Employing the new computer LBET class models with multivariant fitting to the analysis of single and double adsorption isotherms generated by the selected classical equations in different relative pressures

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The aim of this work has been to study the problems related to the reliability evaluation of microporous structure parameters. The new methods of characterization of micropores carbonaceous materials have been explored by employing single and double adsorption isotherms generated by the classical equations for different values of the system parameters and different relative pressures.

KEY WORDS: adsorption, modeling, adsorption properties, microstructure, computational chemistry

1.   Introduction

Gases and vapors adsorption is one of the most widely used techniques for the characterization of microporous carbonaceous materials and multilayer adsorption [1]. The characterization of these materials comprises, among others, a description of microporosity, and energetic heterogeneity [1,2]. A significant effort has recently been devoted to the development of reliable methods of the microporous structure description on the basis of empirical adsorption isotherms. Also many various theories have been proposed to describe multilayer adsorption [3–5]. Among them, the most widely used theory to describe adsorption of gases and vapors on microporous adsorbents has been the theory of micropores volume filling [6]. Several equations have been derived from this theory, e.g., the Dubinin–Radushkevich (DR) or the Dubinin–Astakhov (DA) equations [7,8]. The most popular has been the DR equation, however for carbonaceous solids with a wider pore size distribution it does not describe well the equilibrium data. Moreover, it has not reduced to the Henry's equation at low-relative pressures.

Another popular equation applied to description of the multilayer adsorption process has been the BET equation – one of the most widely used and practically applicable in the analysis of the experimental adsorption data. The BET theory assumes a reversible adsorption/desorption process with multilayer formation [9]. The BET model owes its extensive use to the fact that it is simple to apply. What is more, it provides two of the most significant structure parameters, the monolayer capacity and the C parameter, giving satisfactory results for several adsorbents [9].

In spite of its success and wide applications, the BET theory is also one of the most criticised because of its excessively simplifying assumptions [9]. The main criticism of the BET model comes from two basic assumptions made at its development: (a) all adsorbing sites are energetically homogeneous, (b) any adsorbate-adsorbate interactions are ignored.

The BET equation is applied in the range of relative pressure 0.05–0.35 (exceptionally to 0.5 p/p_0). For the values larger than 0.5 p/p_0 the classical BET equation cannot be applied, because of an overvaluation of physical adsorption process and capilary condensation. For the value smaller than 0.05 p/p_0 this equation is not applicable either, because the energetical effect of the surface heterogenity is difficult to describe. The BET equation gives too small adsorption for a low-pressure and too large for a high-pressure. Thus, many generalizations of the BET model have been proposed in the literature, including lateral interaction among the adsorbed molecules, surface heterogeneity, differences between the adsorption energy of the first layer, and the upper layers. However, one basic feature of the BET model is preserved in all mentioned theories; i.e. the assumption that the adsorbed molecule occupies one adsorption site.

A noteworthy equation based on the BET theory is the Hütting equation assuming that it is possible – unlike in the BET equation – to desorb adsorbate molecules from the deeper adsorption layers. Besides, the Hütting equation assumes that the amount of the molecules adsorbed under the pressure $p = p_0$ is not unlimited, but proportional to the number of layers [10].

These above-mentioned models have played an important role in the characterization of solid surfaces by means of gas adsorption, but the results of the surface structure and energy evaluation based on adsorption at higher pressures are doubtful. Thus, precision and reliability of the structure parameters calculation are not enough and there is still a need to improve and develop uncomplicated and relievable methods of microporous structure characterization. Therefore, to examine microporous carbonaceous adsorbents the mathematical description of heterogeneous adsorption process was elaborated the team the author belongs to. In particular, the new LBET class models for heterogeneous adsorption on microporous carbonaceous materials and multivariant fitting technique was proposed.

These models provide information on pore structure and capacity on the basis of adsorption isotherms of the small molecule adsorbates. The molecules

are located in pores by forming agglomerates, the size of which is limited by the pores geometry. The set of adsorbate molecules, which have been adsorbed mainly due to adhesive interactions with the adsorbent matter, has been treated as the first adsorption layer [11,12]. Joining further molecules is viewed as forming the second, third,..., adsorption layer. The proposed models have been recommended to description of carbonaceous adsorbents with random microporous structure.

2. Theoretical basis

In a presented theory one considers the adsorption subsystems attributed to particular layers $n = 1, \ldots, k$ at agglomerates limited to $k = 1, 2, \ldots \infty$ layers. The same adsorption energy $Q_C \geqslant 0$ is assumed for each subsystem on the second and higher layers at each agglomerate of $k > 1$. The molar adsorption energy Q_{Aa} at the ath subsystem on a primary site is expressed by the following equation [13,14]:

$$Q_{Aa} \overset{\text{def}}{=} U_p - Z_{Aa} \cdot Q_{cp}, \quad Q_A \overset{\text{def}}{=} U_p - Z_A \cdot Q_{cp}, \tag{1}$$

where: U_p is the molar cohesion energy of pure adsorbate; Q_{cp} is the molar adhesion energy for the adsorbate molecules contacting only with adsorbent, Z_{Aa} is the fraction of the effective adsorbent–adsorbate contact surface area [15,16].

In the presented, approach the uniform distribution of Z_{Aa} over the first layer adsorption sites is assumed. The distribution function ranges from Z_{Ak} to Z_{fk}, depending on the site capacity (i.e. on the number k of layers) and $Z_{fk} \leqslant Z_{Ak}, Z_{Ak+1} \leqslant Z_{Ak}, Z_{fk+1} \leqslant Z_{fk}$.

Sites contacting small number of layers are having main effect on adsorption isotherms [3]. Hence, the parameters $Z_{A1}, Z_{f1}, Z_{A2}, Z_{f2}, Z_{A3}$ have been treated individually, respecting possible effects of pore shape and size on the contact surface area in pores of $k < 4$. For $k > 2 + d(d = \{0, 1\}) Z_{Ak}$ and Z_{fk} are calculated as follows [11,12]:

$$Z_{Ak} = Z_{A2+d}, \quad Z_{fk} = \frac{Z_{A2+d} - Z_{f\infty}}{k - \eta} + Z_{f\infty}, \quad \eta = \{0, 1\}, \quad \eta \leqslant d, \tag{2}$$

where: d, η are the binary options $\{0, 1\}$, $\eta \leqslant d$ for different variants of the surface energy distribution function, $\eta = 0$ fields a wider energy spectrum.

The particular set of the parameters $P = \{Z_{A1}, Z_{f1}, Z_{A2}, Z_{f2}, Z_{A3}, Z_{f\infty}, d, \eta\}$ generates a specific step-wise distribution of the first adsorption layer energy $f(Q_{A\kappa})$, depending also on the primary site capacity distribution $m_{hk}(k)$ [11,12].

The LBET class formula of the adsorption models has the following form [11,12]:

$$
\begin{aligned}
\frac{m_{\mathrm{p}}}{m_{hA}} = {} & (1 - \alpha) \left\{ 1 - \frac{1}{\ln(B_{A1}/B_{f1})} \cdot \ln\left(\frac{B_{A1} + \pi}{B_{f1} + \pi}\right) \right\} \\
& + d \cdot \alpha(1 - \alpha)\,(1 + \beta\theta_{22}) \left\{ 1 - \frac{1}{\ln(B_{A2}/B_{f2})} \ln\left(\frac{B_{A2}(1 - \theta_{22})^\beta + \pi}{B_{f2}(1 - \theta_{22})^\beta + \pi}\right) \right\} \\
& + \alpha^{d+1} \left[d + (\beta\theta)^d \left(1 + \frac{\beta\theta}{1 - \alpha\beta\theta}\right) \right] \\
& \times \left\{ 1 - \frac{1}{\ln(B_{A2+d}/B_{f\theta})} \ln\left(\frac{B_{A2+d}(1 - \theta)^\beta + \pi}{B_{f\theta}(1 - \theta)^\beta + \pi}\right) \right\},
\end{aligned}
\tag{3}
$$

where: m_{p} is the amount of adsorbate [mmol/g], m_{hA} is the number of primary sites, θ_{kj} is the coverage ratio of j is the layer at k-type agglomerate, θ is the mean coverage ratio of layers $n > 1$, π is the relative pressure, α is the geometrical parameter of the porous structure, β is the pore shape parameter ($\beta \geqslant 1$), B_{Ak}, B_{fk} is the energetic parameters: $B_{Ak} = \exp(Q_{Ak}/RT)$, $B_{fk} = \exp(Q_{fk}/RT)$.

