, ranging from simple to more advanced, have been derived to characterize microporous materials (Rudziński and Everett 1992). The primary methods for the characterization of a variety of porous materials, e.g. activated carbons, are gases or vapors adsorption techniques based on determining experimental adsorption isotherms (Sing 2001; Aranovich and Donohue 2000; Storck et al. 1998; Jaroniec et al. 1989; Gil 1998). Several different equations have been proposed to describe the adsorption equilibrium, among which the most popular are: the Dubinin–Radushkevich equation (Dubinin 1960,

---

M. Kwiatkowski (✉)
Faculty of Fuels and Energy, AGH-University of Science and Technology, Al. Mickiewicza 30, 30-059 Krakow, Poland
e-mail: kwiatkow@agh.edu.pl

1989), the Dubinin–Astakhov equation (Dubinin and Astakhov 1971; Gil and Grange 1996), and the BET equation (Gregg and Sing 1967; Gomez-Serrano et al. 2001). The development of computer science and the improvements in computational technology have triggered the development of more advanced methods of pore structure description (Rudziński and Everett 1992; Puziy et al. 1997), based on sophisticated numerical tools (Puziy et al. 1997), statistical mechanics (Sánchez-Montero et al. 2005; Cao et al. 2002), computer simulations (Nicholson 1994; Suzuki et al. 1996), the DFT theory (Ryu et al. 1999), fractal geometry (Erdem-Senatalar et al. 2000) and neural networks (Shahsavand and Ahmadpour 2005).

Although ranges of advanced methods are available, the obtained results are still unsatisfactory. Therefore there is still a need to improve and develop simple and reliable methods of their characterization. A new group of models was created, based on the previously elaborated sorption theory (Milewska-Duda et al. 2000; Duda et al. 2005a). This new theory is based on the observation that the surface structure and adsorption energy distribution of irregular microporous materials cannot be determined reliably, but evaluated only by multilateral verification of alternative models of the simplest possible form. In order to achieve this, the original mathematical models, based on the fundamental law of thermodynamics and employing simple adsorption energy were developed (Duda et al. 2005a, 2005b).

The proposed models provide for reliable information on the microporous structure and its capacity based on the empirical adsorption isotherms of vapors and gases. These models consider the adsorption process as the formation of clusters the size of which is limited by pore geometry. The set of adsorbed molecules which have mainly been adsorbed due to adhesive interactions with the adsorbent surface is taken into account as the first adsorption layer in the proposed models. The adsorption of further molecules is viewed as creating the second, the third, and successive adsorption layers.

In the presented mathematical tool, there is a distinction between two types of adsorption models. The first type refers to the adsorption systems in which the number of layers in a cluster is limited due to the expansion of the adjacent clusters. The second type describes the systems in which the limitations in the number of layers in a cluster result from the geometry of pores. According to these models, each cluster starts from a simple molecule. Consequently only one primary adsorption site on the surface can begin the clusterization process. The groups of molecules based on two or more primary sites are treated by these models as independent clusters. This simplification does not take into account the fact that the creation of the considered cluster is determined by the presence of other clusters.

Upon derivation of the general formula of the model, hereinafter referred to as LBET class model, the following assumptions were taken into account (Duda et al. 2005b; Kwiatkowski 2007a):

(a) The layers above the first layer are homogeneous, and energy parameters B_C are the same for all layers above the first layer:

$$\begin{aligned} &B_C \overset{\text{def}}{=} \exp\left(\frac{Q_C}{RT}\right), \\ &Q_C \overset{\text{def}}{=} U_p(1 - 2 \cdot Z_{pp}) - Z_C \cdot Q_{cp}, \end{aligned} \tag{1}$$

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}, Z_C are the correcting factors.

(b) The number of primary adsorption sites is expressed by the formula given below:

$$m_{hAk} = m_{hA}(1 - \alpha)\alpha^{k-1}, \quad \alpha \in \langle 0, 1), \tag{2}$$

where α is the geometrical parameter of the porous structure, $m_{hA\kappa}$ is the amount of κ type primary sites [mmol/g], and k is the cluster type.

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

$$\begin{aligned} &Q_{A\kappa} = U_p - Z_{A\kappa} \cdot Q_{cp}, \\ &Q_A \overset{\text{def}}{=} U_p - Z_A \cdot Q_{cp} = \min_{k=1}(Q_{A\kappa}), \end{aligned} \tag{3}$$

where Z_{Ak} is the factor uniformly distributed over a range depending on k, κ counts kth type clusters of identical energy profile across the layers $n = 1, \ldots, k$, Q_A is the first layer adsorption energy, $Q_{A\kappa}$ is the molar energy contributed by placing an adsorbate molecule on the first layer of κth class clusters, Z_A is the correcting factor of effective adsorbent-adsorbate contact.

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

$$\begin{aligned} &B_{Ak} \overset{\text{def}}{=} B_A \cdot (B_{cp})^{Z_A(1-\zeta_{Ak})}, \\ &B_{fk} \overset{\text{def}}{=} B_A \cdot (B_{cp})^{Z_A(1-\zeta_{fk})}, \\ &f_k(B_{A\kappa}) = \frac{m_{hAk}}{\ln(B_{fk}/B_{Ak})} \frac{1}{B_{A\kappa}}, \end{aligned} \tag{4}$$

$$B_A \overset{\text{def}}{=} \exp(Q_A/RT), \qquad B_{cp} \overset{\text{def}}{=} \exp(Q_{cp}/RT), \tag{5}$$

where the energy parameters B_{Ak} and B_{fk} do not depend on k.

(e) The coverage ratios θ_{kn} are the same for all layers above the first layer.

The heterogeneous adsorption LBET class model derived using the above assumptions has the following mathematical form (Kwiatkowski 2007a):

$$
\begin{aligned}
\frac{m_p}{m_{hA}}
&= (1-\alpha)\left\{1-\frac{1}{\ln(B_A/B_{f1})}\cdot\ln\left(\frac{B_A+\pi}{B_{f1}+\pi}\right)\right\}\\
&\quad + d\cdot\alpha(1-\alpha)(1+\beta\theta_2)\\
&\quad \times\left\{1-\frac{1}{\ln(B_{A2}/B_{f2})}\ln\left(\frac{B_{A2}(1-\theta_2)^{\beta}+\pi}{B_{f2}(1-\theta_2)^{\beta}+\pi}\right)\right\}\\
&\quad + \alpha^{d+1}\left[d+(\beta\theta)^{d}\left(1+\frac{\beta\theta}{1-\alpha\beta\theta}\right)\right]\\
&\quad \times\left\{1-\frac{1}{\ln(B_{A2+d}/B_{f\theta})}\ln\left(\frac{B_{A2+d}(1-\theta)^{\beta}+\pi}{B_{f\theta}(1-\theta)^{\beta}+\pi}\right)\right\},
\end{aligned}
\tag{6}
$$

where m_p is the amount of adsorbate, m_{hA} is the number of primary sites, θ_{kj} is the coverage ratio of jth layer at kth type clusters, θ means the coverage ratio of the layers above the first layer, π is the relative pressure, α is the geometrical parameter of the porous structure, β is the pore shape parameter $\beta \ge 1$, and B_{Ak}, B_{fk} are the energy parameters:

$$
B_{Ak}=\exp\left(\frac{Q_{Ak}}{RT}\right),\qquad B_{fk}=\exp\left(\frac{Q_{fk}}{RT}\right).
\tag{7}
$$

The model (6) is directly applicable to the energy distribution of $h = 1, 2$ (See: Kwiatkowski 2007a, 2007b). For $h > 2$, the following simplified formulas were elaborated to obtain $B_{fk} = B_{f\theta}$ (Duda et al. 2005b; Kwiatkowski 2007a):

$$
\begin{aligned}
&B_{f\theta}\overset{\text{def}}{=}B_A\exp\bigl((Q_{cp}/RT)\cdot(Z_{f\theta}-Z_{f\infty})\bigr),\\
&B_A\overset{\text{def}}{=}\exp\left(\frac{Q_A}{RT}\right),
\end{aligned}
\tag{8}
$$

where Q_{cp} is the molar adhesion energy in the ideal adsorbent-adsorbate contacts, Q_A is the first layer adsorption energy ($Q_L = Q_A/RT$), R is the gas constant, T is the temperature, and $Z_{f\theta}$ denotes an averaged value of the upper boundaries Z_{fk} of the distribution function range.

The LBET models have five adjusted parameters: V_{hA}, Q_A,α, β, B_C and optionally $Z_{f\infty}$. For the first type adsorption $\theta = \Pi^* = \Pi^*_\infty$, where (Duda et al. 2005b; Kwiatkowski 2007a):

$$
\Pi^*\overset{\text{def}}{=}\frac{\pi}{B_C(1-\theta)^{\beta-1}},
\tag{9}
$$

therefore simplifications are unnecessary. However, for the second type the following averaging formula was found to be appropriate (Kwiatkowski 2007a, 2007b):

$$
\begin{aligned}
&\theta=\Pi^*\left(\frac{1+w_H\Pi^*}{1+\Pi^*}\right),\\
&w_H=\frac{\alpha(1+\alpha-\alpha^2)}{2-\alpha}\quad\text{for } d=0,\\
&w_H=\frac{2+\alpha}{3(2-\alpha)}\quad\text{for } d=1.
\end{aligned}
\tag{10}
$$

To avoid numerical problems, multivariant identification procedure was proposed, with a subset of parameters being fixed in each variant (Duda et al. 2005b; Kwiatkowski 2007a).

