

# Computer analyses of new numerical methods for the description of adsorption process and the reliability of identification of microporous structure parameters

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Received: 28 February 2007 / Accepted: 30 November 2007 / Published online: 25 January 2008  
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**Abstract** The aim of this work was the computer analysis of numerical properties of the original mathematical method of the description of adsorption process and the reliability of the identification of structure parameters. The method is based on the theory of multilayer adsorption, the derivation and further theoretical discussion of which was presented in the author's earlier works. The following tasks were given special attention in this paper: the influence of the assumed structure parameters, the influence of the high-pressure section of adsorption isotherms and the influence of the number of simultaneously fitted adsorption isotherms on the quality of identification and the errors of microporous structure parameters. This research provides a basis for the evaluation of the reliability of the parameters calculated for real adsorption systems.

**Keywords** Computer calculation · Heterogeneous · Isotherms · Microporous · Physical adsorption

## Introduction and theoretical basis

At the present time, the microporous materials occupy a major position among adsorbents due to their adsorption, chemical and mechanical properties [1–3]. The characteristic adsorption properties of those materials are connected to the occurrence of micropores, defined as pores with internal width of less than 2 nm [4]. The use of carbonaceous materials requires their characterization, which includes,

among others, description of microporosity and heterogeneity in terms of adsorption energy [5]. Different methods for the characterization of micropores are available, including spectroscopy, electron and tunnel microscopy and adsorption methods [5, 6]. However, the results obtained are not always compatible, resulting in problems with the credibility of the obtained structure parameters. Therefore in the majority of cases applying a single technique does not suffice to provide for precise and reliable information regarding the structure of the pores. Consequently, the acquired data should be compared with those obtained otherwise. The most popular method is the physical adsorption measurement, used widely for the analysis of the texture of porous carbons. Gas and vapours adsorption methods are the techniques applied particularly often for the characterization of microporous carbonaceous materials [5, 6].

Several various equations have been proposed to describe the adsorption equilibrium of small molecules, and many different theories of physical adsorption processes have been developed [5]. They are used for obtaining the characteristics of adsorbents including adsorption energy distribution, pore volume, pore size distribution and surface area on the basis of the empirical adsorption data obtained at lower pressures. Those theories assume different mechanisms of physical adsorption processes and various simplifications of the real adsorption systems. For microporous materials, the Dubinin-Radushkevich (DR) and Dubinin-Astakhov (DA) equations are usually recommended [6]. The DR equation is empirical, but it is based on the adsorption theory of the volume filling of micropores proposed by Dubinin and Radushkevich [7, 8], which has its origins in the potential theory of physical adsorption [8]. The DA equation is in turn a general form of the DR equation, in which the coefficient  $n$  may be optimized [9].

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The DR equation is used widely for the description of vapours adsorption on a variety of microporous carbonaceous adsorbents, including activated carbons. However, it is often emphasized that there are several defects in the Dubinin-Radushkevich equation, which affect the accuracy of the results [6, 9]. In particular, the DR equation does not reduce to the Henry equation as  $p/p_0$  approaches zero. Moreover, adsorption isotherms of many microporous carbonaceous materials usually cannot be fitted to the DR equation and in many cases the fittings are unsatisfactory. Additionally, one can find objections in the literature that the energy parameter of the DR equation is not defined clearly enough [9, 10].

Another popular equation applied to the description of the physical adsorption process is the BET equation [11]. The adsorption model on which the BET equation is based describes the multilayer physical adsorption on the basis of the kinetic model proposed by Langmuir [12]. According to the Langmuir theory the adsorption process is limited to a monolayer and the dynamic equilibrium is reached between the gas phase and the adsorbed state when the rates of adsorption and desorption are equal [11].

The principal assumption of the BET theory is that the Langmuir equation applies to every adsorption layer. Similar to the Langmuir theory, the first adsorption layer is formed on active centers, which are located on the adsorbent surface. Moreover, it is assumed that the probability of occupying a given site is independent of the neighboring sites and the molecules, which may already be placed at these neighboring sites [13]. It is also assumed that there are no lateral interactions between the adsorbed molecules situated on the neighboring sites. Applicability of the linearity range for the BET equation is usually restricted to the range of relative pressures between 0.05 and 0.35  $p/p_0$  and for the number of layers equal to 1 this equation reduces to the Langmuir equation. A major criticism of the BET theory concerns the assumption that all adsorption sites on the solid surface are homogeneous of the energy [14]. Another criticized assumption is that the BET model does not take into account adsorbate-adsorbate interactions. Although several modifications of the BET equation were proposed, none of them found wider appreciation.

In spite of the critical remarks regarding the above assumptions of the BET theory, the equation derived from this theory is commonly applied to the surface analysis of microporous materials. This is connected with the fact that the BET theory, though hardly acceptable as a whole, describes the adsorption process clearly. In particular, the BET adsorption mechanism may be perceived as an adequate representation of the physical process at a lower relative pressure range. Therefore, the BET equation is recommended for the evaluation of the specific surface area of adsorbents by using the initial part of the adsorption

isotherm. Apart from the equations mentioned above, the empirical Freundlich equation is well-known and frequently used in adsorption technology, due to its simplicity and applicability to a number of adsorption systems [15]. This equation describes well the majority of adsorption systems. However, it must be remembered when using this equation that the conformity between the calculated values and the experimental ones is not always acceptable.

As frequently emphasized in the literature, the classical methods of the calculation of microporous structure parameters are not satisfactory in the majority of cases, as the results of the surface structure and energy evaluation based on the adsorption at higher pressures are often doubtful. Notwithstanding, the microporous carbonaceous materials have been studied extensively in the last century, and significant progress has been made in the theoretical description of heterogeneity in terms of structure and energy [5, 16].

Owing to the development of computer science and the increasing knowledge of the phenomena occurring on the surfaces of solids, more advanced methods of micropore structure description have been developed [17]. They use advanced numerical tools, e.g., optimization algorithms, molecular simulations [18, 19], the Monte Carlo method [20], neural networks [21], and genetic algorithms.

In recent years the density functional theory, DFT has become an interesting tool for the characterization of porous materials [22]. In this theory, the adsorbed substance is pictured as inhomogeneous fluid, characterized by its density profile across the pore. Recently, with the availability of commercial software, the DFT method has become more popular, although one should take into account that the DFT schemes are very ill-conditioned [23], and consequently the results are dependent to a considerable degree on the arbitrary assumed regularization criteria [24].

In the last century the fractal approach has also become a valuable tool for the characterization of heterogeneous surfaces [25]. To describe surface heterogeneity in the analysis of the structure of pores the fractal dimension  $D$  is used [26, 27]. The fractal dimension of the surface accessible for physical adsorption is the global measure of surface irregularity providing information about the total surface geometry without taking into account individual pores [28].

### Theoretical basis of the new physical adsorption models

Although many advanced methods are available, the achieved results are still unsatisfactory, and in many cases, these methods are too complicated for a wide range of users. Therefore, simple and reliable methods for their characterization still need to be improved and developed. Notwithstanding, a new group of models were developed,

based on the previously elaborated theory of physical adsorption [29].

The above mentioned theory of adsorption is based on the classical BET theory; however, it takes into account the occurrence of branched clusters and discusses the geometrical and energy-related limitations of creating clusters [30, 31]. The localized adsorption results from the occurrence of the sites which provide for the energetic conditions for the adsorption of the first molecules of cluster thanks to the adhesion forces. According to this theory, the surface of adsorbents can be heterogeneous in terms of both energy and pore geometry. Moreover, in the considered theory there exists a distinction between the two types of adsorption models [32]. The first model type refers to the adsorption system in which the limitation in the number of layers is the effect of a competing physical adsorption. The second model type describes the systems in which the limitations in cluster size result from pore geometry.

Upon deriving the uLBET class models, the following assumptions were made [30, 31]:

- a) The layers above the first one are homogeneous, and energy parameters  $B_C$  are the same for all the layers above the first one; therefore the following formulas are true:

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

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 following function:

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

where  $\alpha$  is the geometrical parameter of the microporous structure,  $m_{hAk}$  is the amount of  $k$  type primary sites, and  $k$  is the cluster type.

- c) The branching of clusters is expressed by the dimensionless pore shape factor  $\beta_{\kappa n}$ .
- d) The physical adsorption energy of the first layer is expressed in the following form [30, 31]:

$$Q_{A\kappa} = U_p - Z_{A\kappa} \cdot Q_{cp}, Q_A \stackrel{def}{=} U_p - Z_A \cdot Q_{cp} = \min_{k=1} (Q_{A\kappa}), \tag{3}$$

where  $Z_{A\kappa}$  is the factor distributed uniformly over a range depending on  $k$ ,  $\kappa$  counts  $k$ th type clusters of the identical energy profile across the layers  $n=1, \dots, k$ ,  $Q_A$  is the physical adsorption energy of the first layer,  $Q_{A\kappa}$  is the molar energy contributed by placing an adsorbate molecule on the first

layer of  $\kappa$ th class clusters, and  $Z_A$  is the correcting factor of the effective adsorbent-adsorbate contact.