The parameter $B_{f\theta}$ is defined as follows [17,18]:

$$
B_{f\theta} \stackrel{\text{def}}{=} B_{\mathrm{A}} \exp\left((Q_{\mathrm{cp}}/RT) \cdot (Z_{f\theta} - Z_{f\infty})\right), \quad B_{\mathrm{A}} \stackrel{\text{def}}{=} \exp\left(Q_{\mathrm{A}}/RT\right),
\tag{4}
$$

where: Q_{cp} is the molar adhesion energy in an 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 average value of the upper boundary Z_{fk} (equation 2) calculated according to the following formula [12,19]:

$$
Z_{f\theta}(\alpha, \beta\theta) = \frac{(Z_{\mathrm{A}2+d} - Z_{f\infty})}{1 - \dfrac{\ln(1 - \alpha) - (\beta\theta)^{1+\eta} \ln(1 - \alpha\beta\theta) + (d - \eta)\alpha \left(1 - (\beta\theta)^{2+\eta}\right)}{\alpha^{1+d-\eta} \dfrac{1 - \beta\theta}{1 - \alpha} \left[d + (\beta\theta)^d \left(1 + \dfrac{\beta\theta}{1 - \alpha\beta\theta}\right) \right]}} \\
+ Z_{f\infty}.
\tag{5}
$$

The LBET class models have five parameters: $m_{\mathrm{hA}}, Q_{\mathrm{A}}, \alpha, \beta$, and B_{C}, which have been calculated by the numerical methods.

In the presented approach two types of adsorption on the top layer k have been considered, corresponding to a different nature of restrictions for the adsorbate agglomerate size represented by k [20,21]. The first type adsorption, assuming the limitations of formal nature, implies $\theta = \Pi_\infty^*$. It may be expected to occure in more compact or flat end large pores. For the second type adsorption (the restrictions are of a geometrical nature, which is observed in small or narrow pores) the ratio θ average over the layers $n = 2, \ldots, k, k = 2 + d, \ldots, \infty$ is taken [21].

Energetic heterogeneity of microporous adsorption systems enlarges uncertainty of the identification results. To solve this problem a set of energy distribution variants, assuming fixed values for $P = \{Z_{f1}, Z_{A2}, Z_{f2}, Z_{A3}, Z_{f\infty}, d, \eta\}$ has been prepared [20]. For different variants the values in P have been selected in such a way, as to get the distributions of accurately diversified shape. The proposed multivariant technique of adsorption system identification based on fitting of the LBET type models, for the evaluation reliability of the deriving structure parameters by employing single or double adsorption isotherm has been used.

3. Numerical analysis of the adsorption isotherms

The purpose of the computer calculations was a comparison of the evaluation reliability of heterogeneous microporous structure parameters by employing single and double adsorption isotherms generated by the selected classical equations and fitted by the LBET class models. Such calculations enabled to evaluate reliably the procedure properties on the basis of the estimation error, which could be calculated because true values of the parameters were known. The research was focused on the analysis of identification errors. The fitting of theoretical isotherms to isotherm data was carried out by a non-linear constrained optimization, which minimizes the least-square error of fitting. During the optimization the following boundaries have been assumed:

$$0 \leqslant \alpha \leqslant 1, \quad 1 \leqslant \beta \leqslant 1.3, \quad Z_{\mathrm{pc}} \geqslant 1/12, \quad B_{\mathrm{C}} \geqslant 1.$$

The reliability of identification was assessed on the basis of a residual deviation and relative errors of parameters calculated for all 30 variants. One may expect that the identification procedure is able to get better results for a particular adsorption type, represented by the subset of 15 variants. In simultaneous identification of multiple isotherms the same values for V_{hA}, α, β, and $\{h, d, \eta\}$ were assumed for all isotherms, but each of them involved two additional parameters Q_A and B_C [11,12]. Since, the energy distribution presumed in each subset differs significantly, a subset of 10 variants may be considered as potentially acceptable. Hence, to get a synthetic measure of the identification uncertainty, the following identifiability index w_{id} was defined [12,17]:

$$w_{id} = 1 - \frac{\sigma_{e\,\min}}{\frac{1}{10} \sum_{\mathrm{opt}=1}^{10} \sigma_{e\,\mathrm{opt}}}, \tag{6}$$

where: $\sigma_{e\,\min}$ and $\sigma_{e\,\mathrm{opt}}$ express the error standard deviation of the best fitting and the sequence of increasing deviation error of ten well fitted models.

Next, three best fitted variants were proposed to be used as a basis for selection of the finally accepted solution. The three variants mentioned above are presented in figures for exemplary systems to show relations between the fitting error deviation and uncertainty of the determined parameters.
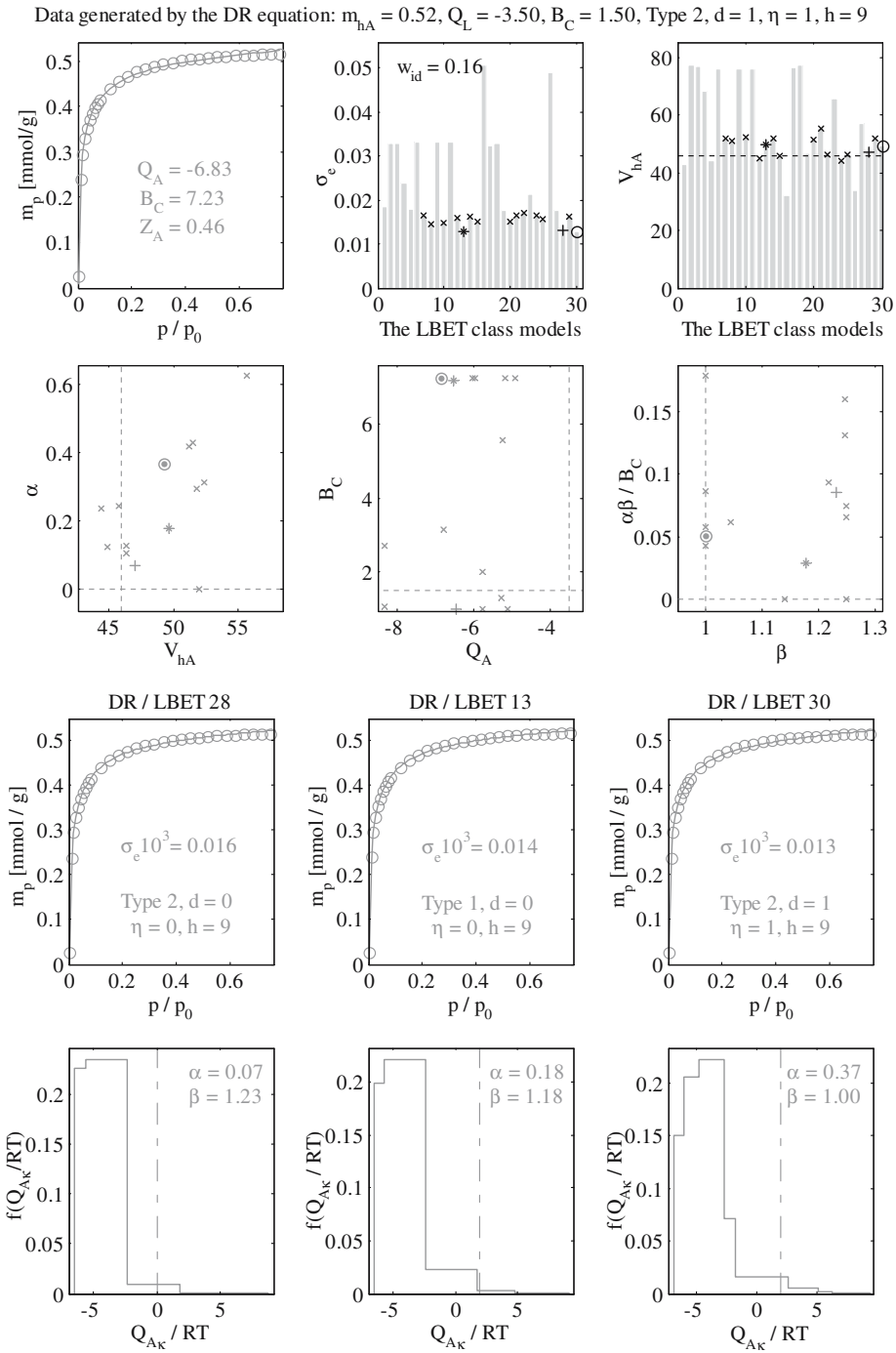
Figure 1. The multivariant identification results for a single isotherm generated by the DR equation and fitted by full set of the LBET class formulas.

Table 1
The classical equations used in the verification of the LBET class models.