2 Numerical calculations

The purpose of the numerical analysis and calculations was to verify the LBET class adsorption models and to test their applicability to the analysis of empirical adsorption isotherms. The research was divided into two stages. In the first stage, numerical investigations of the multivariant identification procedure were carried out. The adsorption isotherms were generated using the LBET formulas for the relative pressure values π ranging from $\pi_{\max} = 0$ to $\pi_{\max} = 0.91$ and with adequate energy and structural parameters taken from the literature. Next, the parameters were identified using the full set of variants of the five- parameters LBET formulas with fixed values of the system parameters and a selected energy distribution variant. In the second stage, the proposed multivariant identification of adsorption systems, based on the fitting of the five- and six-parameters LBET class models, was found to be useful for an analysis of empirical isotherms Ar–1P (Klinik 1994) and C_6H_6–WA1 (Choma 1983) taken from literature. The fitting was done using a typical constrained optimization procedure-minimizing the fitting error dispersion σ_e. The following parameters were adjusted: V_{hA}-volume of the first layer, α, β-geometric parameters of the porous structure, Z_A and Z_C-correction factors used to calculate Q_A, B_C and optionally $Z_{f\infty}$. The reliability of identification was assessed on the basis of residual dispersion σ_e and relative errors of parameters calculated for all 30 variants. To enable the final choice of the best variant, the detailed results were presented for the three best fittings. Moreover, ten well-fitted variants out of the thirty ones were treated as the acceptable ones. In order to get a synthetic measure of the identification uncertainty, the following identifiability index w_{id} was defined (Kwiatkowski 2007a):

$$
w_{\text{id}}=1-\frac{\sigma_{e\,\min}}{\frac{1}{10}\sum_{\text{opt}=1}^{10}\sigma_{e\,\text{opt}}},
\tag{11}
$$

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 ten best fitted models. The identifiability index is a fac-

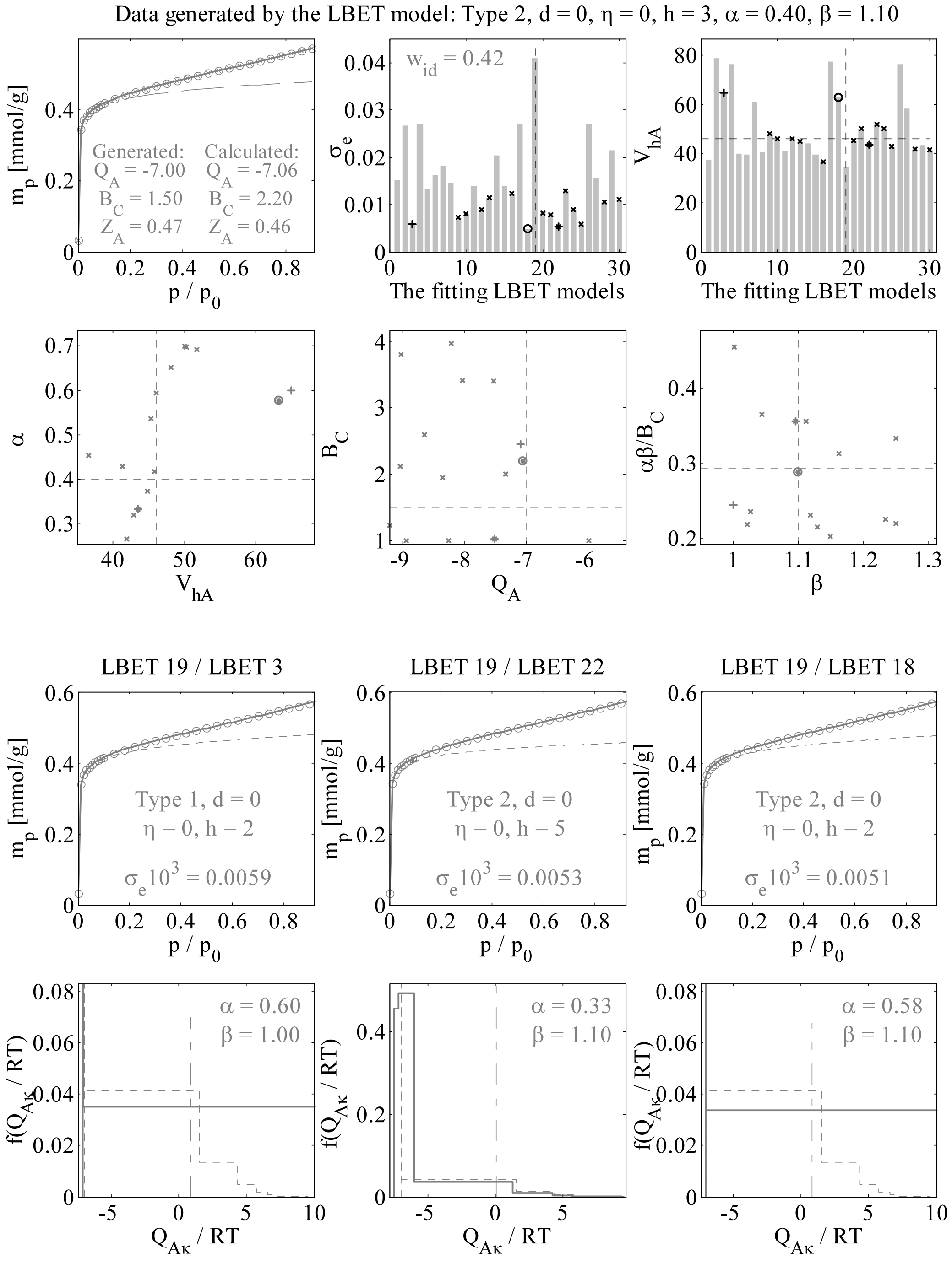


Fig. 1 The multivariant identification results for an isotherm generated by the *LBET* class model (*Type* 2, $d = 0, \eta = 0, h = 3$) and fitted by the *LBET* formulas

tor specific for this method and it provides for information regarding identification uncertainty. For example, where ten acceptable solutions differ considerably from one another at low fitting error values, it can be assumed that the best fitted variant may not be the one closest to reality. The higher the index, the better reliability of the determined parameters.

The obtained calculation results were presented in Table 1 and three best fittings for all analyzed adsorption systems were presented on Figs. 1 though 12 in full detail to

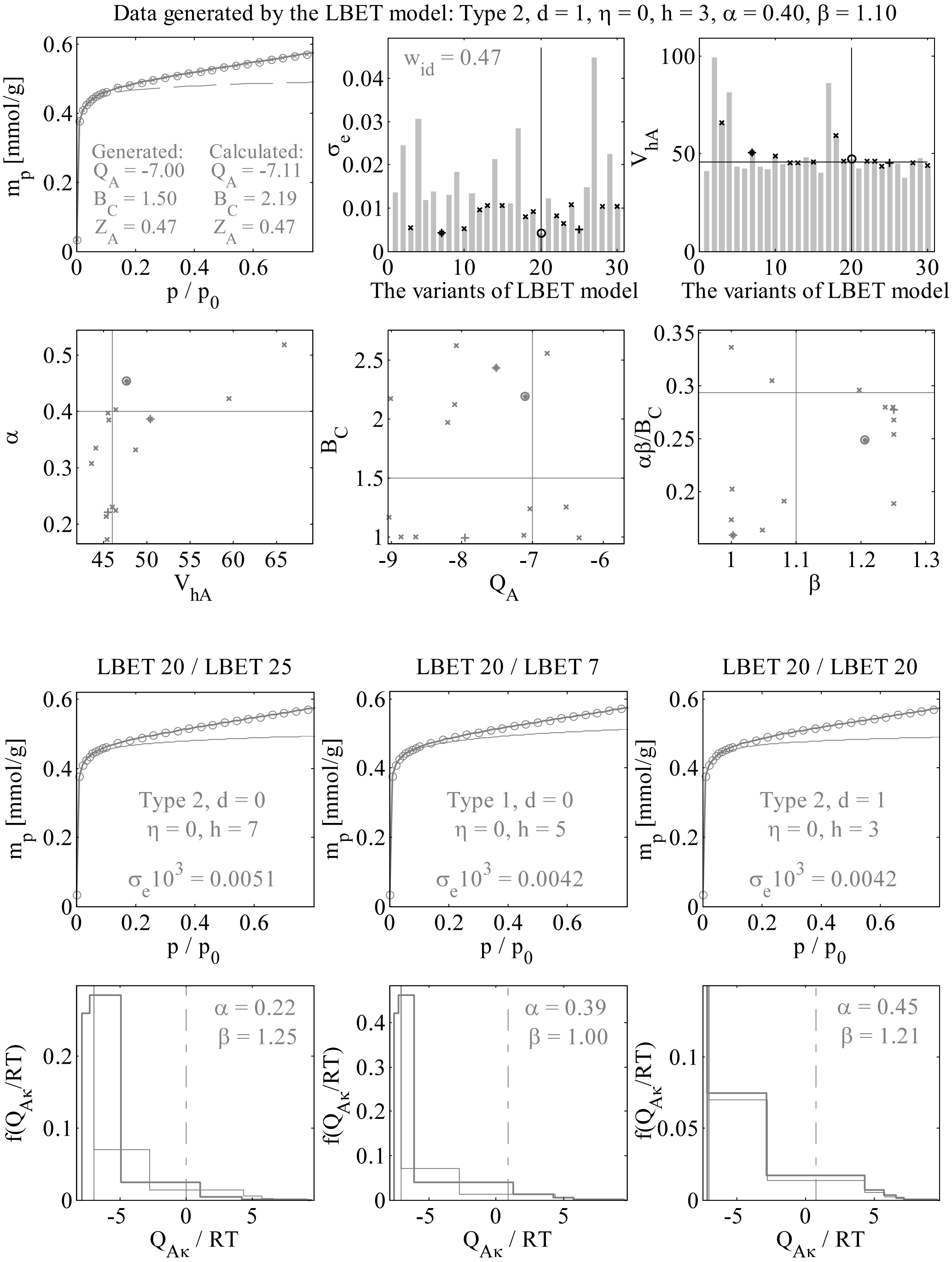


Fig. 2 The multivariant identification results for an isotherm generated by the *LBET* class model (*Type* 2, $d = 1, \eta = 0, h = 3$) and fitted by the *LBET* formulas