- e) The distribution function related to the energy parameter  $B_{A\kappa} \in (B_{Ak}, B_{j\kappa})$  is [30, 31]:

$$B_{Ak} \stackrel{def}{=} B_A \cdot (B_{cp})^{Z_A(1-\zeta_{Ak})}, B_{j\kappa} \stackrel{def}{=} B_A \cdot (B_{cp})^{Z_A(1-\zeta_{j\kappa})}, f_k(B_{A\kappa}) = \frac{m_{hAk}}{\ln(B_{j\kappa}/B_{Ak})} \frac{1}{B_{A\kappa}}, \tag{4}$$

$$B_A \stackrel{def}{=} \exp(Q_A/RT), B_{cp} \stackrel{def}{=} \exp(Q_{cp}/RT). \tag{5}$$

The uLBET model based on the above assumptions takes the following form [30, 31]:

$$m_p = m_{hA}(1 - \alpha) \left\{ 1 - \frac{1}{\ln(B_A/B_{f1})} \ln \left( \frac{B_A + \pi}{B_{f1} + \pi} \right) \right\} + m_{hA}(1 - \alpha) \sum_{k=2}^K \alpha^{k-1} \left( 1 + \sum_{n=2}^k \prod_{j=2}^n (\beta\theta_{kj}) \right) \left\{ 1 - \frac{1}{\ln(B_{Ak}/B_{jk})} \ln \left( \frac{B_{Ak}(1-\theta_{k2})^\beta + \pi}{B_{jk}(1-\theta_{k2})^\beta + \pi} \right) \right\} \tag{6}$$

where  $m_p$  is the amount of adsorbate,  $m_{hA}$  is the number of primary sites,  $\theta_{kj}$  is the coverage ratio of  $j$ th layer at  $k$ th type clusters,  $\theta$  is the coverage ratio of layers  $n > 1$ , and  $\pi$  is the relative pressure. The uLBET model involves the following five or six parameters:  $m_{hA}$ ,  $Z_A$ ,  $\alpha$ ,  $\beta$ ,  $B_C$  and optionally  $\zeta_{f\infty}$  which can be adjusted by fitting Eq. (6) to the empirical adsorption data, with a selected variant of the surface energy distribution function. To make the calculations more effective numerically, the analytical formulas approximating the uLBET model (6) with negligible errors were developed.

The uLBET formula can be expressed in the analytical form based on the assumptions given below:

- a) The coverage ratios  $\theta_{kn}$  are the same for all  $k > 1 + d$ ,  $n > 1 + d$ ,
- b) The energy parameters  $B_{Ak}$  and  $B_{j\kappa}$  do not depend on  $k$ , at least for  $k > 1 + d$ , where  $d = \{0,1\}$  is the binary variable; for  $d=1$ , a more accurate variant of the model with the bimolecular clusters treated separately is obtained.

The heterogeneous adsorption model based on the above assumptions takes the following form, referred to as the LBET formula [30, 33]:

$$\frac{m_p}{m_{hA}} = (1 - \alpha) \left\{ 1 - \frac{1}{\ln(B_A/B_{f1})} \cdot \ln \left( \frac{B_A + \pi}{B_{f1} + \pi} \right) \right\} + d \cdot \alpha(1 - \alpha) \left( 1 + \beta\theta_2 \right) \left\{ 1 - \frac{1}{\ln(B_{A2}/B_{f2})} \ln \left( \frac{B_{A2}(1-\theta_2)^\beta + \pi}{B_{f2}(1-\theta_2)^\beta + \pi} \right) \right\} + \tag{7}$$

+ $\alpha^{d+1}[d + (\beta\theta)^d(1 + \frac{\beta\theta}{1-\alpha\beta\theta})]\{1 - \frac{1}{\ln(B_{A2+d}/B_{f\theta})} \ln(\frac{B_{A2+d}(1-\theta)^\beta + \pi}{B_{f\theta}(1-\theta)^\beta + \pi})\}$ , where  $m_{hA}$  is the total number of the primary sites. The quantity  $\Pi^*$  was defined as [33]:

$$\Pi^* \stackrel{def}{=} \frac{\pi}{B_C(1-\theta)^{\beta-1}} \tag{8}$$

For the 1st type adsorption  $\theta = \Pi^* = \Pi_\infty^*$ , therefore simplifications are not required, although for the 2nd type the following averaging formula was found to be appropriate [33]:

$$\theta = \Pi^* \left( \frac{1 + w_H \Pi^*}{1 + \Pi^*} \right), \quad w_H = \frac{\alpha(1 + \alpha - \alpha^2)}{2 - \alpha} \text{ for} \tag{9}$$

$$d = 0, \quad w_H = \frac{2 + \alpha}{3(2 - \alpha)} \text{ for } d = 1.$$

The model (7) is directly applicable to the energy distribution of  $h=1, 2$ . For  $h>2$ , the following simplified formulas were elaborated to obtain  $B_{jk} = B_{fq}$  [33]:

$$B_{f\theta} \stackrel{def}{=} B_A \exp((Q_{cp}/RT) \cdot (Z_{f\theta} - Z_{f\infty})), \quad B_A \stackrel{def}{=} \exp(Q_A/RT), \tag{10}$$

where  $Z_{f\theta}$  denotes the averaged value of the upper boundary parameter of the distribution function range.

The heterogeneity of microporous adsorption systems deteriorates the numerical conditioning of the system identification tasks. To avoid the problem of identification procedures the fast multivariant fitting of the LBET class models was proposed [30, 31]. The group of heterogeneity options  $h_i$ , with the binary factors ( $d, \eta$ ), creates an energy distribution variant [30, 33]. Such a distribution variant is fitted during the identification by adjusting the parameters involved in the homogeneous adsorption equations of the LBET type. The 15 different variants with the values of the fixed parameters selected this way to yield the energy distributions of the properly diversified shapes related to the real cases were defined. They were both used for the 1st and the 2nd type adsorption models. Therefore, the total numbers of 30 variants were developed to find the best fitted model for each isotherm.

**Numerical calculations**

The aim of the numerical calculations of the multivariant procedure was to evaluate:

- The influence of the high-pressure section of the adsorption isotherms on the quality of the identification,
- The influence of the number of the fitting points on the uncertainty of estimation of the physical adsorption system parameters, including the relevance of the simultaneous analysis of more than one adsorption isotherm,

- The influence of the microporous structure parameters on the quality of the identification,
- The effect of the assumed simplifications on the LBET class models.

For that purpose, single and double adsorption isotherms were generated using all the variants of the LBET formulas and the corresponding formulas of the uLBET class for the following two values of the parameter  $\alpha$  ( $\alpha=0.4, \alpha=0.8$ ) and the following two values of the relative pressure ( $\pi_{max}=0.9$  and  $\pi_{max}=0.6$ ). The isotherms generated by the uLBET and LBET formulas were calculated for the assumed hypothetical microporous adsorbent.

Next, these generated adsorption systems were identified using the full set of variants of the LBET formulas. The following quantities were selected for fitting during the optimization procedure:  $V_{hA}$  - the molar volume of the first layer,  $\alpha, \beta$  - the geometric parameters of the microporous structure,  $Z_A, Z_C$  - the correction factors used to calculate  $Q_A$  and  $B_C$ , and  $Z_{f\infty}$  in the case of the six-parameter models. In the case of the simultaneous analysis of double isotherms, the same values of the parameters  $V_{hA}, \alpha, \beta$  and the same types of the energy distribution for all such isotherms were used, although each of these isotherms required introducing two additional parameters:  $Z_A$  and  $B_C$ .

The reliability of the identification was assessed based on the residual dispersion and the relative errors of the parameters calculated for all 30 variants of the LBET model. To make the final choice of the best variant possible, the results for the best three fittings were presented. Moreover, ten out of the 30 well fitted variants were treated as the acceptable results. In order to get the synthetic measure of the identification uncertainty and the estimation certainty the following indices were defined:

- The identifiability index  $w_{id}$ , which is the synthetic measure of the identification uncertainty [30, 33]:

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

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

- The direct index  $w_{epi}$  which is the ratio of the relative estimation error of a given parameter in the best fitted variant to an average from the group of the ten well fitted variants [30] is defined by the following formula:

$$w_{epi} = \frac{|\Delta b_{i\opt}|}{\frac{1}{10} \sum_{wo=1}^{10} |\Delta b_{iwo}|}, \tag{12}$$

where  $\Delta b_{i\ opt}$  is the error for the parameter  $b_i$  in the best fitted variant and  $\Delta b_{i\ wo}$  is the error for the parameters  $b_i$  in the ten well fitted variants.

- The weighed estimation index  $w_{ew}$  which is the reliable measure of the practical usefulness of the studied models is defined by the following equation [30]:

$$w_{ewi} = \frac{1}{\sigma_{e\ min}} \frac{|\Delta b_{i\ opt}|}{\frac{1}{10} \sum_{wo=1}^{10} |\Delta b_{i\ wo}| \frac{1}{\sigma_{ewo}}} \tag{13}$$

The identification results for the analyzed adsorption systems are presented in the original color scale diagrams (Figs. 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11) and additionally the obtained indices are presented in Table 1. It should be emphasized that Figs. 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11 present the quality indices for the particular parameters of the analyzed isotherms. The presentation of detailed figures with the analyzed adsorption isotherms is impossible, since 900 isotherms were analyzed for all the adsorption systems. However, this approach to the analysis of the model provides for the thorough information on its properties.