Model name	Adsorption equation	Parameters of the models
Dubinin – Radushkevich	$a = a_0 \exp\left(-B_{DR}\left(RT \ln \frac{p_0}{p}\right)^2\right)$	a is the volume of the adsorbate condensed within the micropores at temperature T and relative pressure p/p_0 a_0 is the total volume of the micropores accessible to the given adsorbate B_{DR} is the energetic-structural parameter
Freundlich	$a = k_{FR} p^{1/n_{FR}}$	p is the partial pressure of the adsorbate k_{FR}, n_{FR} is the empirical constants characteristic for adsorbate–adsorbent system
Hütting	$a = \left(a_m C_{HUT} \frac{p}{p_0}\right)\left(1 + \frac{p}{p_0}\right) \cdot \frac{1}{1+C_{HUT}\frac{p}{p_0}}$	a is the amount in moles adsorbed on 1 g of adsorbent a_m is the monolayer capacity C_{Hut} is the Hütting equation constant

The relative errors of the parameters evaluated for the best fitted variants are compared with those obtained with the homogeneous LBET model (table 1). The detailed results of the analysis are presented in figures 1–12, additionally the most important indicators, fitting errors and obtained parameters are gathered in table 2. In all figures, the first column of the first row shows the fitting isotherm pointed by circles "o". The solid line "−" presents a theoretical isotherm calculated with the uLBET model (see [12]) with the parameters of the best fitted variant of the LBET model. The second figure in this row includes a grey bars diagram of the deviation error of the fitting with different variants of the LBET model. The bold "o" refers to the best fitted variant. Next "+" and "*" mean, the second and the third best fitting. In addition, the value of the index w_{id} is shown. The more diversified heights of the individual bars and the bigger the differences between the lowest bar and the remaining bars, the better the identyfication of the adsorption system. In this case factor w_{id} has a big value. The third figure in the discussed row shows the values of the most important structure parameter i.e.: monolayer capacity $V_{hA} \sim m_{hA}$, obtained in the individual variants. The three best fitted variants are marked in the same way as in the previous figure. The headline of the frst line of the set of figures gives the name of the adsorption system, i.e.: adsorbat symbol, the carbonaceous adsorbent symbol, binary options h, d, η and parameters α, β. Figures in the second row present diversification of the model parameters, obtained in ten good fittings. The marks "o"

Table 2
Comparison of the detailed results of calculations for different adsorption systems.

Nr	Generated data	p/p_0	Number of isotherm	w_{id}	The best fitting fitting variants	Parameters of the best variants						
						Type	d	η	h	α	β	$\sigma\,10^3$
1	DR	0.76	single	0.16	1st	2	1	1	9	0.37	1.00	0.013
					2nd	1	0	0	9	0.18	1.18	0.014
					3th	2	0	0	9	0.07	1.23	0.016
2	DR	0.76	double	0.07	1st	2	1	1	9	0.07	1.08	0.013
					2nd	2	1	1	9	0.22	1.00	0.015
					3th	1	1	1	9	0.66	1.00	0.016
3	DR	0.5	single	0.18	1st	2	1	1	9	0.22	1.00	0.012
					2nd	2	0	0	9	0.01	1.24	0,013
					3th	1	1	1	9	0.66	1.00	0.013
4	DR	0.5	double	0.10	1st	2	1	1	7	0.25	1.00	0.012
					2nd	2	1	1	9	0.12	1.24	0.013
					3th	2	0	0	7	0.18	1.25	0.013
5	Freundlich	0.76	single	0.18	1st	2	1	0	9	0.52	1.08	0.019
					2nd	1	1	0	3	0.97	1.17	0.021
					3th	1	0	0	3	0.92	1.04	0.021
6	Freundlich	0.76	double	0.11	1st	2	1	0	9	0.64	1.00	0.018
					2nd	2	1	0	7	0.89	1.00	0.019
					3th	2	1	1	9	0.60	1.00	0.020
7	Freundlich	0.5	single	0.08	1st	1	0	0	3	0.95	1.00	0.018
					2nd	2	0	0	5	0.95	1.01	0.019
					3th	1	1	1	3	1.00	1.23	0.021
8	Freundlich	0.5	double	0.07	1st	2	1	0	9	0.64	1.01	0.017
					2nd	1	1	0	9	0.80	1.00	0.018
					3th	2	1	1	9	0.82	1.00	0.019
9	Hütting	0.76	single	0.25	1st	2	0	0	5	0.56	1.00	0.0085
					2nd	2	0	0	3	0.68	1.12	0.0086
					3th	1	1	0	9	0.17	1.05	0.0090
10	Hütting	0.76	double	0.20	1st	2	0	0	0	0.69	1.00	0.0095
					2nd	1	0	0	0	0.73	1.00	0.01
					3th	1	1	1	5	0.41	1.00	0.011
11	Hütting	0.5	single	0.36	1st	2	0	0	5	0.65	1.05	0.0039
					2nd	2	1	0	3	0.55	1.00	0.0042
					3th	1	0	0	5	0.64	1.09	0.005
12	Hütting	0.5	double	0.15	1st	1	0	0	0	0.44	1.07	0.0072
					2nd	2	1	1	5	0.57	1.22	0.0075
					3th	2	1	1	3	0.5	1.25	0.0075

show optimum fitting parameters, while "*", "+" – the second and the third quality fitting, "x" the seven remaining acceptable fittings. They are presented in rectangular coordinates of two parameters. When the best results are close to one another or cover one another, the parameters are calculated with a small error.

Data generated by the DR equation: $Q_A = -7.00$, $B_C = 1.50$, $Z_A = 0.47$, Type 2, d = 1, η = 1, h = 9
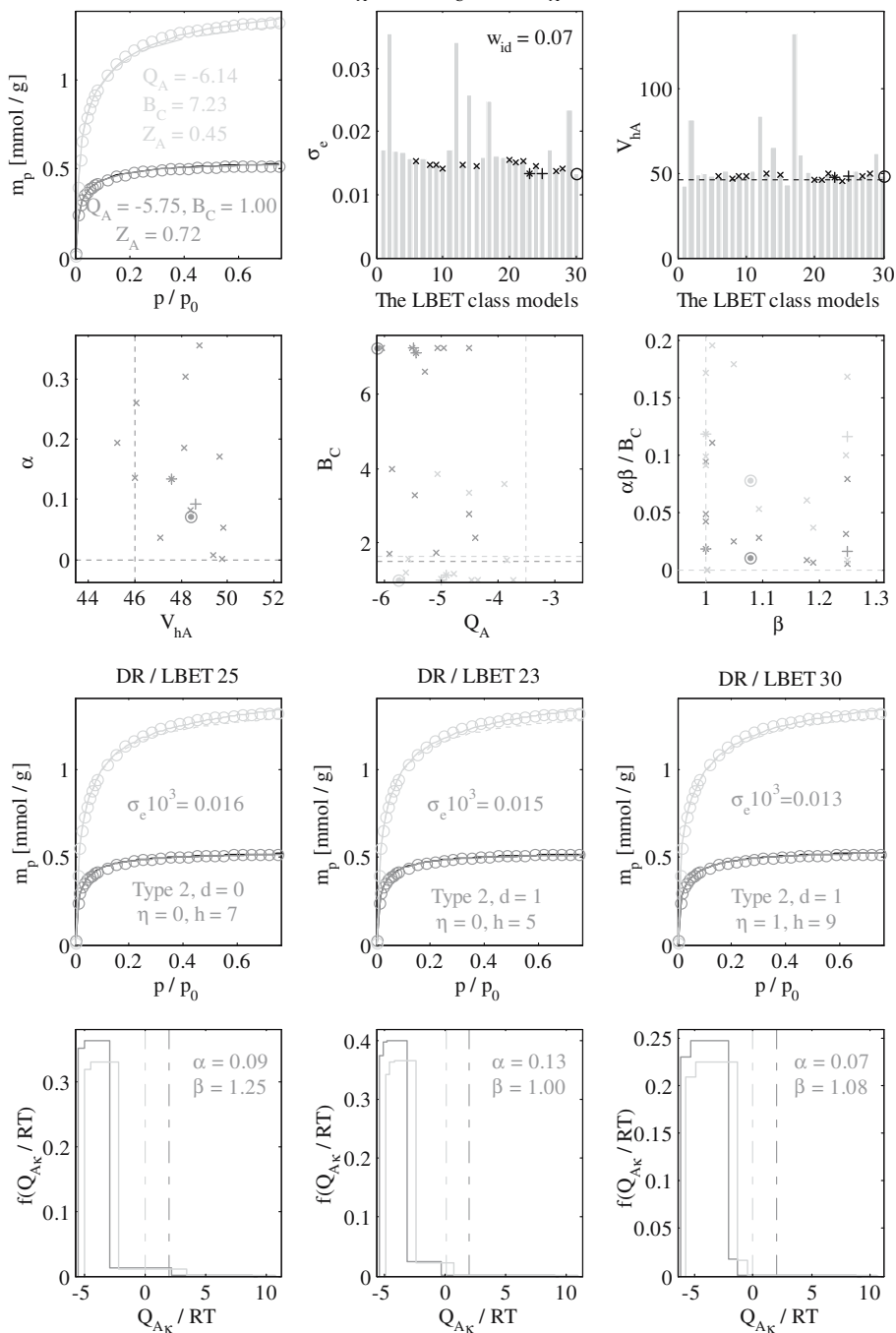