show the relations between the fitting error dispersion and the 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 first column of the first row shows the fitting isotherm marked by circles “o”. The solid line “—“presents a theoretical isotherm calculated with the uLBET model (Duda et al. 2005b; Kwiatkowski 2007a) with the parameters of the best fitted variant of the LBET model. The second figure in this row includes a grey bar diagram of the deviation error of the fitting with different variants of the LBET model. The red bold “o” refers to the best fitted variant. Next

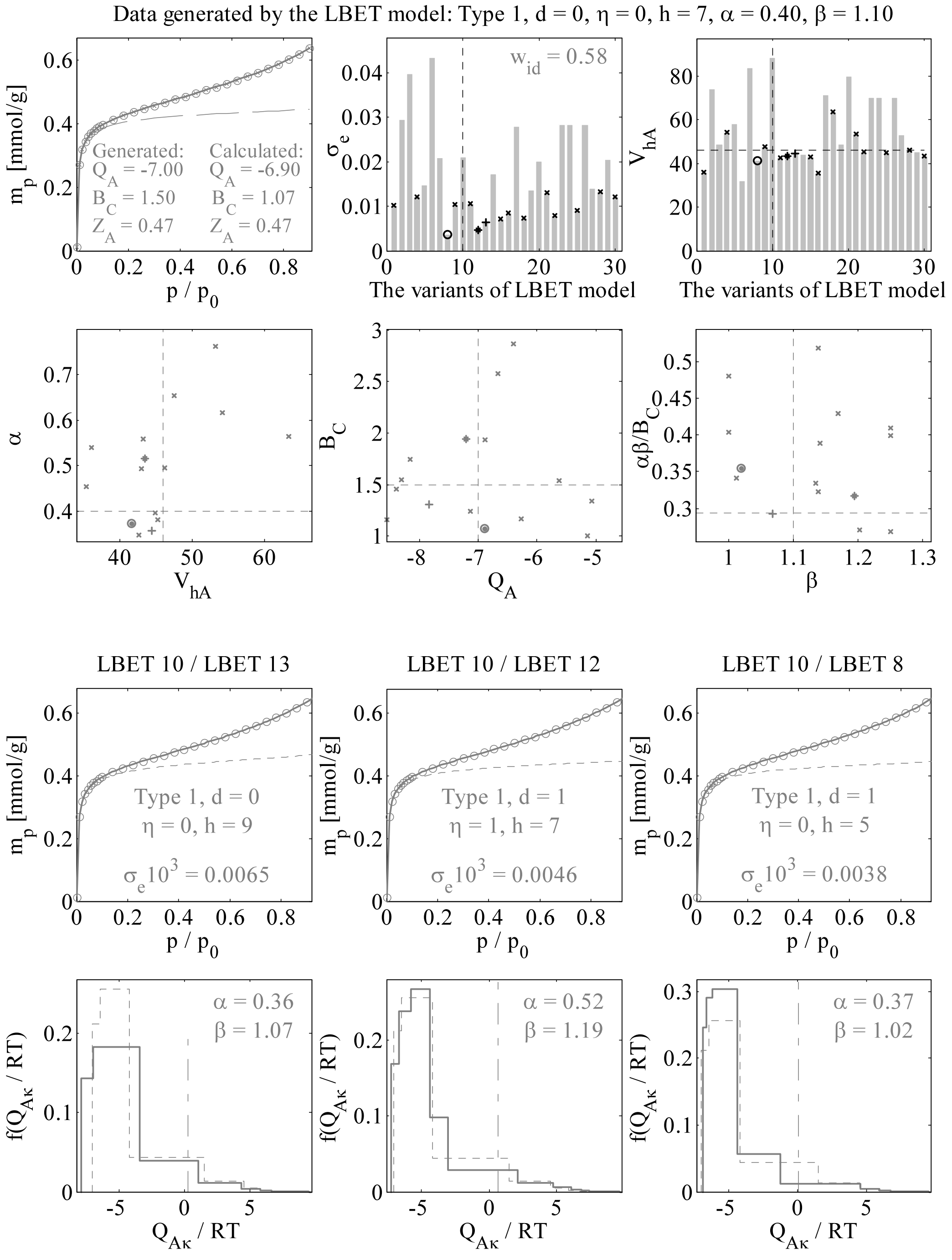


Fig. 3 The multivariant identification results for an isotherm generated by the *LBET* class model (*Type* 1, $d = 0, \eta = 0, h = 7$) and fitted by the *LBET* formulas

"+" and "*" mean the second and third best fitting. The value of the index w_{id} is shown there as well. The more diversified heights of individual bars and the bigger the differences between the lowest bar and the remaining bars, the better identity of the adsorption system. In this case, the factor w_{id} has is high, as mentioned above. The third figure in the first row shows the values of the most important structure parameter, i.e. monolayer capacity $V_{hA} \sim m_{hA}$, obtained in individual variants (grey bars). The three best fitted variants were marked in the same way as in the previous figure. The

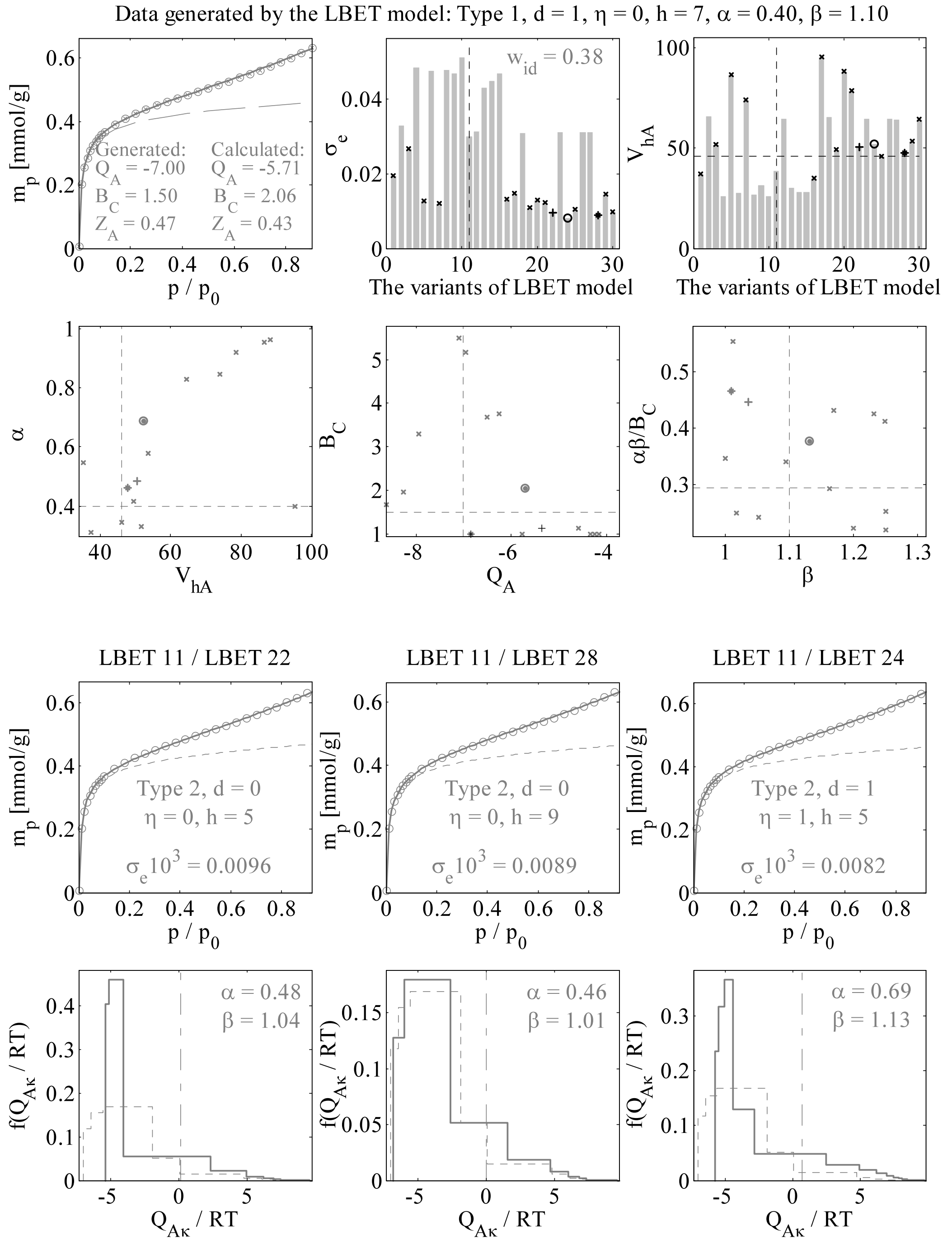


Fig. 4 The multivariant identification results for an isotherm generated by the *LBET* class model (*Type* 1, $d = 1, \eta = 0, h = 7$) and fitted by the *LBET* formulas

figures in the second row present diversification of the LBET model parameters obtained in ten good fittings. The symbol "o" means the optimum fitting parameters, "*", "+" means the second and third best fittings, and "x" marks the seven remaining acceptable fittings. They were presented in pairs in the rectangular coordinate systems. The third row of figures shows three best fittings of the LBET models. The diagram captions include the symbol of the adsorption system, and the number of the LBET model variant was divided by a slash. In the lower part of each diagram, the value of the