For each of the analyzed systems, there are eight grouped diagrams on which a range of color was used to show the adequate qualities of:

- The dispersion of the fitting error and the error of the relative evaluation of the parameters,
- The relative errors of the aggregated parameter  $\alpha/B_C$  representing the combined effect of the energy and geometrical limitations of the multilayer physical adsorption,
- The relative errors of the aggregated parameter  $\alpha\beta/B_C$ , which can be considered as the parameter of the actual distribution of the size and volume of the clusters.

The figures show the positions of the best three fittings in the two-dimensional space of the studied model variants. The first three rows and columns of each quarter denote the distribution {1, 2, 3} of the type different from the remaining heterogeneous adsorption systems, i.e., homogeneous for the mono-molecular clusters and uniform heterogeneous for the larger ones. The remaining columns have been grouped into triples separated with solid lines, having the energy distribution of the same value of the parameter  $h$ , i.e., with the similar shape of the left side of the distribution function, and different in width. In every column, the best-fitted isotherm is distinguished by “o”. The second and the third fittings were marked with “\*” and “+”, respectively. In the ideal case all “o” marks should be placed on the main diagonal of the diagram.

The position of these marks on the upper diagonal of the left quarter denotes correct recognition of the energy distribution class with incorrect qualification of the adsorp-

tion type. Similarly, the position of marks on the bottom diagonal of the right quarter denotes incorrect interpretation of the adsorption type 2 as the adsorption type 1, with the accurate qualification of the energy distribution.

The range of color of the square ruling shows the quality of the adequate variant for the simulated isotherms (the columns) and the fitting model variants (the rows). The minor errors are colored blue, while the major ones are colored red. This dependence is linear for the error fitting dispersion, while the relative errors of the system parameter evaluation have been submitted to the following transformation:

$$\begin{aligned} \text{The code of the range of color} &= (100/W) \\ &\cdot \ln(1 + 5 \cdot \text{The relative error fitting}) \end{aligned} \tag{14}$$

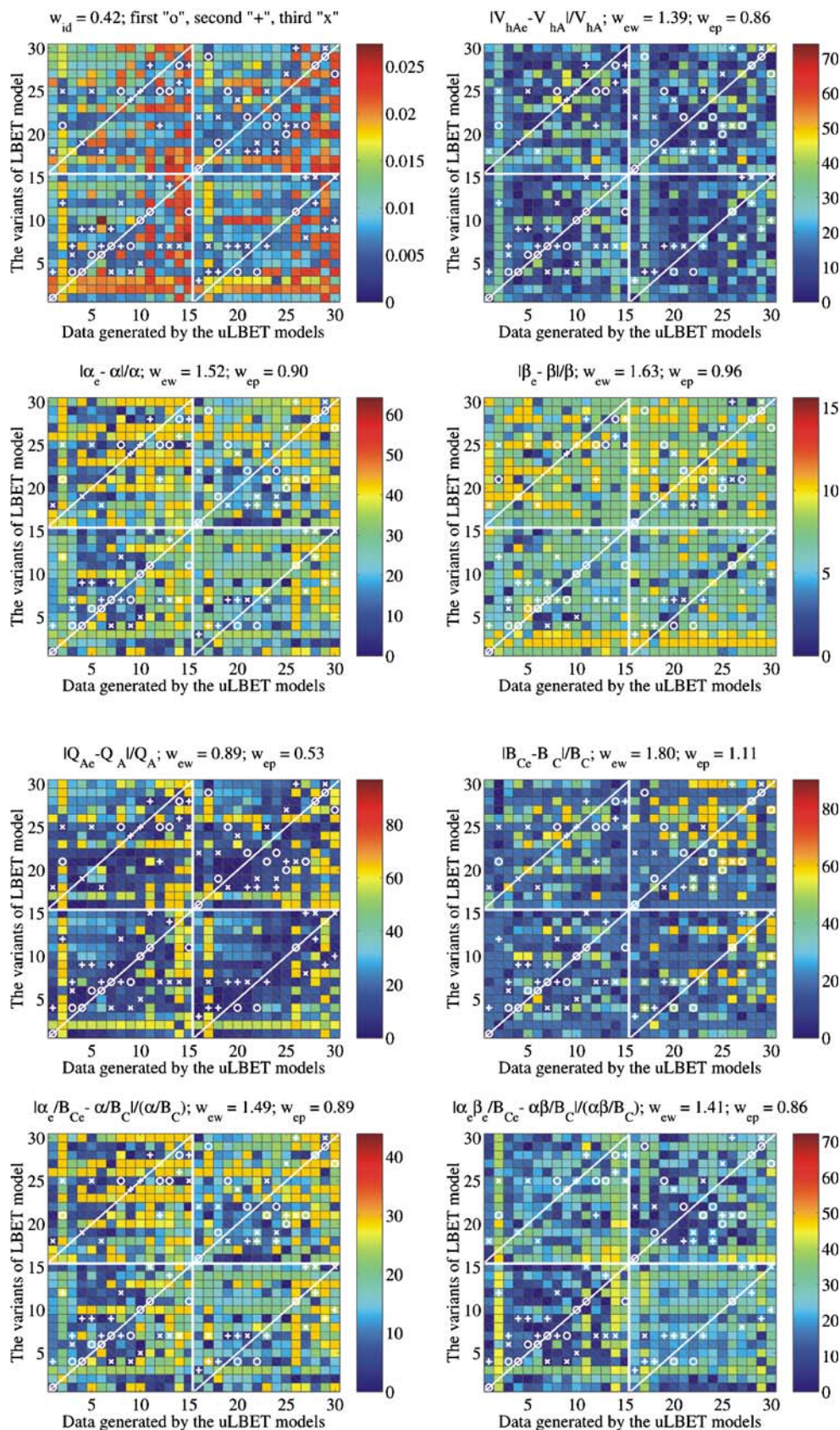
The aim of the above transformation was to neutralize the influence of the major errors on the presentation accuracy of the minor errors. The justification for the above draws from the fact that the presence of the major estimation errors is a normal phenomenon in the proposed fast multivariant fitting technique; therefore it does not have to be exposed. The group of the fitting variants proposed in this paper is selective, i.e., it offers reliable parameter estimations only if the model compatible with the data generating model is applied. This is also concerned with the dispersion of the fitting errors, which should be strongly differentiated.

Generally speaking, one can say that the given diagram describes good properties of the model if the blue squares in the surrounding of the main diagonals or the diagonals in the upper and bottom quarters of the diagram are more dominant than in the remaining parts of the diagram. All “o” signs should be placed on the diagonal against the blue background. In the case when one of the best fittings is placed against the blue background, the results are also acceptable. The summarized results of all the simulation experiments performed are listed in Table 1. In this table, the indices  $w_{id}$  for all the adsorption systems and the indicators  $w_{ep}$ ,  $w_{ew}$  for all the parameters have been provided.