Figure 2. The multivariant identification results for a double isotherm generated by the DR equation and fitted by full set of the LBET class formulas.
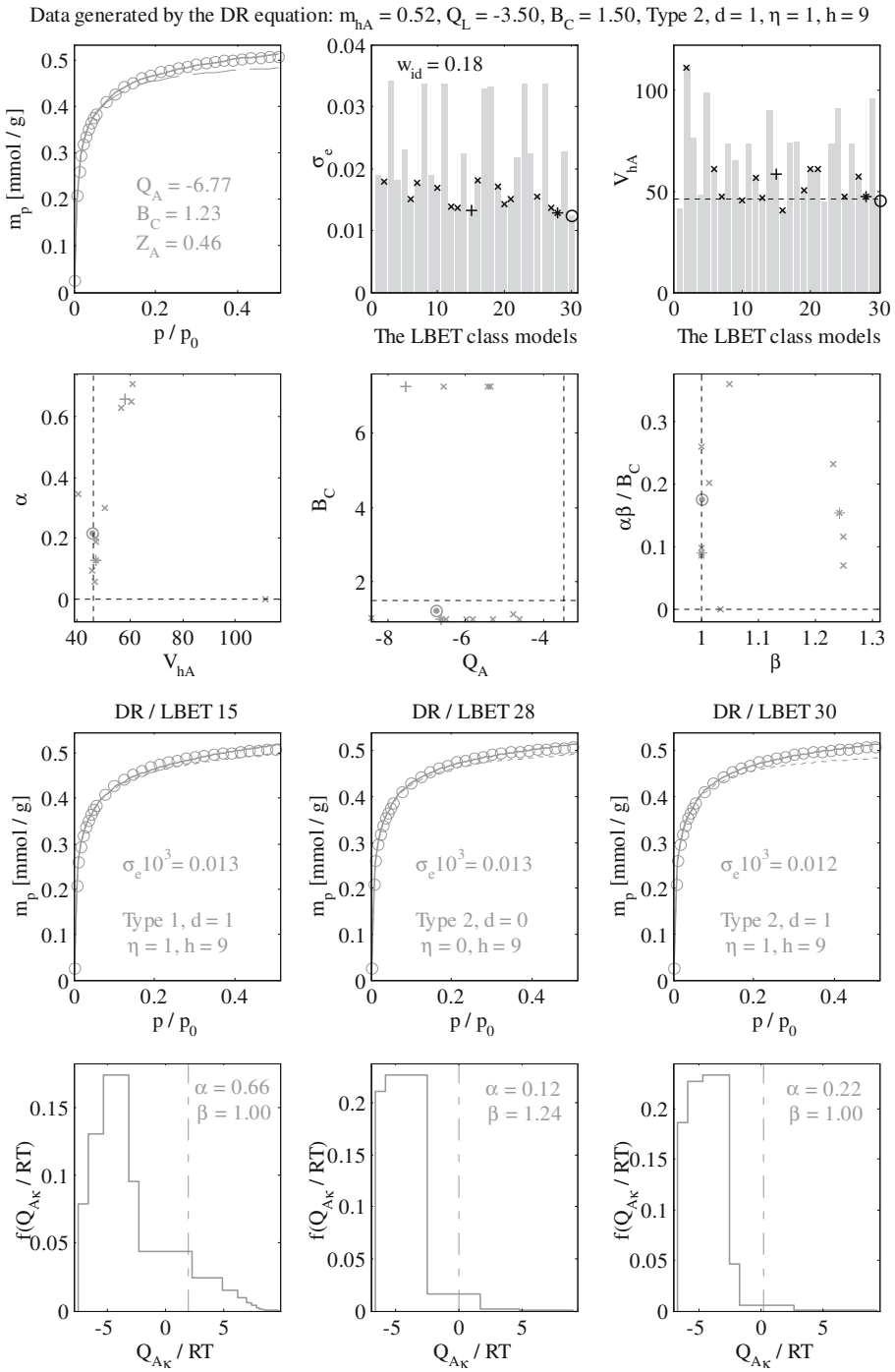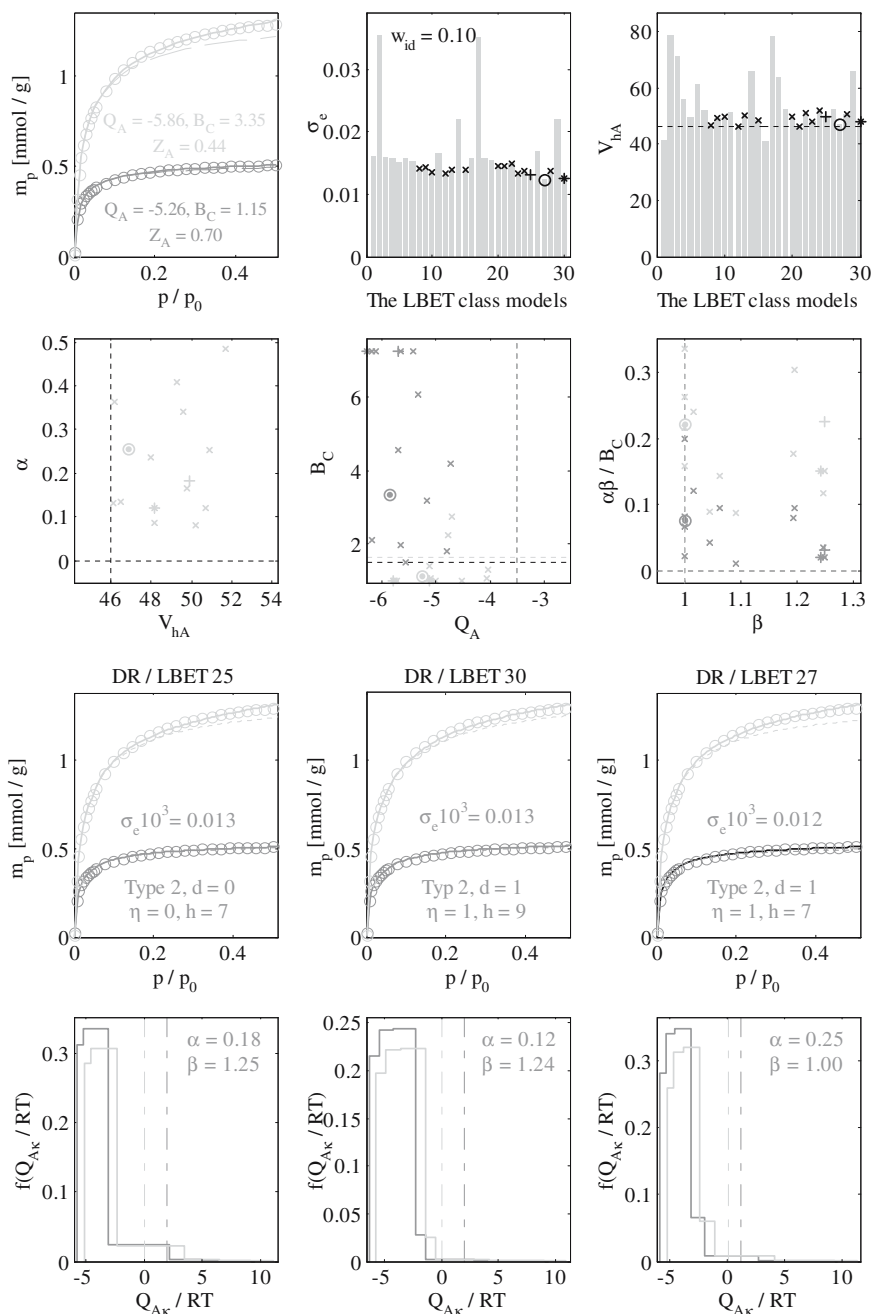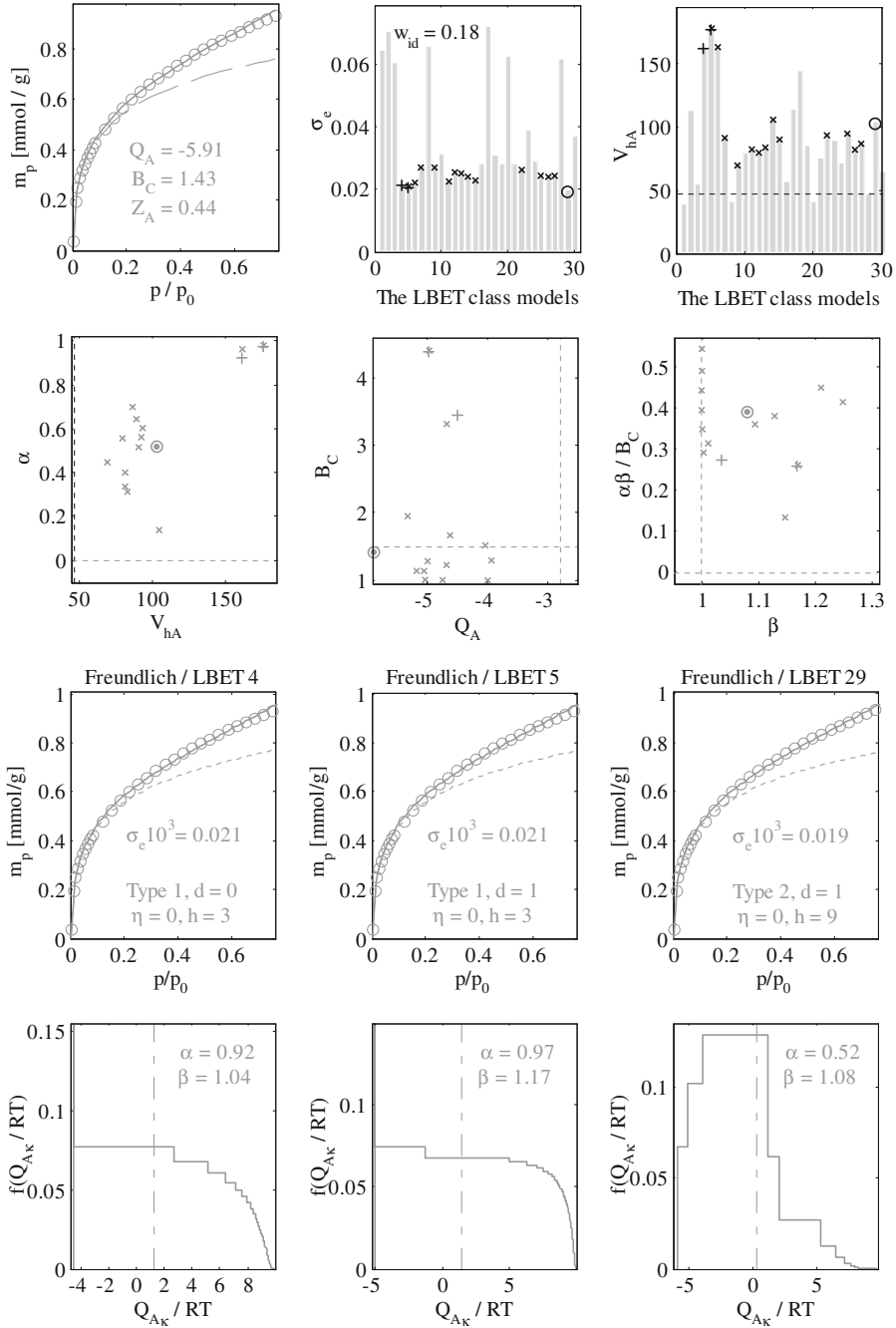