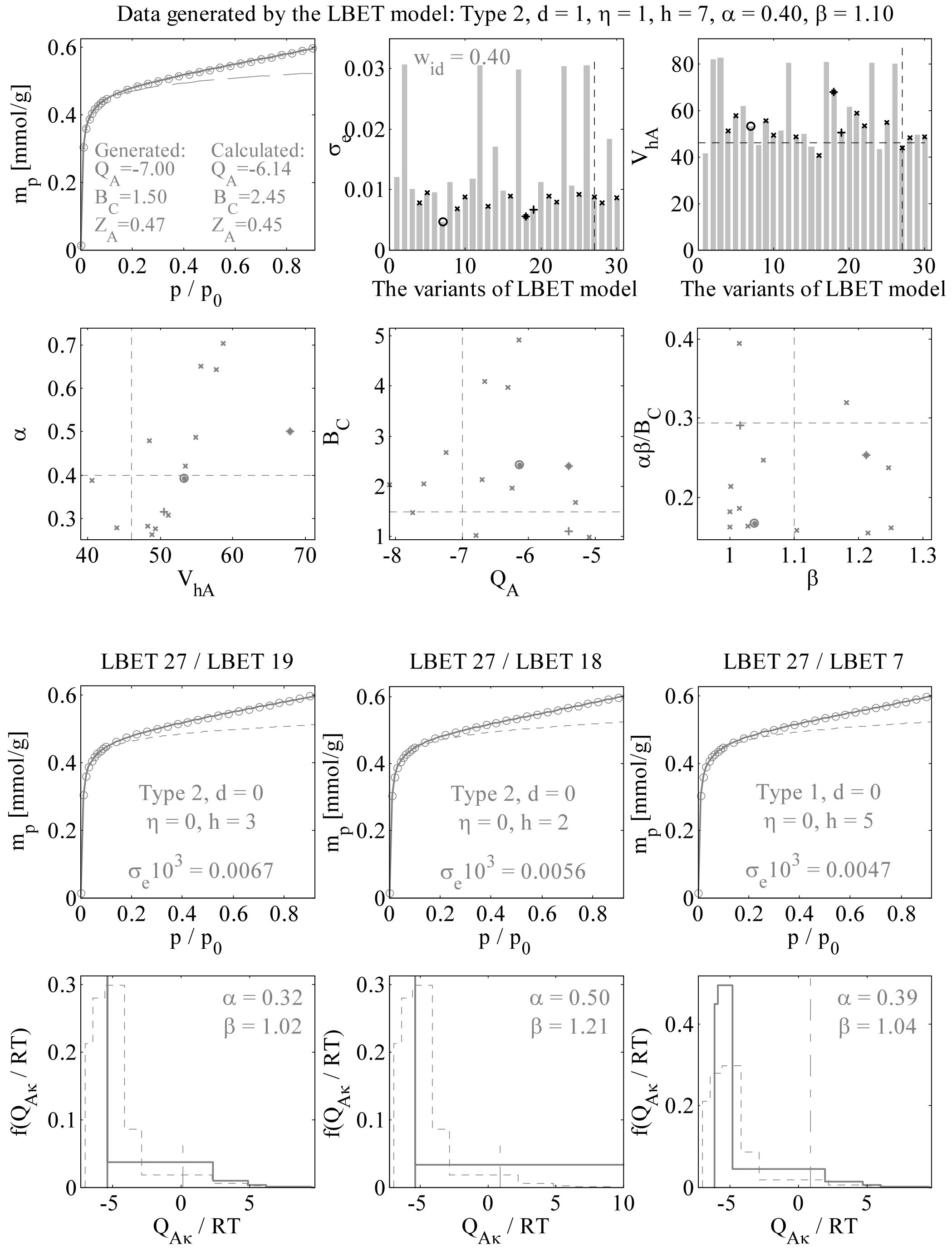


Fig. 5 The multivariant identification results for an isotherm generated by the *LBET* class model (*Type* 2, $d = 1$, $\eta = 1$, $h = 7$) and fitted by the *LBET* formulas

fitting quality measure σ_e is given. In the fourth row, the energy distributions corresponding to the respective previous subfigures are shown. The vertical lines represent the value of the adsorption energy on the second and successive layers.

3 Discussion of the obtained results

An analysis of the results presented in Figs. 1–8 and listed in Table 1 allows one to claim that in the case of data generated with the *LBET* model and recognized with the

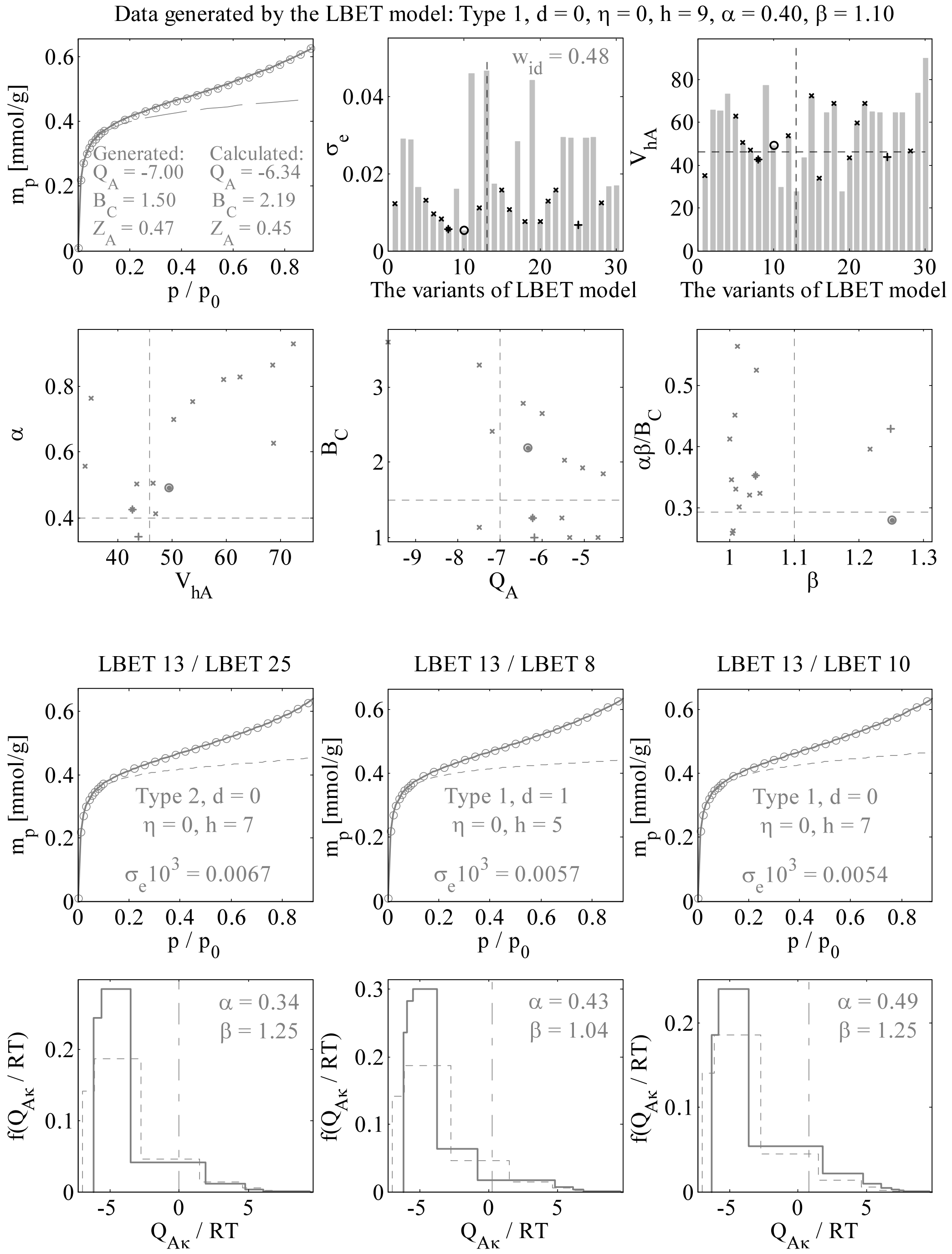


Fig. 6 The multivariant identification results for an isotherm generated by the *LBET* class model (*Type* 1, $d = 0$, $\eta = 0$, $h = 9$) and fitted by the *LBET* formulas

same *LBET* class models good identification indices are obtained. In the most cases the adsorption type is recognized correctly. Nevertheless, the heterogeneous type is not recognized in a satisfactory way. However, it should be taken into account that the *LBET* models constitute certain simplifications of the *uLBET* models presented in the earlier papers (See: Kwiatkowski 2007a). The aim of those simplifications was to obtain a significant decrease in the calculation time, which unfortunately lowered their accuracy.