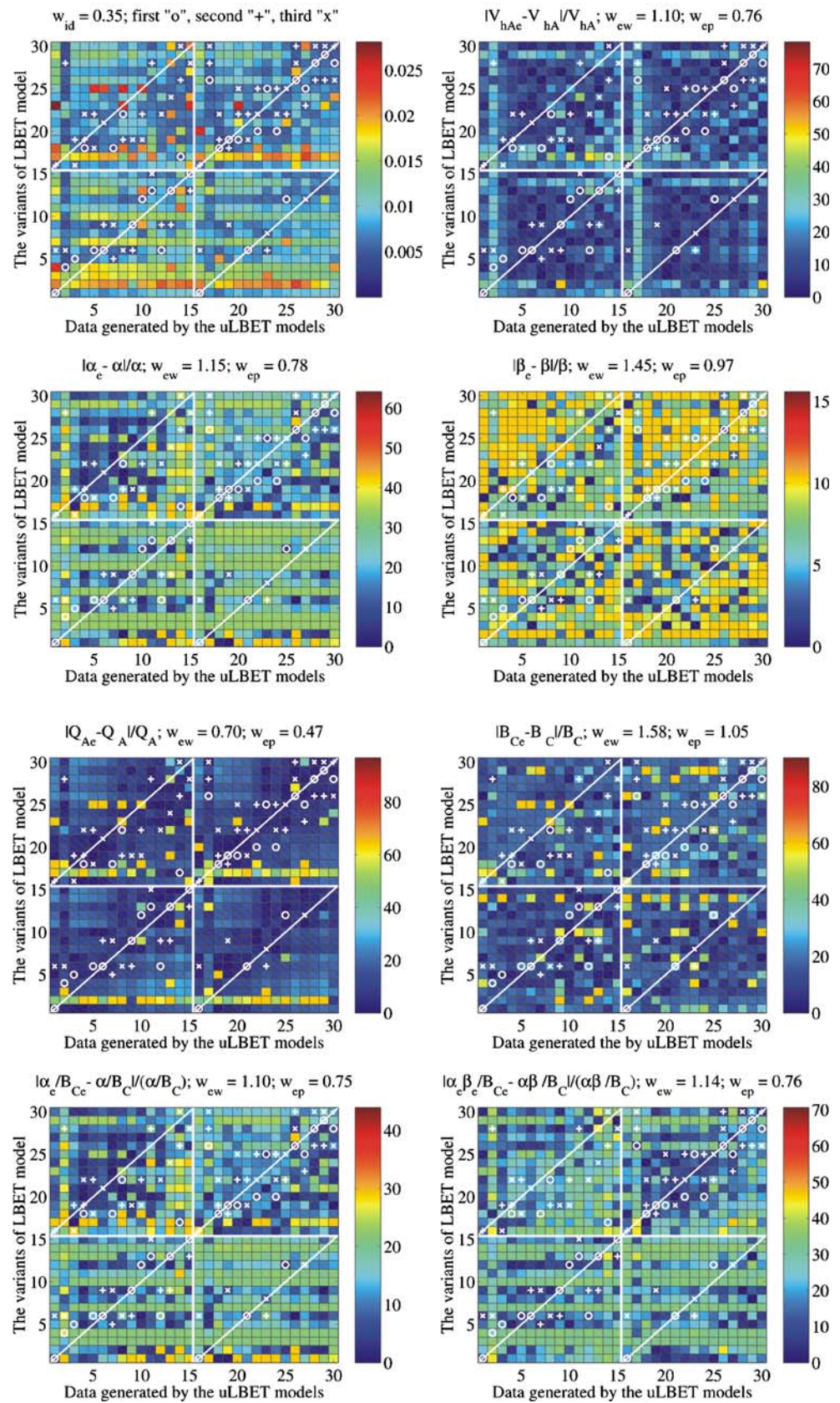
### Discussion of the obtained results

A visual analysis of all the diagrams shows good identifiability of the adsorption systems parameters. In the majority of the analyzed systems, the optimal fittings have significantly smaller errors than the rest (the high indicators  $w_{ew}$ ). The optimal variants can be found near the main diagonal and only a minor group of the variants occurs elsewhere. However, wrong recognitions of the adsorption type where the type 1 is recognized as the type 2 can also be observed, which confirms the theoretical predictions assumed earlier. In all the figures, the first diagram in the right-hand column,

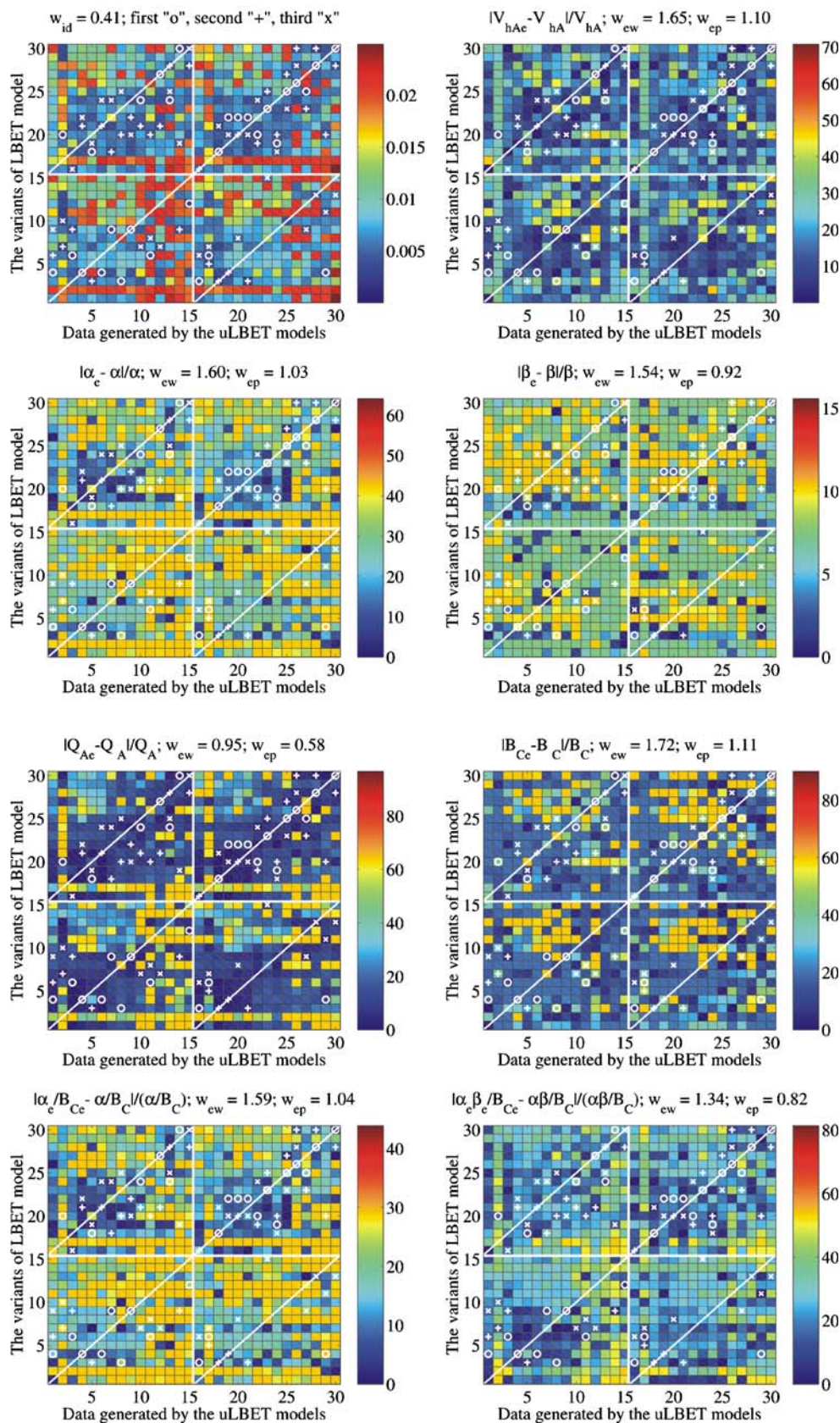
**Fig. 1** The comparison of the calculation results for the single adsorption isotherms generated by the uLBET models and fitted by the LBET class models ( $Q_A/RT=4.5$ ,  $\alpha=0.4$ ,  $\pi_{max}=0.9$ )



**Fig. 2** The comparison of the calculations results for the double adsorption isotherms generated by the uLBET models and fitted by the LBET class models ( $Q_A/RT=4.5$ ,  $\alpha=0.4$ ,  $\pi_{max}=0.9$ )

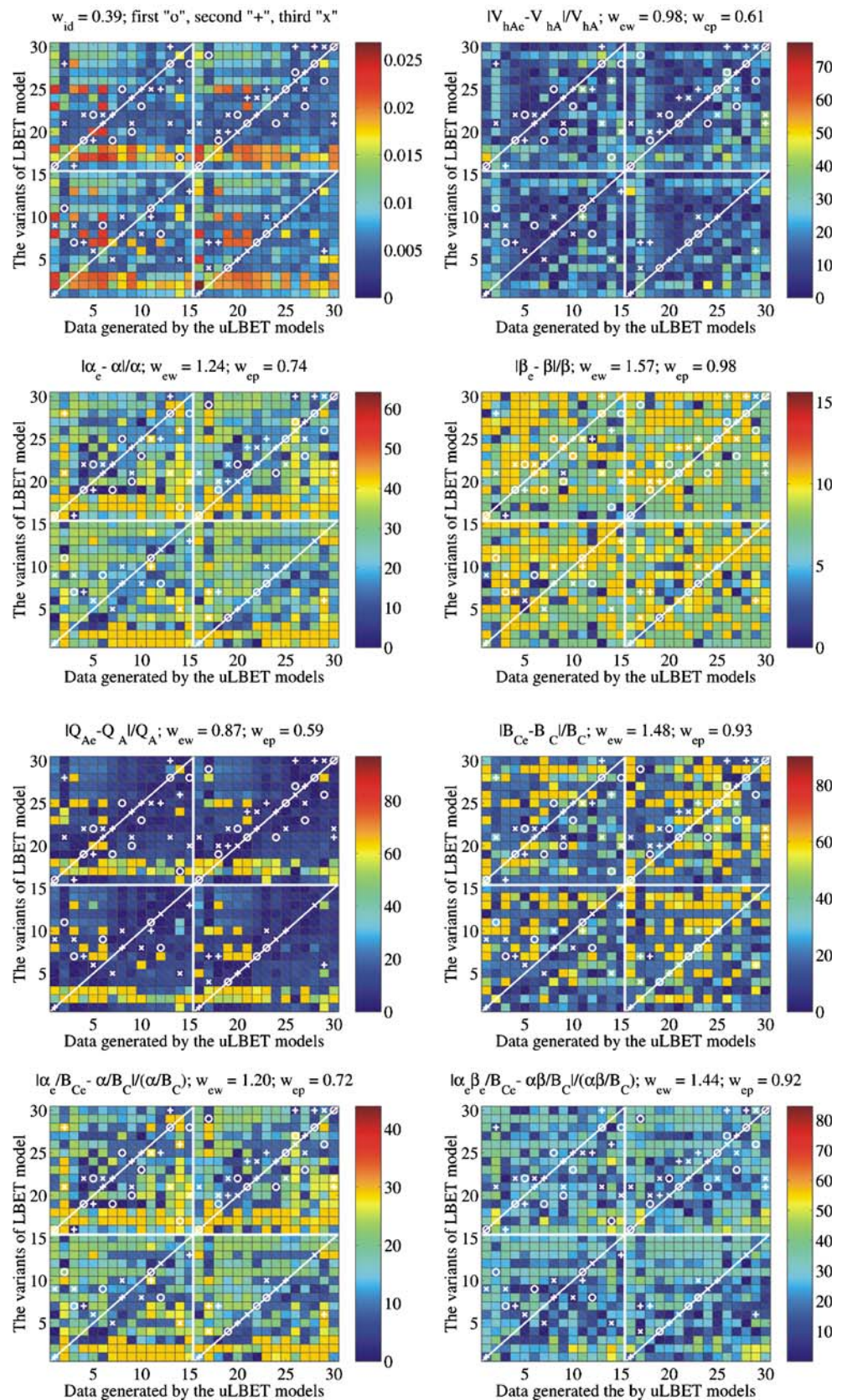


**Fig. 3** The comparison of the calculations results for the single adsorption isotherms generated by the uLBET models and fitted by the LBET class models ( $Q_A/RT=4.5$ ,  $\alpha=0.4$ ,  $\pi_{max}=0.6$ )