Figure 3. The multivariant identification results for a single isotherm generated by the DR equation and fitted by full set of the LBET class formulas.
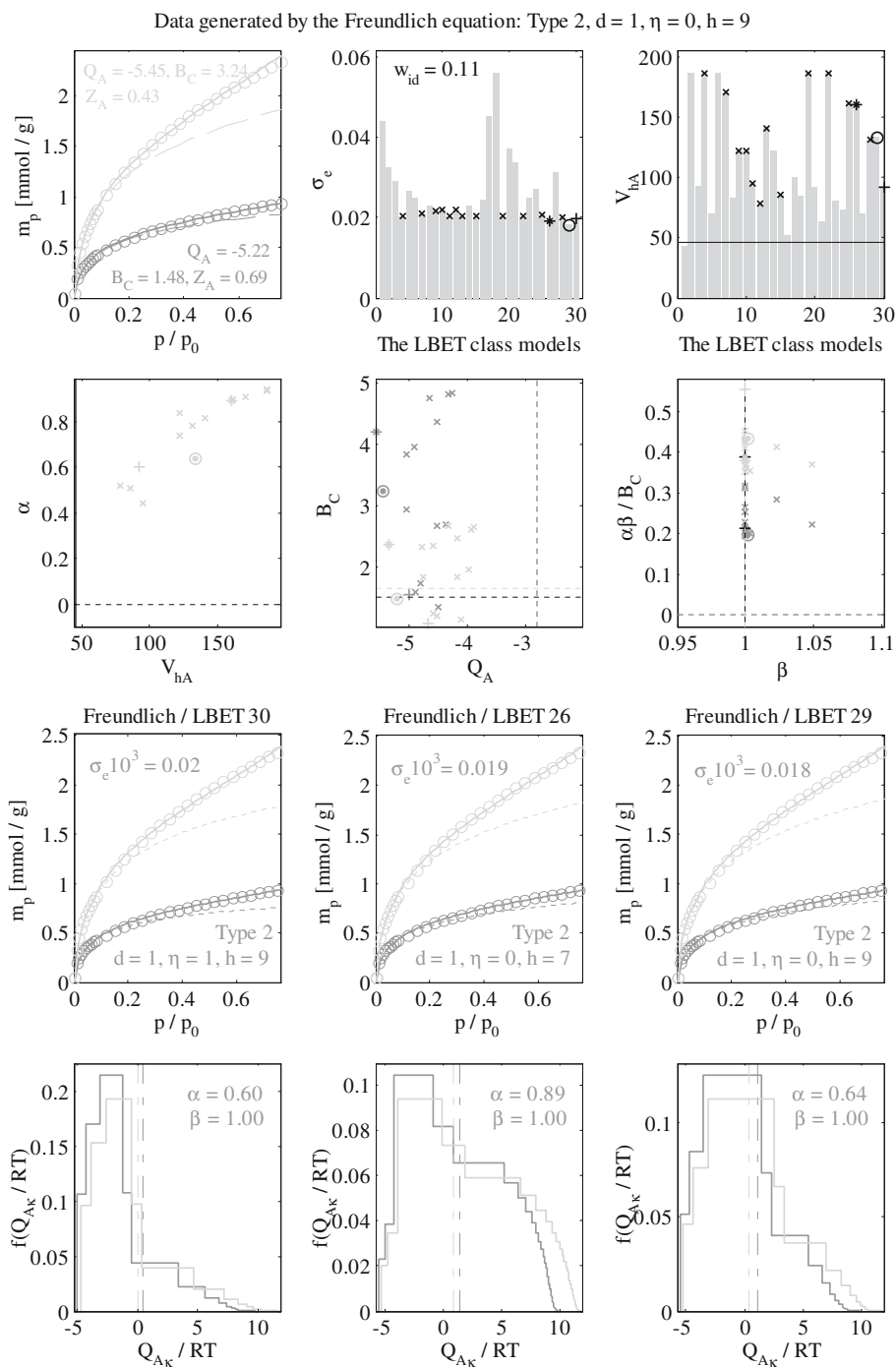
Data generated by the DR model: Type 2, d = 1, η = 1, h = 7, α = 0.25, β = 1.00