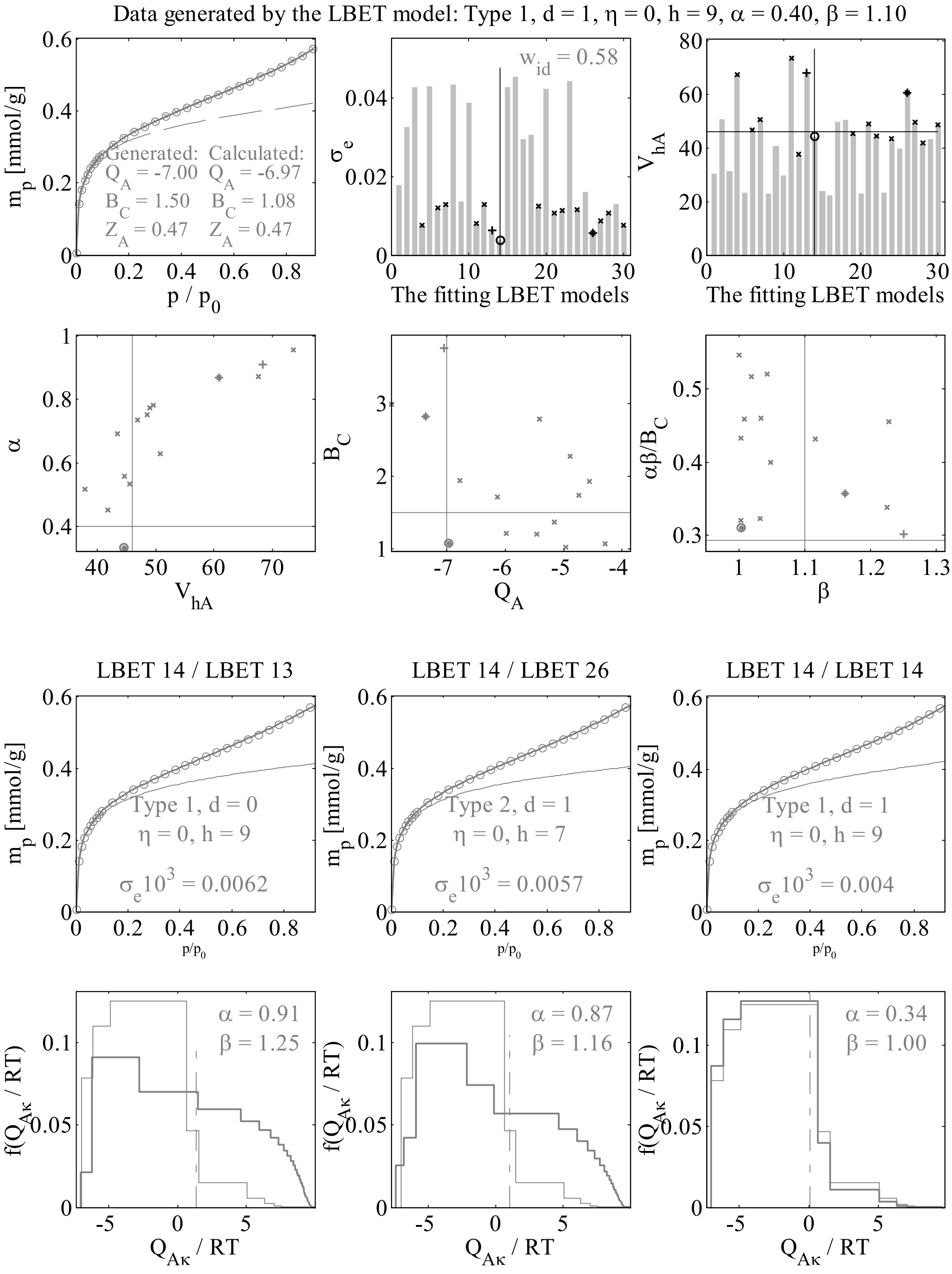


Fig. 7 The multivariant identification results for an isotherm generated by the *LBET* class model (*Type* 1, $d = 1$, $\eta = 0$, $h = 9$) and fitted by the *LBET* formulas

In the case of an analysis of the Ar–1P (77.5 K) adsorption system using the five-parameter LBET class models (Fig. 9), very precise calculations of V_{hA} parameter by all the fitted models are obtained. However, the identifiability index w_{id} is very low ($w_{\mathrm{id}} = 0.06$), which points to low identifiability of the discussed system-probably, due to a relatively small accuracy of empirical data. In the case of using the six-parameter *LBET* class models (Fig. 10) an insignificantly higher value of the identifiability index was obtained ($w_{\mathrm{id}} = 0.09$) in comparison to the analysis carried out using the five-parameter *LBET* models ($w_{\mathrm{id}} = 0.06$). In both cases the same second type of adsorption

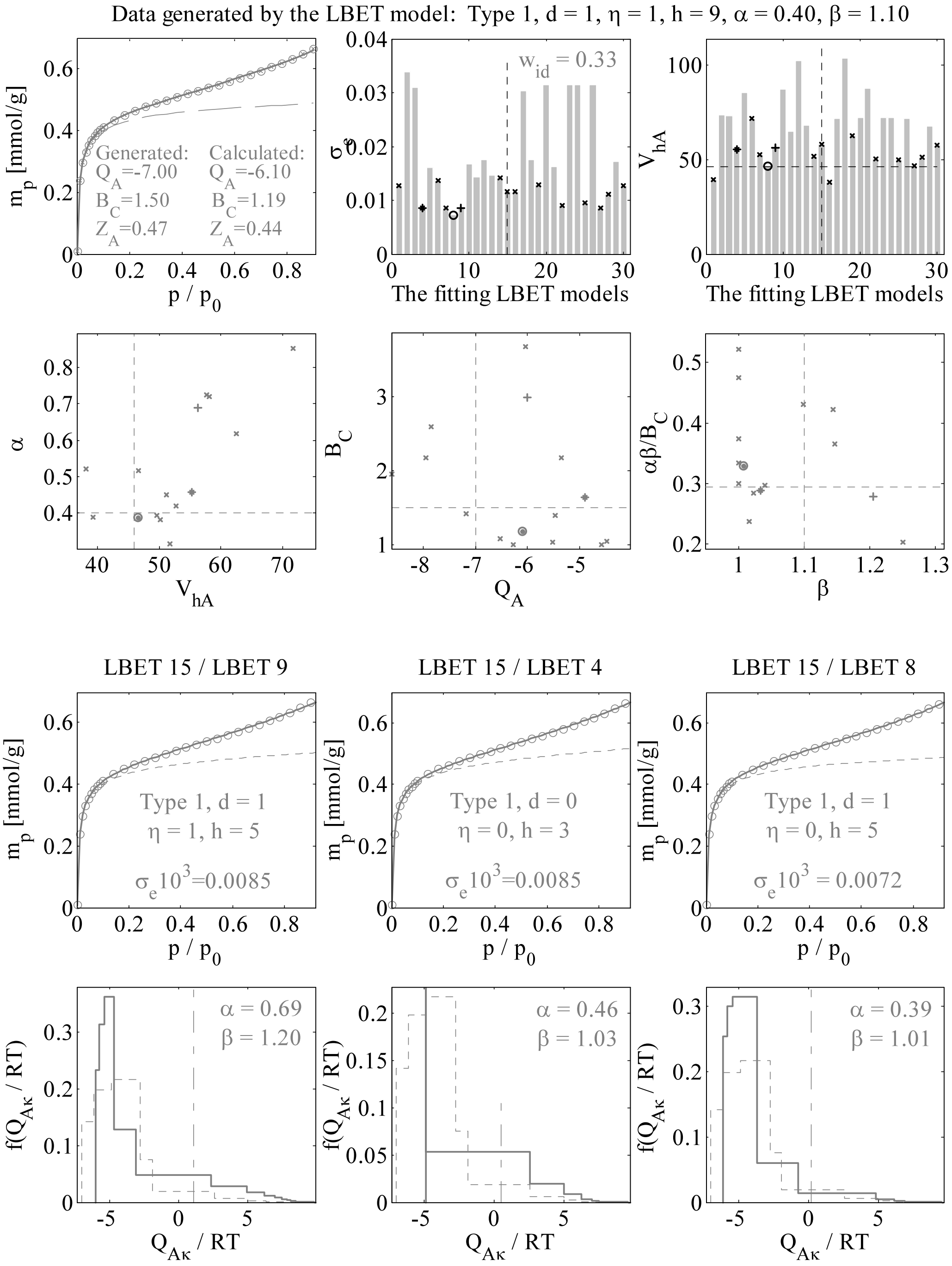


Fig. 8 The multivariant identification results for an isotherm generated by the *LBET* class model (*Type* 1, $d = 1$, $\eta = 1$, $h = 9$) and fitted by the *LBET* formulas

was recognized and the same variant of *LBET* model was best fitted. It can be concluded that the surface of the analyzed adsorbent is homogeneous with the uniformly distributed energy, and the size range of micropores is wide.