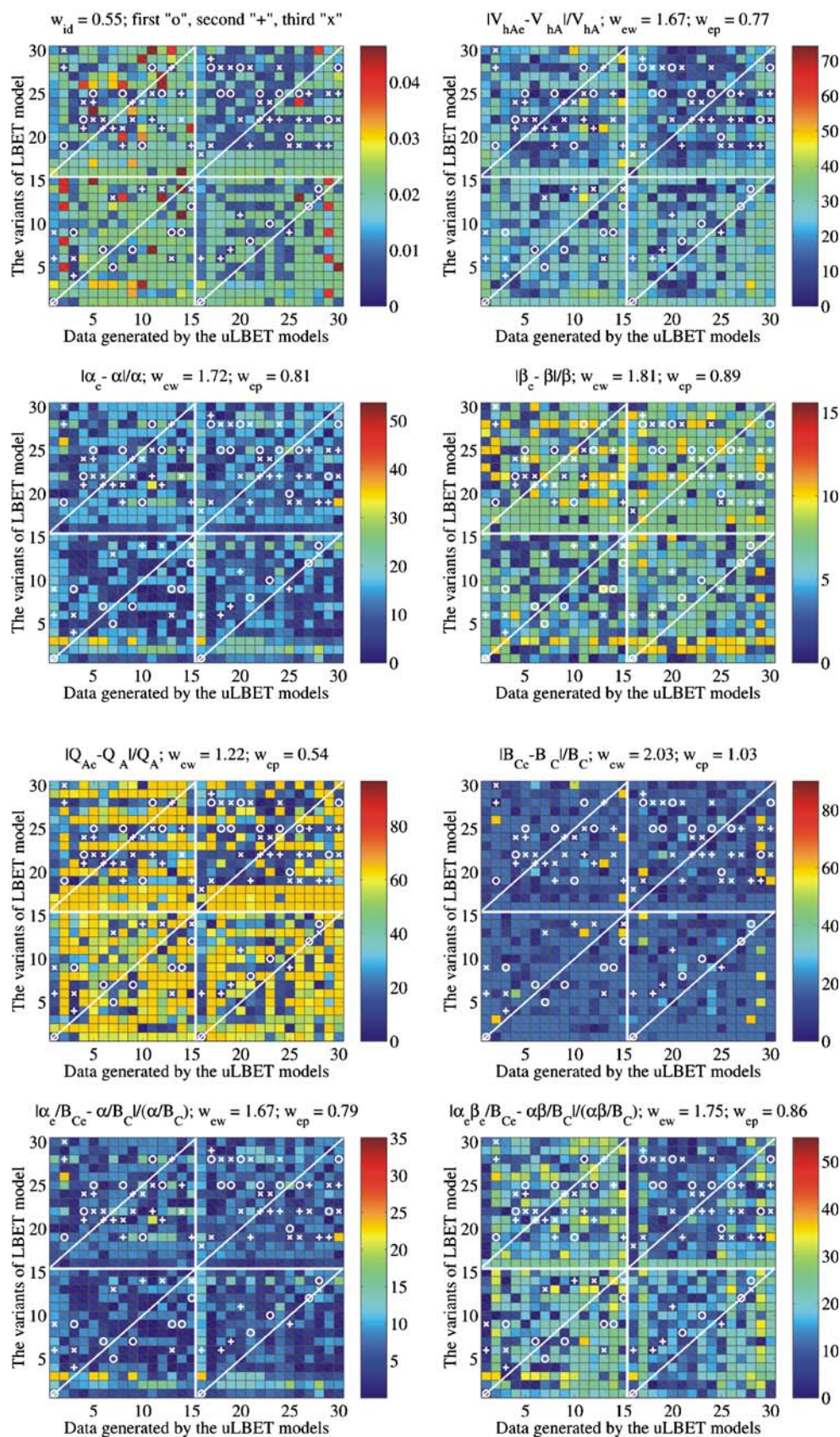




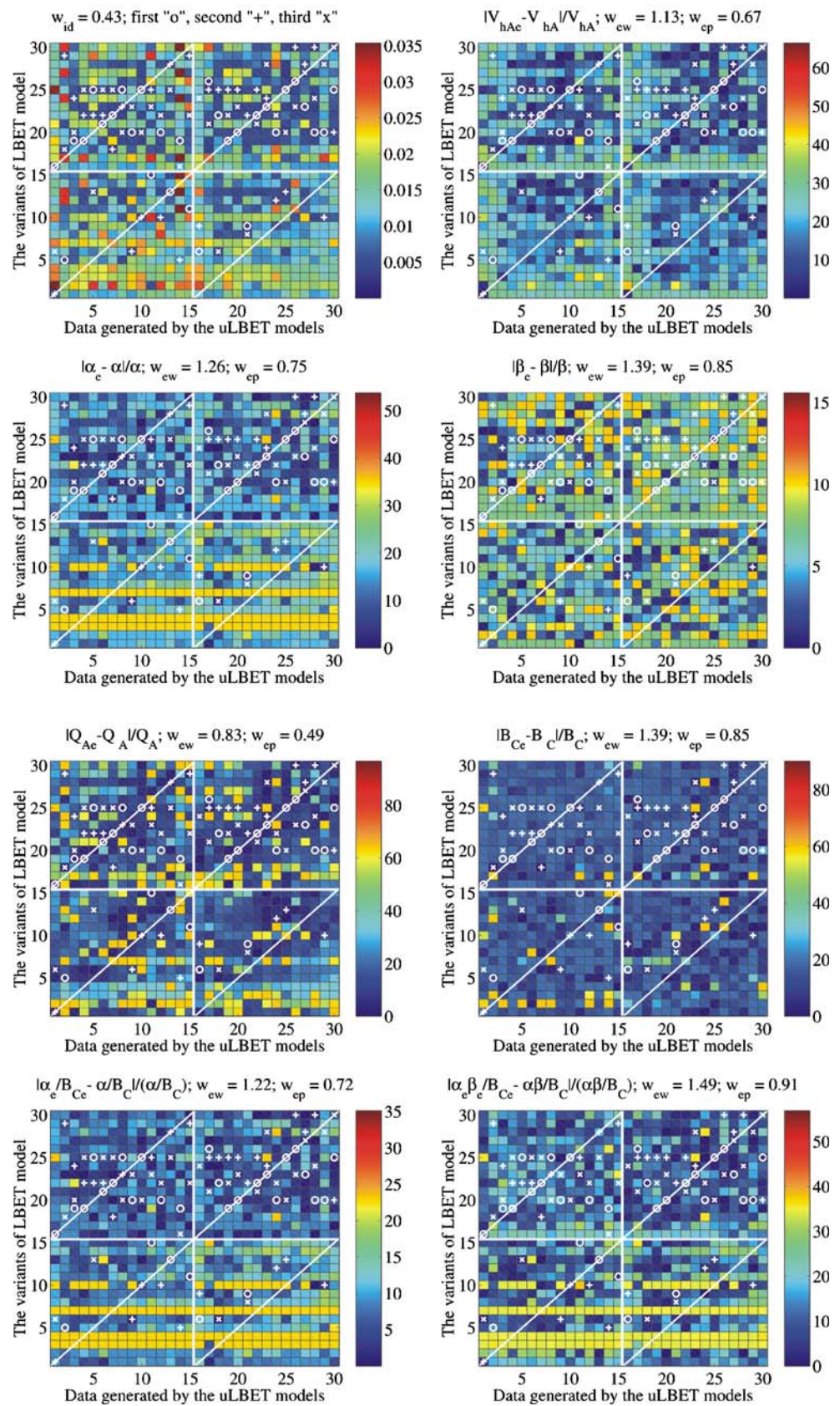
**Fig. 4** The comparison of the calculations results for the double adsorption isotherms generated by the uLBET models and fitted by the LBET class models ( $Q_A/RT=-4.5$ ,  $\alpha=0.4$ ,  $\pi_{max}=0.6$ )