Figure 4. The multivariant identification results for a double isotherm generated by the DR equation and fitted by full set of the LBET class formulas.

Data generated by the Freundlich equation: $m_{hA} = 0.52$, $Q_L = -2.80$, $B_C = 1.50$, Type 2, $d = 1$, $\eta = 0$, $h = 9$
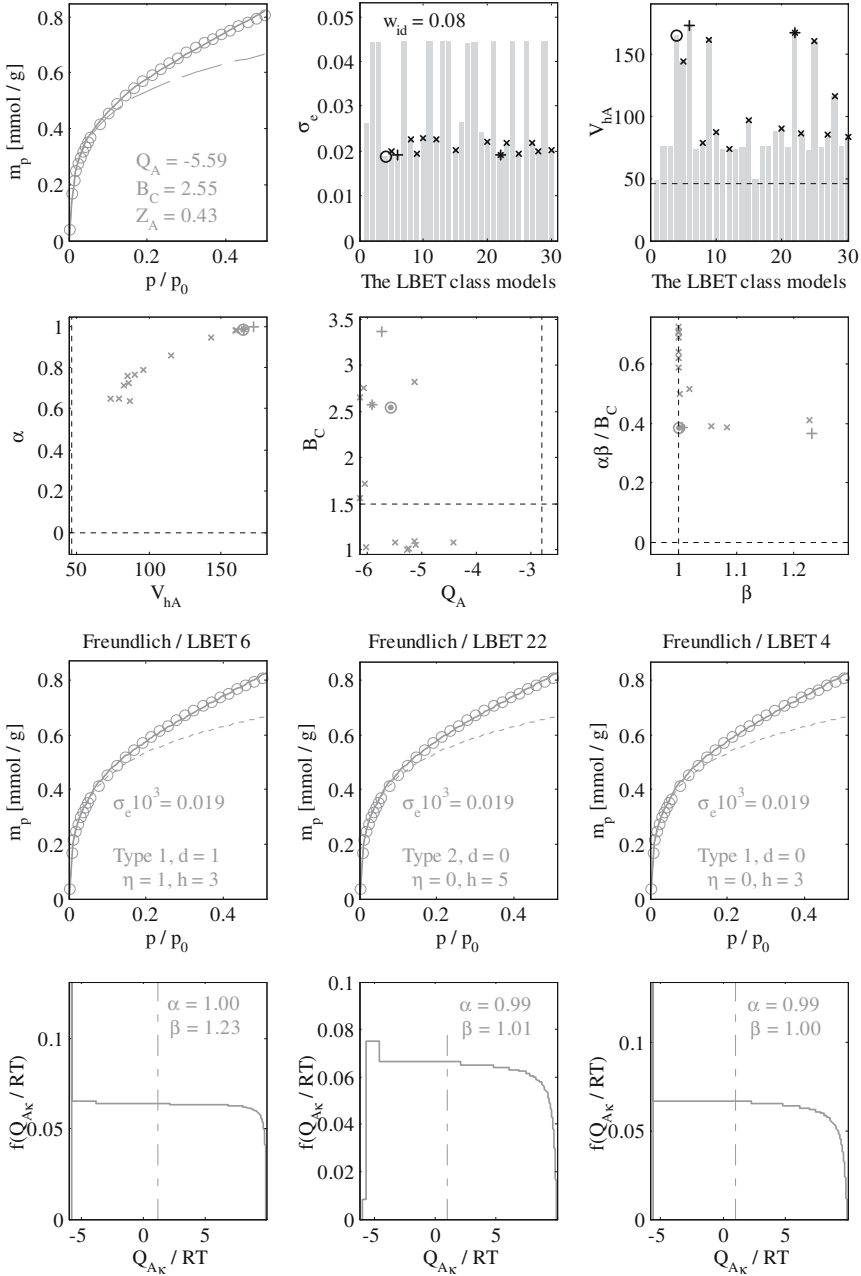

Figure 5. The multivariant identification results for a single isotherm generated by the Freundlich equation and fitted by full set of the LBET class formulas.
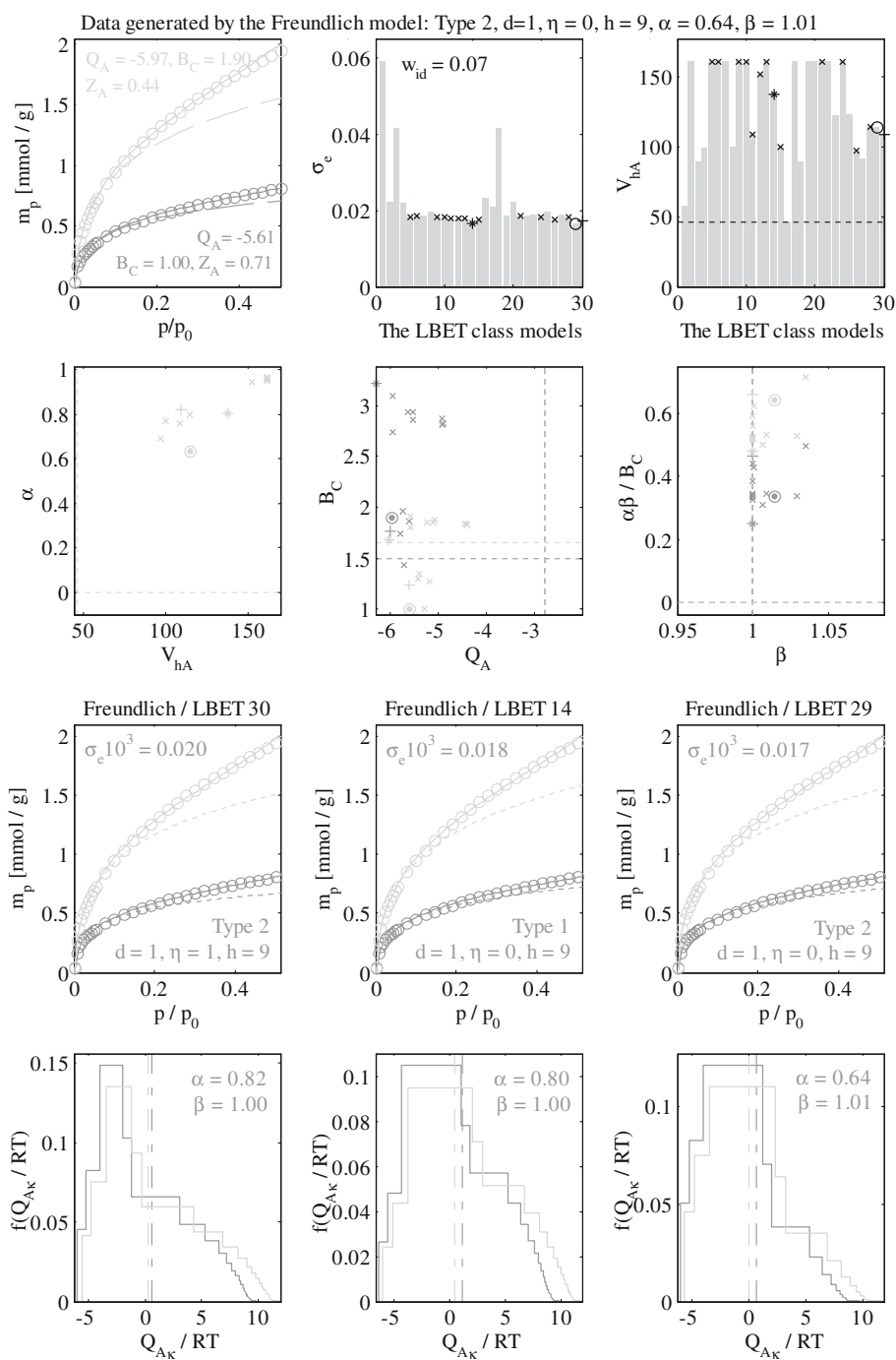
Data generated by the Freundlich equation: Type 2, d = 1, η = 0, h = 9

Figure 6. The multivariant identification results for a double isotherm generated by the Freundlich equation and fitted by full set of the LBET class formulas.