The results for another analyzed system C_6H_6–WA1 (293 K) presented in Fig. 11 show that the adsorption system is characterized by a low identifiability index ($w_{\mathrm{id}} = 0.05$). It should be noticed that the values of parameters calculated for all best fittings are similar, which points to high

Table 1 A comparison of the detailed results of calculations for isotherms generated by the *LBET* class models and fitted by the five parameters *LBET* formulas

Nr	The model generated data	w_{id}	Parameters obtained for the first best-fitted variants			The best fitted variants	Parameters of the best fitting variants						
			$-Q_A$	B_C	Z_A		T	d	η	h	α	β	$\sigma 10^3$
1	*Type* 2												
	$d=0$	0.42	7.06	2.20	0.46	1st	2	0	0	2	0.58	1.10	0.0051
	$\eta=0$					2nd	2	0	0	5	0.33	1.10	0.0053
	$h=3$					3th	1	0	0	2	0.60	1.00	0.0059
2	*Type* 2												
	$d=1$	0.47	7.11	2.19	0.47	1st	2	1	0	3	0.45	1.21	0.0042
	$\eta=0$					2nd	1	0	0	5	0.39	1.00	0.0042
	$h=3$					3th	2	0	0	7	0.22	1.25	0.0051
3	*Type* 1												
	$d=0$	0.58	6.90	1.07	0.47	1st	1	1	0	5	0.37	1.02	0.0038
	$\eta=0$					2nd	1	1	1	7	0.52	1.19	0.0046
	$h=7$					3th	1	0	0	9	0.36	1.07	0.0065
4	*Type* 1												
	$d=1$	0.38	5.71	2.06	0.43	1st	2	1	1	5	0.69	1.13	0.0082
	$\eta=0$					2nd	2	0	0	9	0.46	1.01	0.0089
	$h=7$					3th	2	0	0	5	0.48	1.04	0.0096
5	*Type* 2												
	$d=1$	0.40	6.14	2.45	0.45	1st	1	0	0	5	0.39	1.04	0.0047
	$\eta=1$					2nd	2	0	0	2	0.50	1.21	0.0056
	$h=7$					3th	2	0	0	3	0.32	1.02	0.0067
6	*Type* 1												
	$d=0$	0.48	6.34	2.19	0.45	1st	1	0	0	7	0.49	1.25	0.0054
	$\eta=0$					2nd	1	1	0	5	0.43	1.04	0.0057
	$h=9$					3th	2	0	0	7	0.34	1.25	0.0067
7	*Type* 1												
	$d=1$	0.58	6.97	1.08	0.47	1st	1	1	0	9	0.34	1.00	0.0040
	$\eta=0$					2nd	2	1	0	7	0.87	1.16	0.0057
	$h=9$					3th	1	0	0	9	0.91	1.25	0.0062
8	*Type* 1												
	$d=1$	0.33	6.10	1.19	0.44	1st	1	1	0	5	0.39	1.01	0.0072
	$\eta=1$					2nd	1	0	0	3	0.46	1.03	0.0085
	$h=9$					3th	1	1	1	5	0.69	1.20	0.0085

system identification reliability. Moreover all three best fittings recognized the same second type of adsorption model, which points to the occurrence of geometrical limitations for cluster growth in the analyzed adsorption system. In this case it can also be observed that the adsorption energy distribution in the pores with similar molecular sizes is almost homogeneous. In the case of using the six-parameter *LBET* class models to analyze the C_6H_6–WA1 (293 K) adsorption system (the results of which are shown on Fig. 12), slightly smaller identifiability index was obtained ($w_{\mathrm{id}} = 0.04$), but as in previous adsorption system in all three best fittings the same second type of adsorption was recognized. What is more, identical structure parameters were obtained ($\alpha = 0.17, \beta = 1.25$), which shows that despite low *wid* value the system was identified correctly. This example perfectly depicts the idea behind presenting three best fittings. Other-

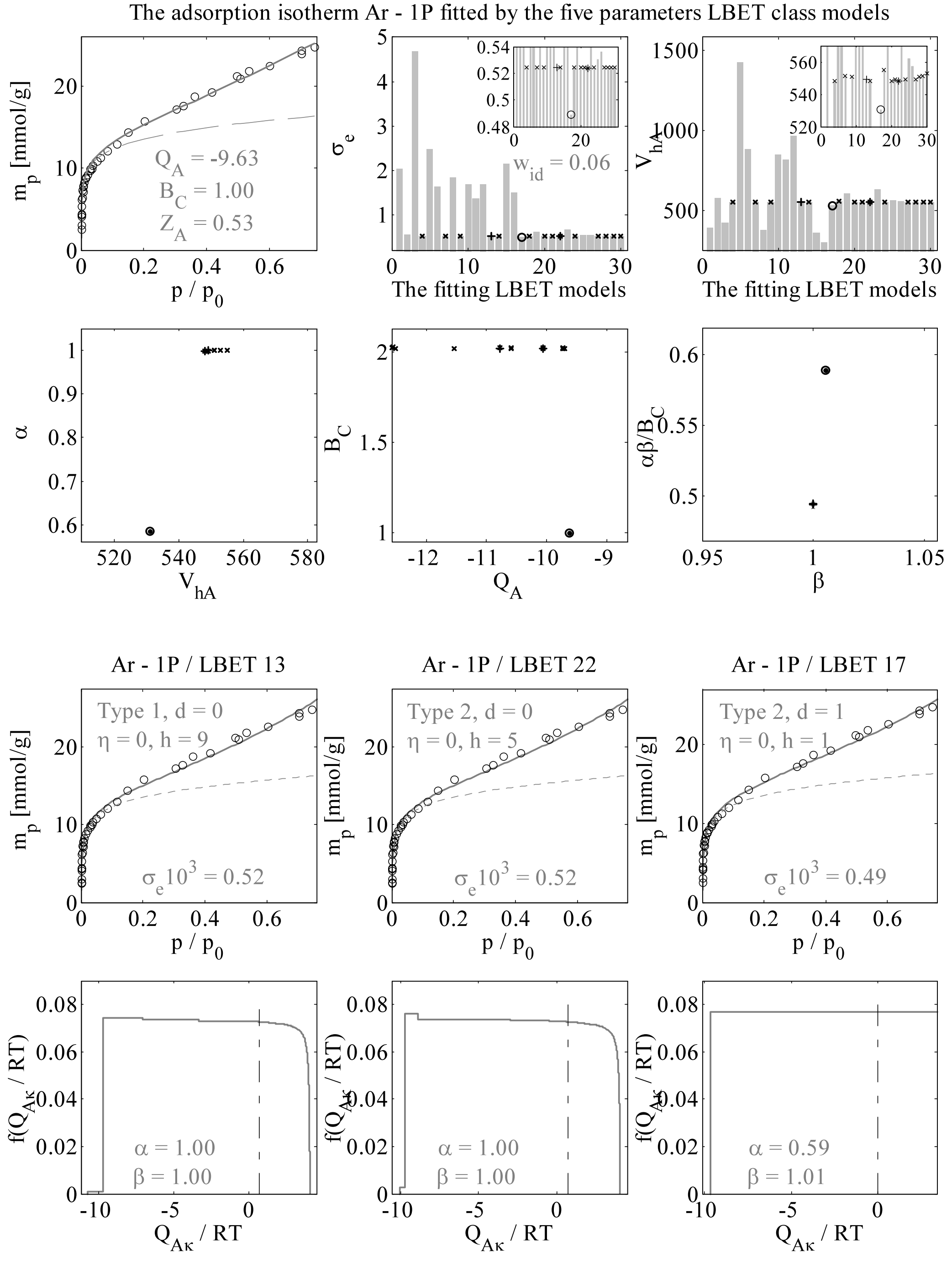


Fig. 9 The best results of application of the five parameters *LBET* class models to the analysis of Ar (argon) adsorption isotherm on the active carbon 1P (77 K)

wise, if the values of the parameters obtained for three best fittings, with insignificant differences in the fitting error itself, differed considerably, the system would be identified incorrectly, i.e. it would not be known which of the three best fittings is closest to reality.