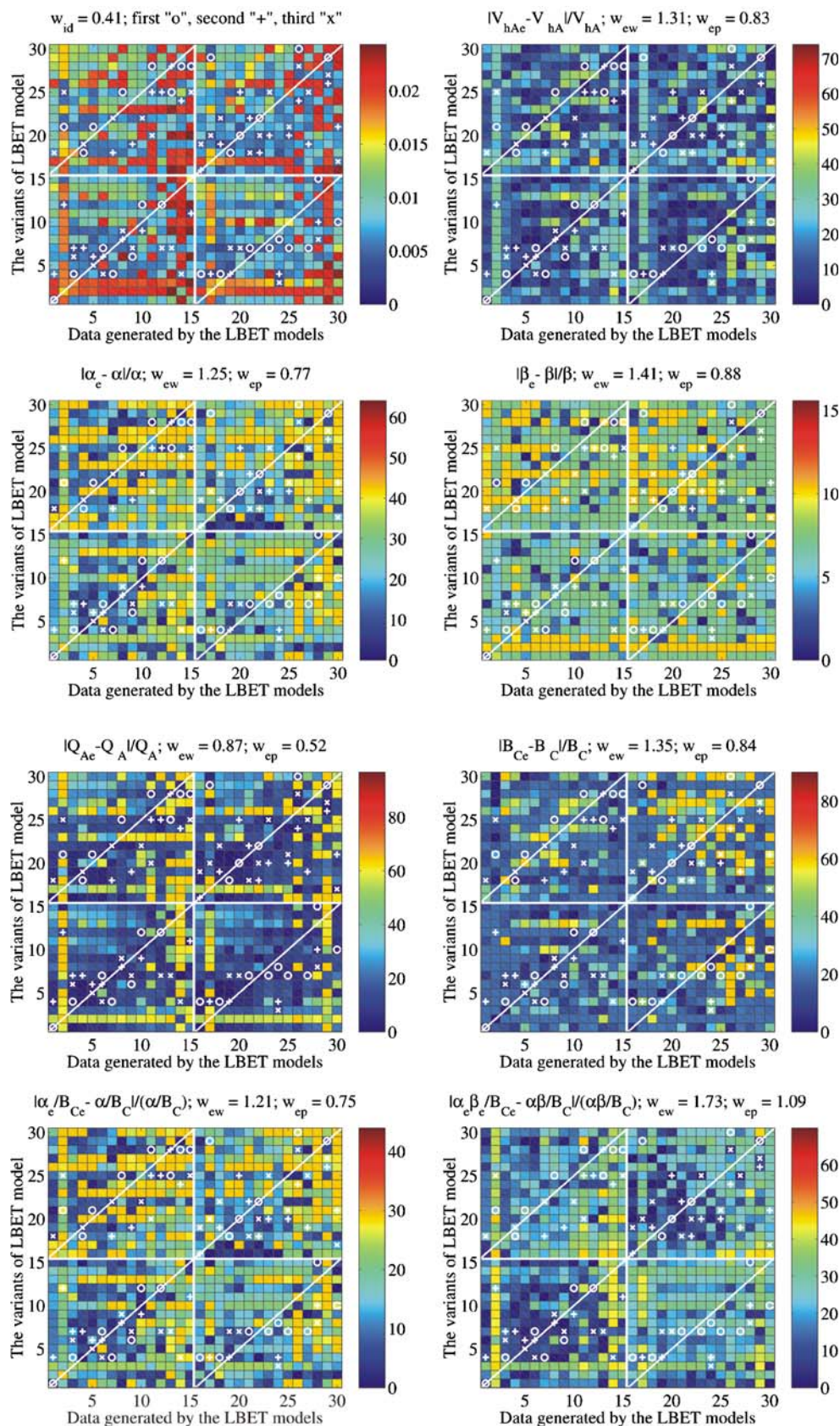
**Fig. 5** The comparison of the calculations results for the single adsorption isotherms generated by the uLBET models and fitted by the LBET class models ( $Q_A/RT=4.5$ ,  $\alpha=0.8$ ,  $\pi_{max}=0.9$ )



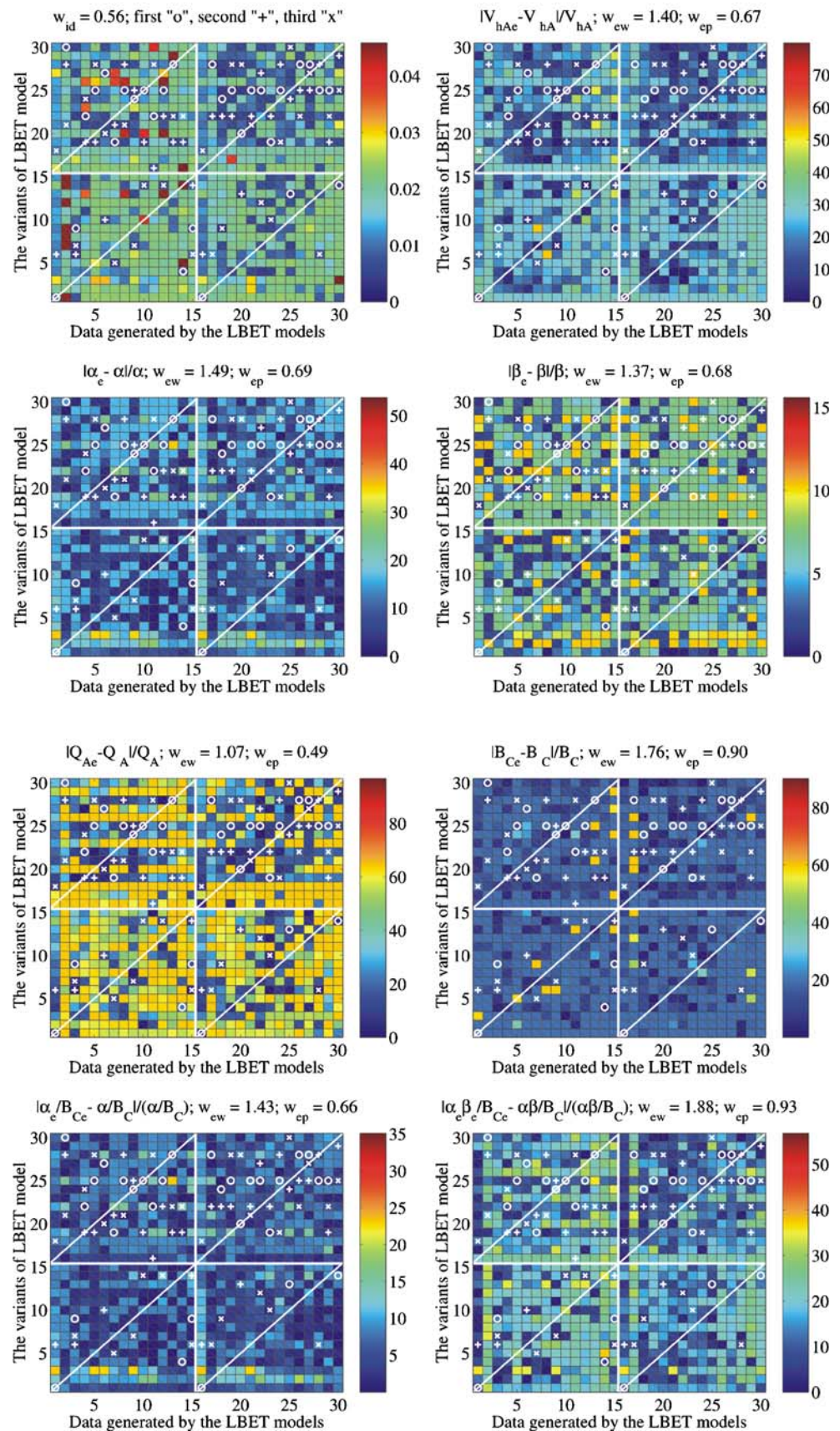
**Fig. 6** The comparison of the calculations results for the double adsorption isotherms generated by the uLBET models and fitted by the LBET class models ( $Q_A/RT=4.5$ ,  $\alpha=0.8$ ,  $\pi_{max}=0.9$ )



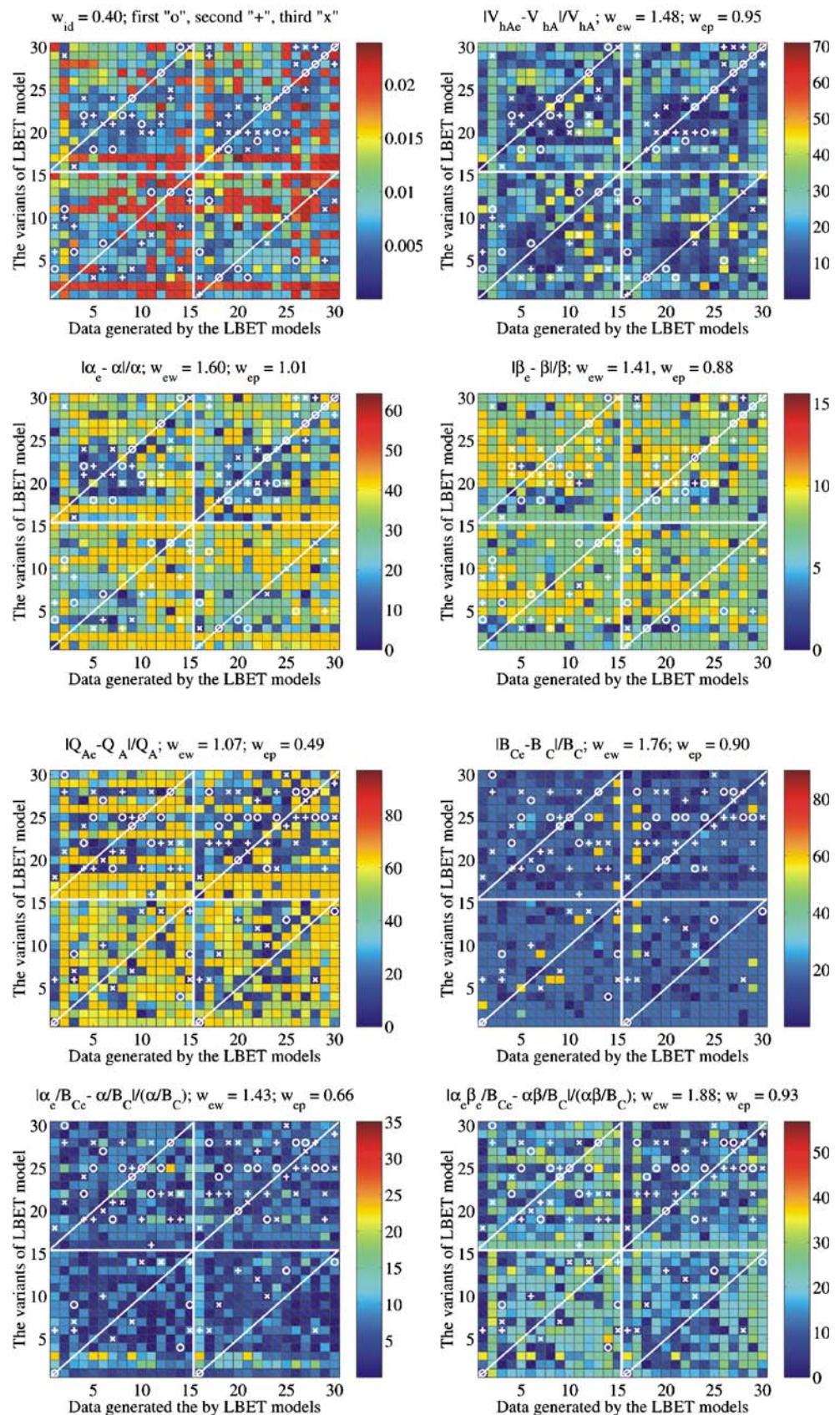
**Fig. 7** The comparison of the calculations results for the single adsorption isotherms generated by the LBET models and fitted by the LBET class models ( $Q_A/RT=4.5$ ,  $\alpha=0.4$ ,  $\pi_{max}=0.9$ )