Data generated by the Freundlich equation: $m_{hA} = 0.52$, $Q_L = -2.80$, $B_C = 1.50$, Type 1, $d = 0$, $\eta = 0$, $h = 3$
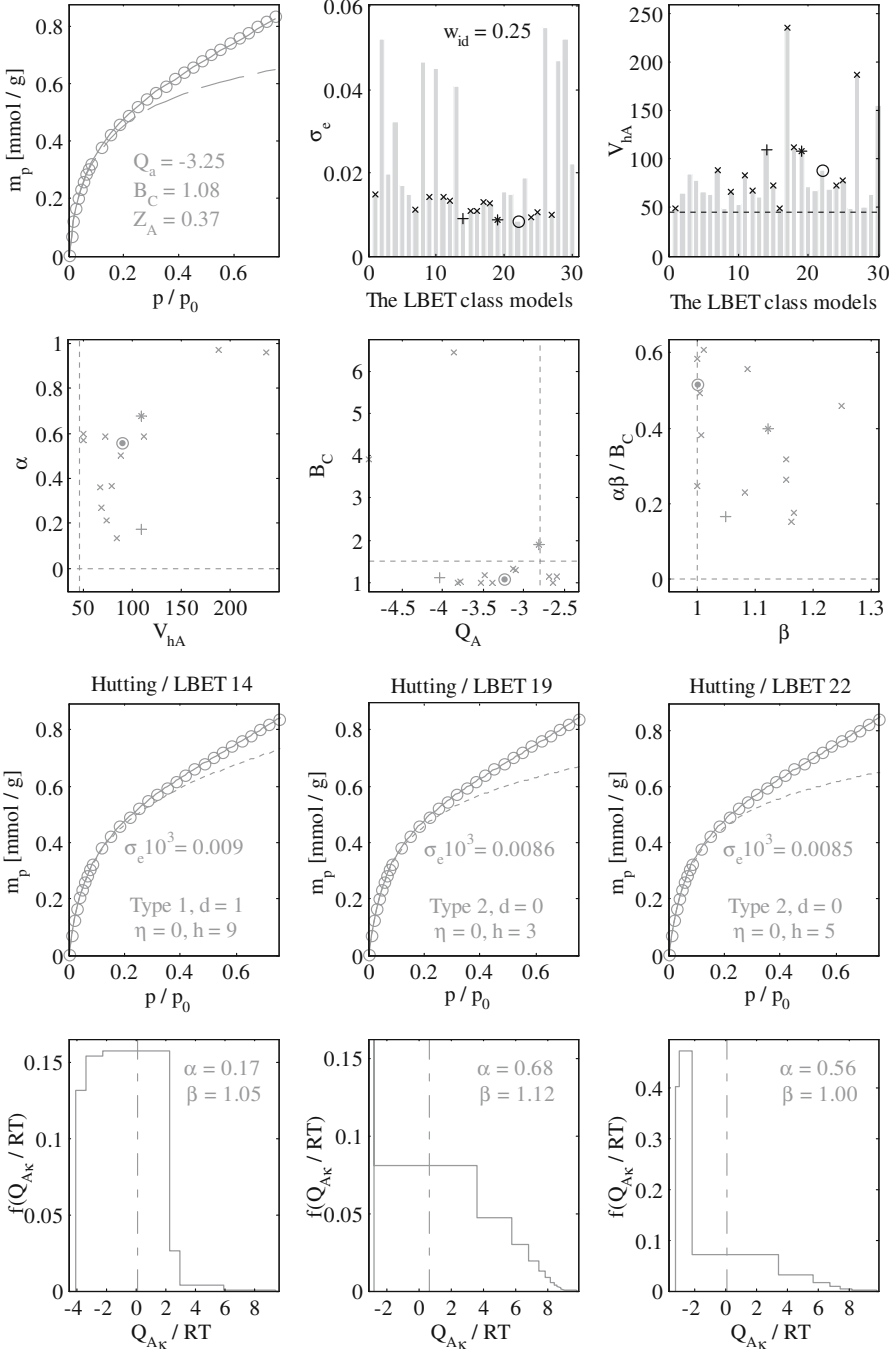

Figure 7. The multivariant identification results for a single isotherm generated by the Freundlich equation and fitted by full set of the LBET class formulas.

Figure 8. The multivariant identification results for a double isotherm generated by the Freundlich equation and fitted by full set of the LBET class formulas.

Data generated by the Hutting equation: m_{hA} = 0.52, Q_L = -2.80, B_C = 1.50, Type 2, d = 0, η = 0, h = 5

Figure 9. The multivariant identification results for a single isotherm generated by the Hütting equation and fitted by full set of the LBET class formulas.
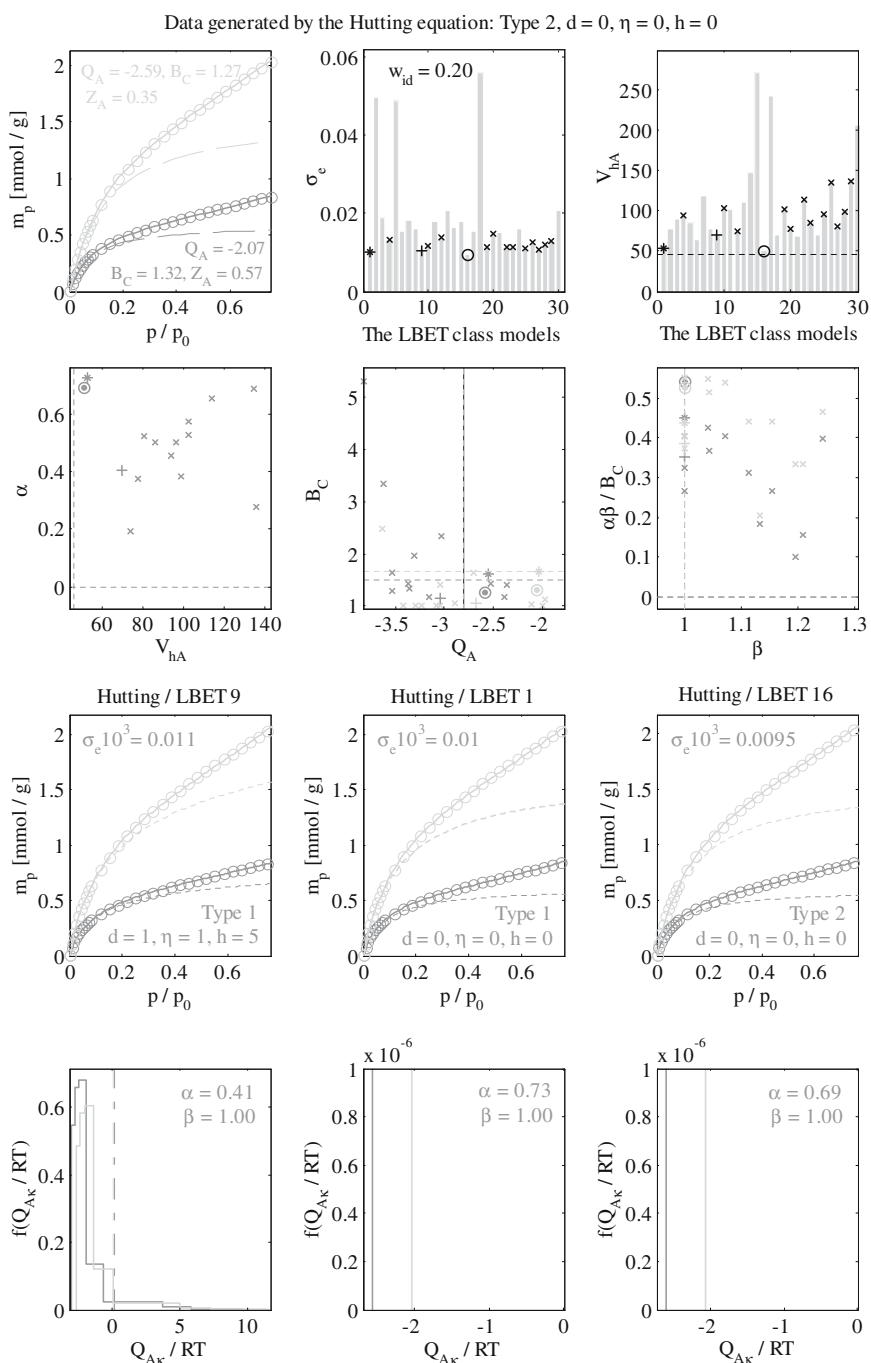
Data generated by the Hutting equation: Type 2, d = 0, η = 0, h = 0