4 Conclusion

The above results show that the *LBET* class models give better insight into the adsorption mechanisms and the structure

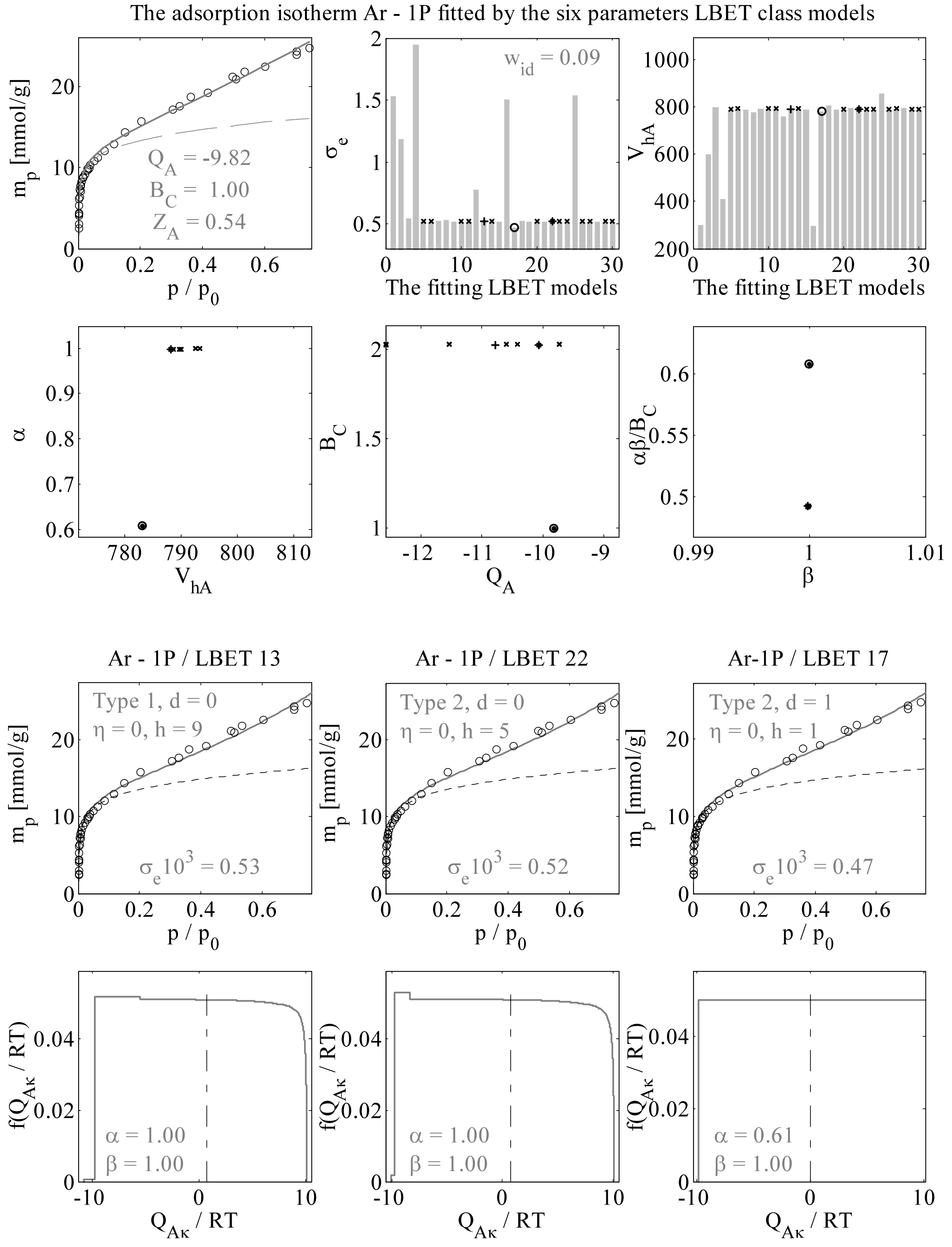
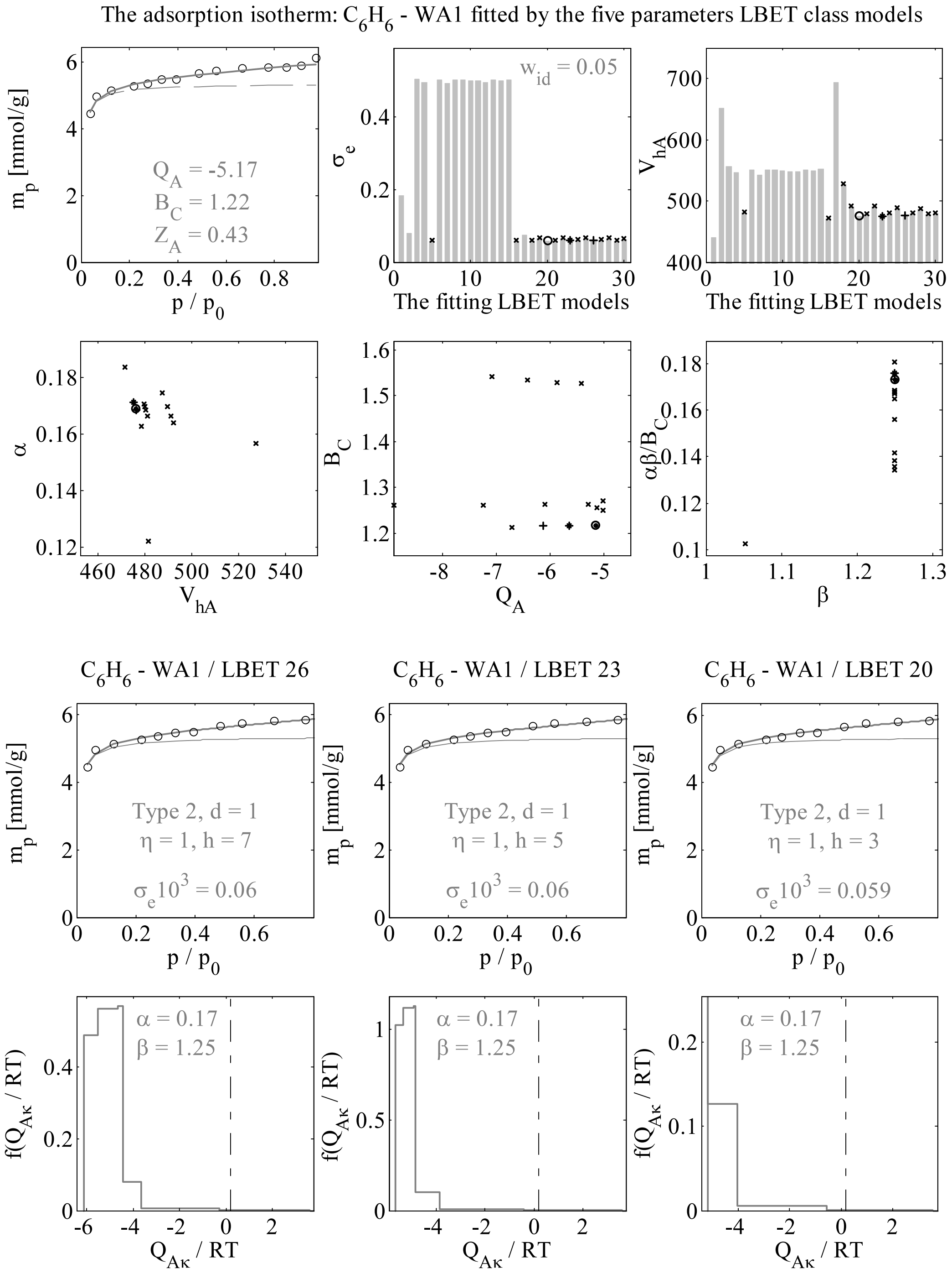


Fig. 10 The best results of application of the six parameters *LBET* class models to the analysis of Ar (argon) adsorption isotherm on the active carbon 1P (77 K)

of pores. The *LBET* models provide for semiquantitative information on pore structure, adsorbate clusterization mechanisms and surface energy distribution and may be well fitted to different adsorption data in a wide pressure range. The *LBET* formulas can be recommended for use directly in the adsorption system identification procedures. The fitting of the *LBET* class models also provides for information on the properties of adsorbate clusters deposed in the material. Additionally, it enables deducing the properties of pore structure.


The adsorption isotherm: C_6H_6 - WA1 fitted by the five parameters LBET class models

C_6H_6 - WA1 / LBET 26

C_6H_6 - WA1 / LBET 23

C_6H_6 - WA1 / LBET 20

Fig. 11 The best results of application of the five parameters *LBET* class models to the analysis of C_6H_6 (benzene) adsorption isotherm on the active carbon WA1

The procedure of multivariant identification of adsorption systems based on fitting LBET class models to either empirical or simulated data, with the surface energy distribution structure being presumed in each variant, enables to avoid numerical problems caused by a large number of the system parameters to be determined. Moreover, an analysis of the three best and seven acceptable fittings provides for information regarding not only the value of the obtained structure parameters, but also on the reliability of their determination.