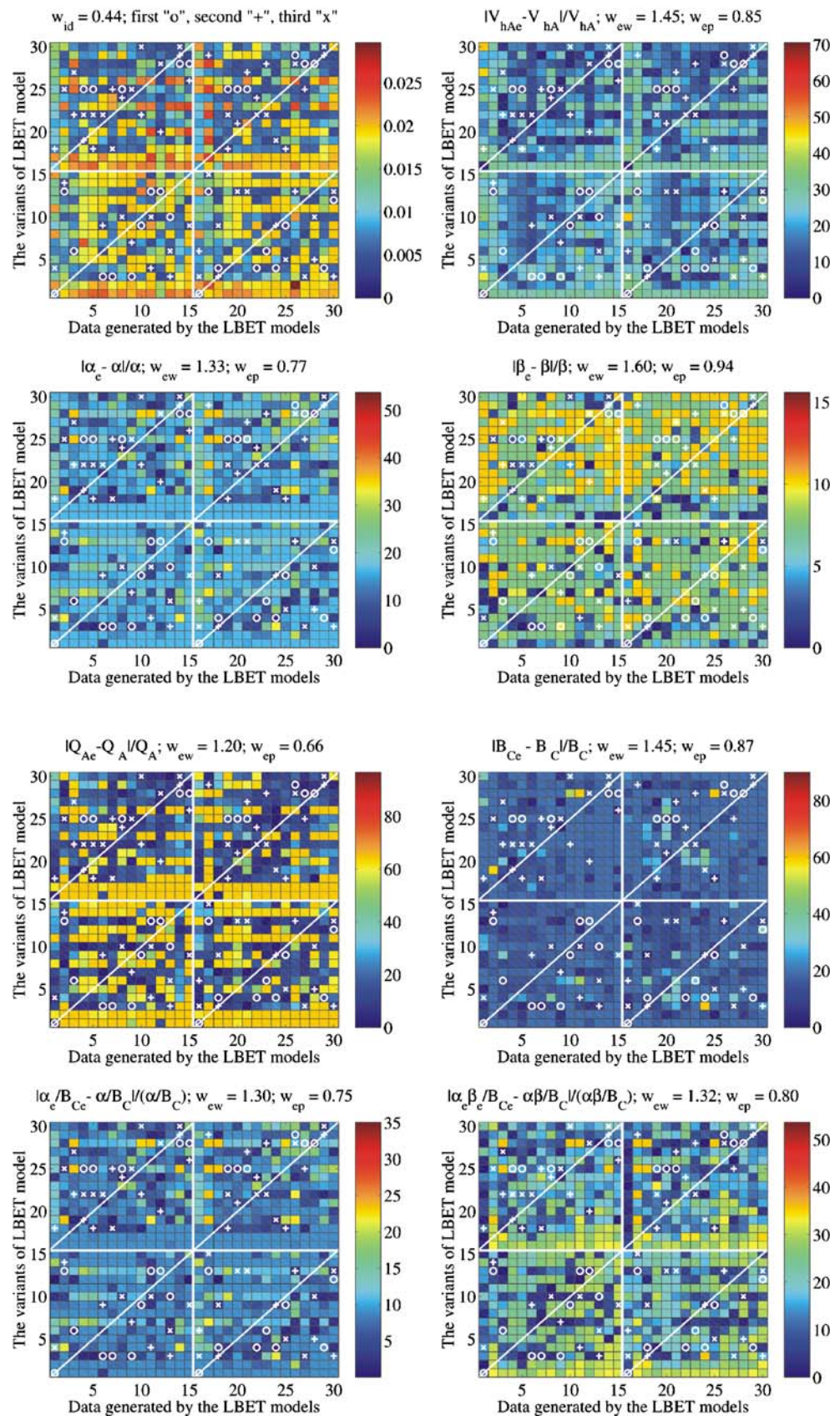
**Fig. 8** The comparison of the calculations results for the single adsorption isotherms generated by the LBET model and fitted by the LBET class models ( $Q_A/RT=-4.5$ ,  $\alpha=0.8$ ,  $\pi_{max}=0.9$ )



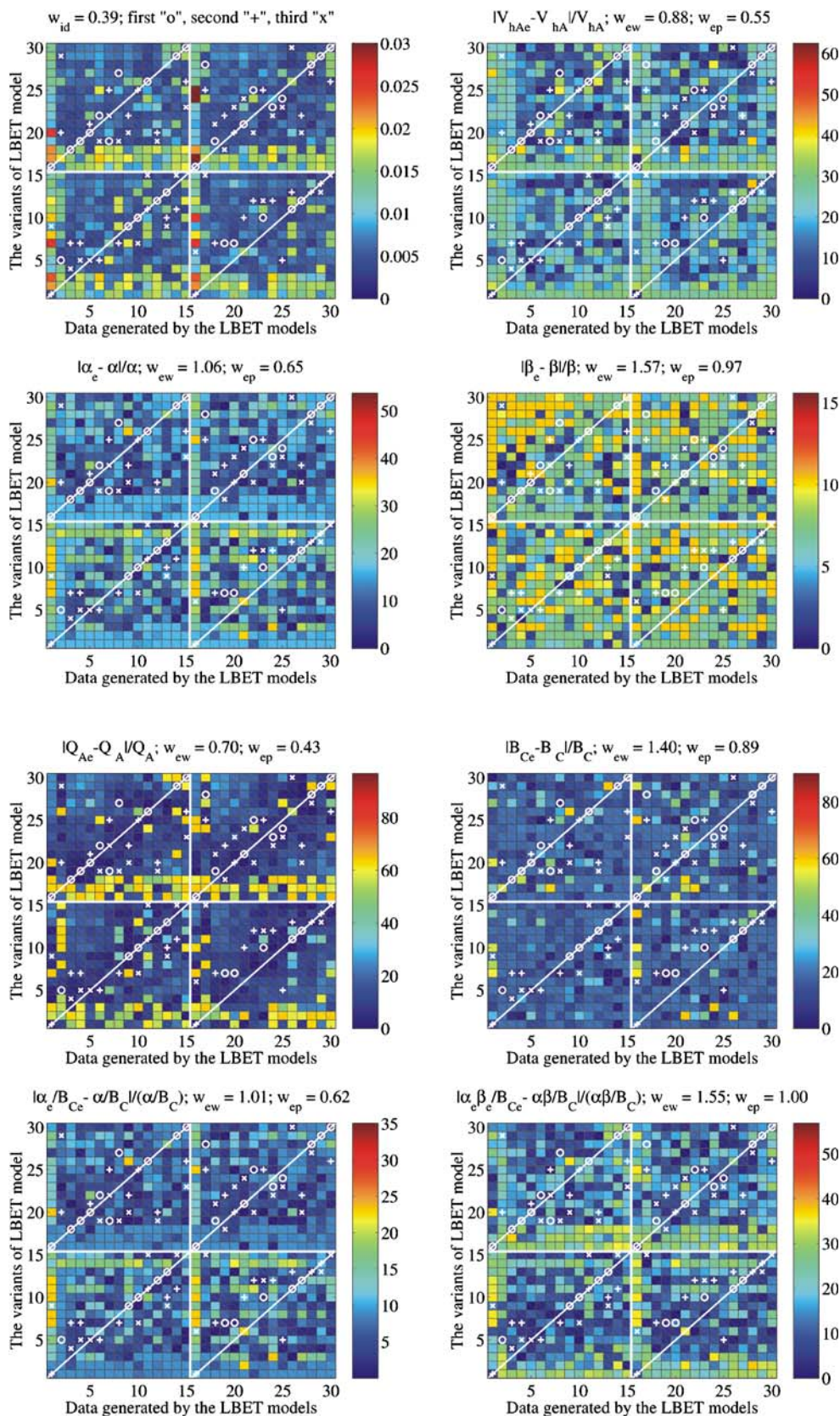
**Fig. 9** The comparison of the calculations results for the single adsorption isotherms generated by the LBET models and fitted by the LBET class models ( $Q_A/RT=4.5$ ,  $\alpha=0.4$ ,  $\pi_{max}=0.6$ )