Figure 10. The multivariant identification results for a double isotherm generated by the Hütting equation and fitted by full set of the LBET class formulas.
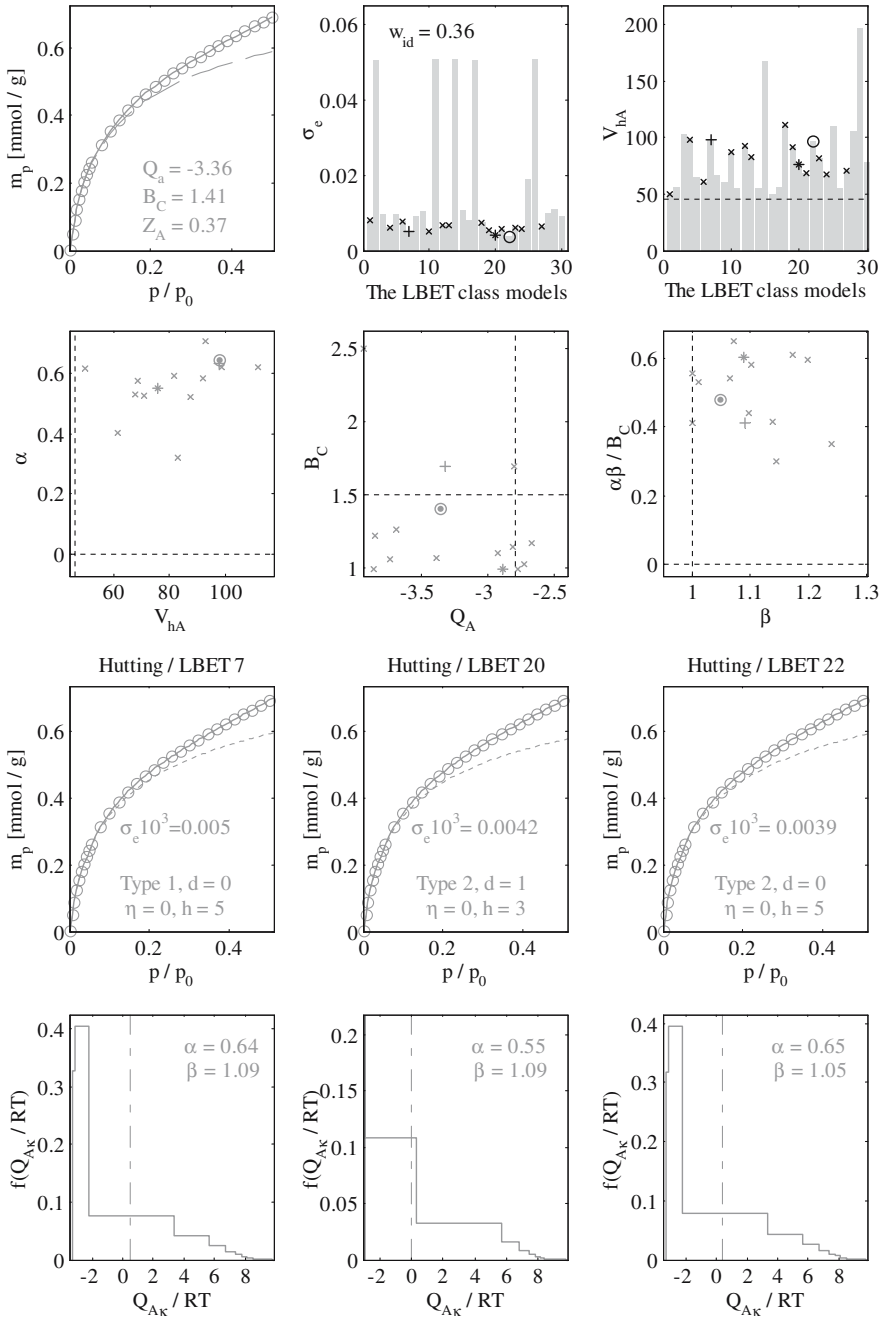
Figure 11. The multivariant identification results for a single isotherm generated by the Hütting equation and fitted by full set of the LBET class formulas.

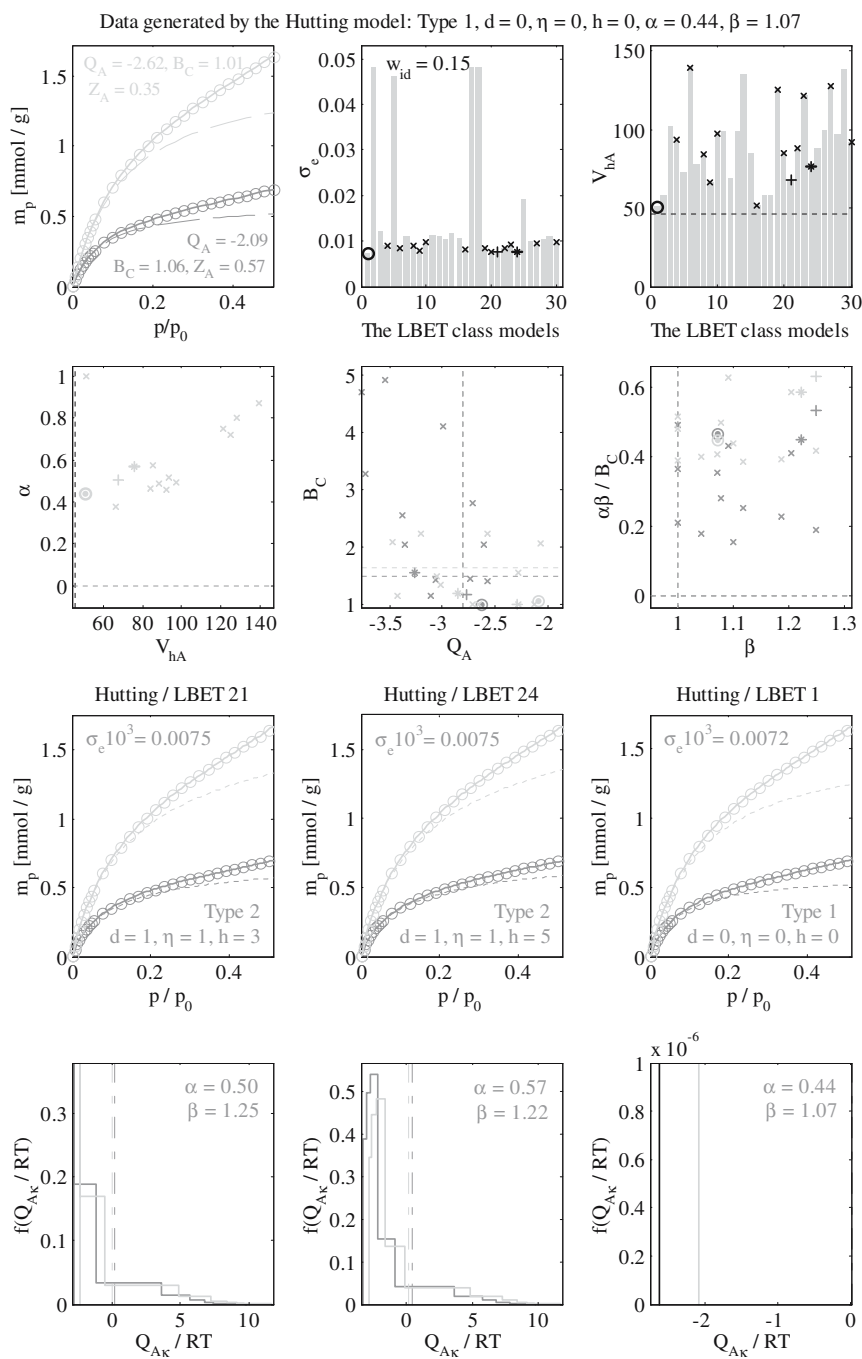Data generated by the Hutting model: Type 1, d = 0, η = 0, h = 0, α = 0.44, β = 1.07

Figure 12. The multivariant identification results for a double isotherm generated by the Hütting equation and fitted by full set of the LBET class formulas.

Figures in the third row show the three best fittings of adsorption models (solid line) to the empirical data marked as bold black "o" in the coordinate system: the amount of adsorbate substances *mmol/g* versus relative pressure p/p_0. In the diagram headlines the symbol of the adsorption system is placed and the number of the LBET model variant follows the slash. In the lower part of each diagram the value of the fitting quality factor is shown (the lower value of the factor means the better fitting).

In the fourth row of the figure, profiles of the obtained adsorption energy distribution are placed. They refer to the corresponding diagram in the third row. The vertical line shows the value of the adsorption energy of the second and the next layers.

4.   Conclusions

On the basis of the results presented in figures 1–12 and table 2 it is shown that in the case of data generated with the DR model, the analysis of double isotherm significantly deteriorates the identification of the adsorption system parameters. However, this identification both for single and double isotherms, improves for narrower range of the relative pressure. This confirms earlier predictions connected with the fact that the errors of determining high-pressure part of isotherm may significantly influence the reliability of the obtained system parameters. In the case of data generated with the Freundlich model with simultaneous analysis of double isotherms, the identification deteriorates as well. Moreover, in this case for narrower range of relative pressure the increase of fitting errors is also observed. In the next case, in which data have been generated with the Hütting model, similarly to the above the analysis of double isotherms deteriorates the possibility of the system parameters identification.

The studies presented in this paper suggest that single isotherms are usually enough to derive adsorption systems parameters especially if, we have empirical data obtained with an average accuracy. Moreover, in some cases, the use of double isotherms worsens the task conditioning. What is more, the significant improvement of identification for narrower range of relative pressure in the case of the single isotherm and significant deterioration of identification during analysing double isotherms is also observed. Comparing the results obtained for $0.5 – 0.76$ p/p_0 brings equally interesting conclusions. In summing up, the analysis of isotherms determined in a narrower range of relative pressures gives better results than those obtained for a wider range of relative pressures. That is why, the analysis of narrower range of relative pressures is recommended.

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