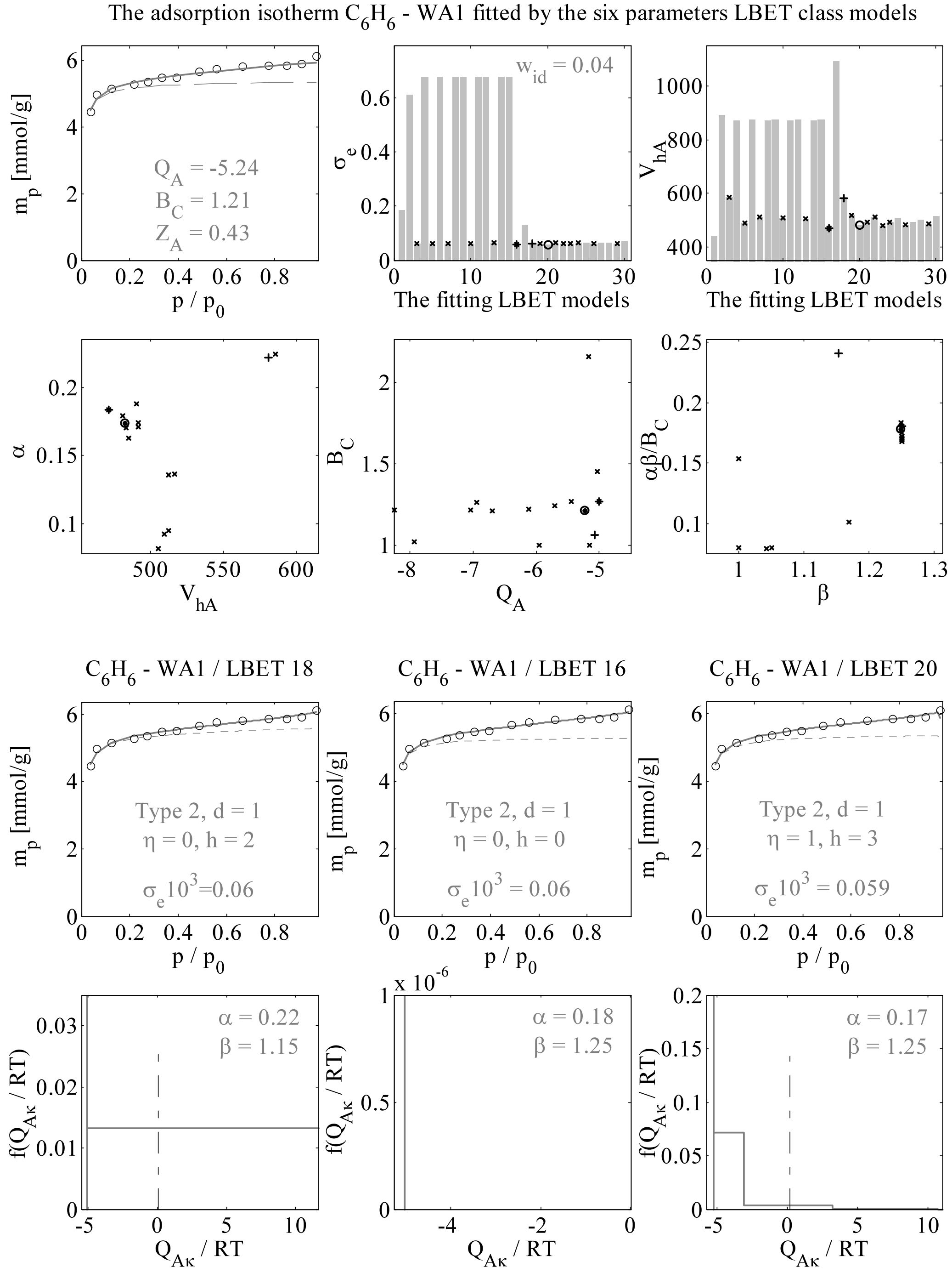


Fig. 12 The best results of application of the six parameters *LBET* class models to the analysis of C_6H_6 (benzene) adsorption isotherm on the active carbon WA1

To sum up, the proposed approach to the examination of microporous structure may be considered an alternative for the classical techniques and more complex methods. However, this requires a more thorough understanding of the theoretical grounds for these models and of the methodology of interpreting results. Still, the effects are worth the effort.

Acknowledgements The research was carried out as a part of the AGH-University of Science and Technology in Krakow grant No. 10.10.210.52/23.

References

Aranovich, G.L., Donohue, M.D.: Vapor adsorption on microporous adsorbents. Carbon **38**, 701–708 (2000)

Cao, D., Wang, W., Shen, Z., Chen, J.: Determination of pore size distribution and adsorption of methane and CCl on activated carbon by molecular simulation. Carbon **40**, 2359–2365 (2002)

Choma, J.: Mikroporowate adsorbenty węglowe w ujęciu zmodyfikowanej zależności potencjałowej teorii adsorpcji. Przem. Chem. **62**(11), 634–637 (1983)

Dubinin, M.M.: The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surfaces. Chem. Rev. **60**, 235–241 (1960)

Dubinin, M.M.: Fundamentals of the theory of adsorption in micropores of carbon adsorbents characteristics of their adsorption properties and microporous structures. Carbon **27**, 457–467 (1989)

Dubinin, M.M., Astakhov, V.A.: Description of adsorption equilibrium of vapors on zeolites over wide ranges of temperatures and pressure. Adv. Chem. Ser. **102**, 69–85 (1971)

Duda, J.T., Milewska-Duda, J., Kwiatkowski, M.: Evaluation of adsorption energy distribution of miscroporous materials by a multivariant identification. Appl. Surf. Sci. **252**, 570–581 (2005a)

Duda, J.T., Kwiatkowski, M., Milewska-Duda, J.: Computer modeling and analysis of heterogeneous structures of microporous carbonaceous materials. J. Mol. Model. **11**(4–5), 416–430 (2005b)

Erdem-Senatalar, A., Tatller, M., Sirkecioglu, A.: The relationship of the geometric factor in the Dubinin–Astakhov isotherm equation with the fractal dimension. Colloids Surf. A: Physicochem. Eng. Aspects **173**, 51–59 (2000)

Gil, A.: Analysis of the micropore structure of various microporous materials from nitrogen adsorption at 77 K. Adsorption **4**, 197–206 (1998)

Gil, A., Grange, P.: Application of the Dubinin–Radushkevich and Dubinin–Astakhov equations in the characterization of microporous solids. Colloids Surf. A: Physicochem. Eng. Aspects **113**, 39–50 (1996)

Gomez-Serrano, V., Gonzalez-Garcia, C.M., Gonzalez-Martin, M.L.: Nitrogen adsorption isotherms on carbonaceous materials. Comparison of BET and Langmuir surface areas. Powder Technol. **11**, 6103–6108 (2001)

Gregg, S.J., Sing, K.S.W.: In: Adsorption, Surface Area and Porosity, pp. 7–297. Academic Press, London (1967)

Jaroniec, M., Madey, R., Choma, J., McEnaney, B., Mays, T.J.: Comparison of adsorption methods for characterizing the microporosity of activated carbons. Carbon **27**, 77–83 (1989)

Klinik, J.: The comparison of various methods used for the determination of mesopore structure of porous solids. In: Rouquerol, J., Rodriguez-Reinoso, F., Sing, K.S.W., Unger, K.K. (eds.) Studies in Surface Science and Catalysis Characterisation of Porous Solids III Proceedings of the UPAC Symposium, pp. 119–128. Elsevier, Amsterdam (1994)

Kwiatkowski, M.: Computer analysis of microporous structure by employing the LBET class models with various variants of the adsorption energy distribution in comparison to the classical equations. Langmuir **23**, 2569–2581 (2007a)

Kwiatkowski, M.: Comparison of the evaluation reliability of microporous structure parameters by employing single and double adsorption isotherms. Colloids Surf. A: Physicochem. Eng. Aspects **294**, 92–101 (2007b)

Milewska-Duda, J., Duda, J., Jodłowski, G., Kwiatkowski, M.: A model for multilayer adsorption of small molecules in microporous materials. Langmuir **16**, 7294–7303 (2000)

Nicholson, D.: Simulation study of nitrogen adsorption in parallel-sided micropores with corrugated potential functions. J. Chem. Soc. Faraday Trans. **90**, 181–185 (1994)

Puziy, A.M., Volkov, V.V., Poznayeva, O.I., Bogillo, V.I., Shkilev, V.P.: Comparison of various numerical procedures for analysis of structural heterogeneity. Langmuir **13**, 1303–1306 (1997)

Rodrıguez-Reinosou, F., Molina-Sabio, M.: Textural and chemical characterization of microporous carbons. Adv. Colloid Interface Sci. **76–77**, 271–294 (1998)

Rudziński, W., Everett, D.H.: Adsorption of Gases on Heterogeneous Surfaces. Academic Press, London (1992)

Ryu, Z., Zheng, J., Wang, M., Zhang, B.: Characterization of pore size distributions on carbonaceous adsorbents by DFT. Carbon **37**, 1257–1264 (1999)

Sánchez-Montero, M.J., Herdes, C., Salvador, F., Vega, L.F.: New insights into the adsorption isotherm interpretation by a coupled molecular simulation—experimental procedure. Appl. Surf. Sci. **252**(3), 519–528 (2005)

Sing, K.: The use of nitrogen adsorption for the characterisation of porous materials. Colloids Surf. A: Physicochem. Eng. Aspects **187–188**, 3–9 (2001)

Shahsavand, A., Ahmadpour, A.: Application of optimal RBF neural networks for optimization and characterization of porous materials. Comput. Chem. Eng. **29**(10), 2134–2143 (2005)

Storck, S., Bretinger, H., Maier, W.F.: Characterization of micro- and mesoporous solids by physisorption methods and pore-size analysis. Appl. Catal. A Gen. **174**, 137–146 (1998)

Suzuki, T., Kaneko, K., Setoyama, N., Maddox, M., Gubbins, K.: Grand Canonical Monte Carlo Simulation for nitrogen adsorption in graphic slit micropores: effect of interlayer distance. Carbon **34**, 909–912 (1996)