**Fig. 10** The comparison of the calculations results for the single adsorption isotherms generated by the LBET models and fitted by the LBET class models ( $Q_A/RT=-4.5$ ,  $\alpha=0.8$ ,  $\pi_{max}=0.6$ )



**Fig. 11** The comparison of the calculations results for the double adsorption isotherms generated by the LBET models and fitted by the LBET class models ( $Q_A/RT=-4.5$ ,  $\alpha=0.8$ ,  $\pi_{max}=0.6$ )





**Table 1** The comparison of the identification quality for all the analysed adsorption systems

| No. | Model generated data/Number of isotherms | $p/p_0$ | $\alpha$ | $w_{id}$ | Indices  | $V_h$ | $\alpha$ | $\beta$ | $Q_A$ | $B_C$ | $\alpha/B_C$ | $\alpha\beta/B_C$ |
|-----|--|---------|----------|----------|----------|-------|----------|---------|-------|-------|--------------|-------------------|
| 1   | uLBET/single                             | 0.9     | 0.4      | 0.42     | $w_{ew}$ | 1.36  | 1.52     | 1.63    | 0.89  | 1.80  | 1.49         | 1.41              |
|     |  |         |          |          | $w_{ep}$ | 0.86  | 0.90     | 0.96    | 0.53  | 1.11  | 0.89         | 0.86              |
| 2   | uLBET/double                             | 0.9     | 0.4      | 0.35     | $w_{ew}$ | 1.10  | 1.15     | 1.45    | 0.70  | 1.58  | 1.10         | 1.14              |
|     |  |         |          |          | $w_{ep}$ | 0.76  | 0.78     | 0.97    | 0.47  | 1.05  | 0.75         | 0.76              |
| 3   | uLBET/single                             | 0.6     | 0.4      | 0.41     | $w_{ew}$ | 1.65  | 1.60     | 1.54    | 0.95  | 1.72  | 1.59         | 1.34              |
|     |  |         |          |          | $w_{ep}$ | 1.10  | 1.03     | 0.92    | 0.58  | 1.11  | 1.04         | 0.82              |
| 4   | uLBET/double                             | 0.6     | 0.4      | 0.39     | $w_{ew}$ | 0.98  | 1.24     | 1.57    | 0.87  | 1.48  | 1.20         | 1.44              |
|     |  |         |          |          | $w_{ep}$ | 0.61  | 0.74     | 0.98    | 0.59  | 0.93  | 0.72         | 0.92              |
| 5   | uLBET/single                             | 0.9     | 0.8      | 0.55     | $w_{ew}$ | 1.67  | 1.72     | 1.81    | 1.22  | 2.03  | 1.67         | 1.75              |
|     |  |         |          |          | $w_{ep}$ | 0.77  | 0.81     | 0.89    | 0.54  | 1.03  | 0.79         | 0.86              |
| 6   | uLBET/double                             | 0.9     | 0.8      | 0.43     | $w_{ew}$ | 1.19  | 1.26     | 1.39    | 0.83  | 1.39  | 1.22         | 1.49              |
|     |  |         |          |          | $w_{ep}$ | 0.67  | 0.75     | 0.85    | 0.49  | 0.85  | 0.72         | 0.91              |
| 7   | LBET/single                              | 0.9     | 0.4      | 0.41     | $w_{ew}$ | 1.31  | 1.25     | 1.41    | 0.87  | 1.35  | 1.21         | 1.73              |
|     |  |         |          |          | $w_{ep}$ | 0.83  | 0.77     | 0.88    | 0.52  | 0.84  | 0.75         | 1.09              |
| 8   | LBET/single                              | 0.9     | 0.8      | 0.56     | $w_{ew}$ | 1.40  | 1.49     | 1.37    | 1.07  | 1.76  | 1.43         | 1.88              |
|     |  |         |          |          | $w_{ep}$ | 0.67  | 0.89     | 0.68    | 0.49  | 0.90  | 0.66         | 0.93              |
| 9   | LBET/single                              | 0.6     | 0.4      | 0.40     | $w_{ew}$ | 1.48  | 1.60     | 1.41    | 1.07  | 1.76  | 1.43         | 1.88              |
|     |  |         |          |          | $w_{ep}$ | 0.95  | 1.01     | 0.88    | 0.49  | 0.90  | 0.60         | 0.93              |
| 10  | LBET/single                              | 0.6     | 0.8      | 0.44     | $w_{ew}$ | 1.45  | 1.33     | 1.60    | 1.20  | 1.45  | 1.30         | 1.32              |
|     |  |         |          |          | $w_{ep}$ | 0.85  | 0.77     | 0.94    | 0.66  | 0.87  | 0.75         | 0.80              |
| 11  | LBET/double                              | 0.6     | 0.8      | 0.39     | $w_{ew}$ | 0.88  | 1.06     | 1.57    | 0.70  | 1.40  | 1.01         | 1.55              |
|     |  |         |          |          | $w_{ep}$ | 0.55  | 0.65     | 0.97    | 0.43  | 0.89  | 0.62         | 1.00              |

which presents the estimation errors for the parameter  $V_{hA}$  and the third one in the left-hand column, which presents the estimation errors for the adsorption energy  $Q_A$  are evidently contrasted. However, more significant errors are observed for the model variants 1 through 3.

As has already been mentioned in the previous section, one of the aims of the numerical calculations presented in this paper was to evaluate the influence of the high-pressure section of the adsorption isotherms on the quality of the identification. Based on the analysis of the results presented in Figs. 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11, as well as the results compiled in Table 1, it can be concluded that the wider the range of the analyzed relative pressures, the more reliable results can be obtained. The particularly reliable evaluation of the microporus structure parameters, such as  $V_h$ ,  $\alpha$ , the first layer adsorption energy  $Q_A$ , and the aggregated parameter  $\alpha/B_C$  were obtained.

It is worth pointing out that the worst estimated parameter of the microporous structure in the majority of adsorption systems is the  $\beta$  parameter. Moreover, as it can be observed, the estimation of the  $B_C$  parameter is strongly differentiated. It should be emphasized that the errors of the aggregated parameters  $\alpha/B_C$  and  $\alpha\beta/B_C$  are usually smaller than for the individual parameters  $\alpha$  and  $\beta$ . Yet more significant errors of the determination of the aggregated parameter  $\alpha\beta/B_C$  can be observed, which is not surprising having regard to the earlier observations.

Another analyzed problem was the influence of the number of the fitting points on the uncertainty of estimation

of the physical adsorption system parameters, including the legitimacy of the simultaneous analysis of two adsorption isotherms. It occurred that the simultaneous analysis of two adsorption isotherms significantly improves the identifiability of the system parameters. The  $\alpha$  parameter estimation errors are considerable, yet in the case of the simultaneous identification of two isotherms significantly improves the parameter estimation reliability. However, it should be taken into account that in some cases such simultaneous analysis can have a bad influence, which is due to the increasing number of the optimized parameters.

The highly significant analyzed problem was the analysis of the influence of the assumed microporous structure parameters on the quality of the identification.

For that purpose, single and double adsorption isotherms were generated for the hypothetical microporous adsorbent by all the variants of the LBET formulas and the accurate formulas of the uLBET class for two values of the microporous structure parameter  $\alpha$ . Significant errors are observed for  $\alpha = 0.8$ , i.e., in the cases where higher clusters occur in the micropores. It can also be concluded from the obtained results that in the case of the adsorbents with branched clusters, i.e., having high values of the micropore shape parameter  $\beta$ , the identification of the system would be worse than in the case of the narrow micropores for which  $\beta=1$ .

The last of the analyzed problems was the evaluation of the significance of the assumed simplification in the LBET class models in which in order to shorten the calculation time the energy distribution with the diverse maximum energy

was replaced with the energy distribution of the averaged energy range for all types of the  $k$  sites. The analysis of the diagrams and results presented in Table 1 also confirms the lack of significant differences in the identification quality in the cases of the data generated by the LBET and uLBET models. This evidences the appropriateness of the simplifications applied in the LBET formulas.

## Conclusions

To sum up, based on the research carried out, it can be claimed that in the case of analyzing microporous carbonaceous adsorbents using the proposed fast multivariant fitting procedure had a considerable effect of the analyzed range of the relative pressures and the microporous structure parameters on the quality of the obtained results is observed. However, this is natural and does not downgrade the applicability of the proposed procedure. The LBET based multivariant identification of the adsorption systems, with the surface energy distribution structure being presumed in each variant, makes it possible to avoid numerical problems caused by a large number of the system parameters to be evaluated. The final analysis of a number of the best-fitted variants provides complementary information on the adsorption mechanisms, thus enabling more reliable evaluation of the studied pore structure.

The presented approach to the examination of the adsorbents having random porous structure may be viewed as an alternative for the classical techniques and methods that are more complicated, and the model verification method used can be very helpful in the verification of different models by providing reliable information regarding these models.

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

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