Incorporating heterogeneity into the osmotic theory of adsorption

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A new theoretical approach of adsorption equilibrium description founded on the Osmotic Theory of Adsorption (OTA) proposed by Bering and Serpinsky is presented. In the first part the new general derivation of the adsorption equations basing on the regularities of the osmotic equilibrium is proposed. One of the developed isotherm formulas leads, after simplifications, to the fundamental Freundlich isotherm equation, another to the OTA isotherm equation (sometimes also called empirical Bradley's adsorption isotherm). Taking into account that in real adsorption space the energy of adsorption as well as the value of the osmotic coefficient should be distributed, the new general heterogeneous version of the OTA model, and corresponding isosteric enthalpy of adsorption equation are derived. Next, two different distribution functions are assumed, and the results of simulations of adsorption isotherms and enthalpy data are presented. It can be concluded that developed models generate the shapes of adsorption isotherms and enthalpy very similar to those observed experimentally. Finally, the applicability of presented model to description of experimental data is presented.

1. INTRODUCTION – DEVELOPING THE OTA EQUATIONS

The Osmotic Theory of Adsorption (OTA) [1] is one of the most interesting and valuable approaches developed in the 20th century. Originating from the so-called "Russian school of adsorption" this concept was in fact the alternative to

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the second important idea, i.e. the Theory of Volume Filling of Micropores (TVFM) founded by Dubinin et al [2]. The major difference in both approaches is the treatment of the adsorption system. While the TVFM postulates the creation of a quasi-liquid adsorbate in the potential field of pores, the OTA assumes the formation of the adsorbent-adsorbate-two component solution. The comparative discussion of the both approaches in adsorption thermodynamics was discussed recently [3]. Now the short presentation of the OTA theory is given; however, in the alternative (to the original) new form.

Consider the system in which a pure solvent is separated from the two-component solution (solute "1" and solvent "0") by a membrane permeable only for the solvent (Figure 1). Osmotic system is at equilibrium, i.e. the flow $J_0=0$, and the difference in the pressure is equal to the osmotic pressure $\Delta p=\pi$. The solvent will penetrate into the solution side until its chemical potential on both sides of a membrane becomes the same because of the increasing Δp on the solute side. Moreover,
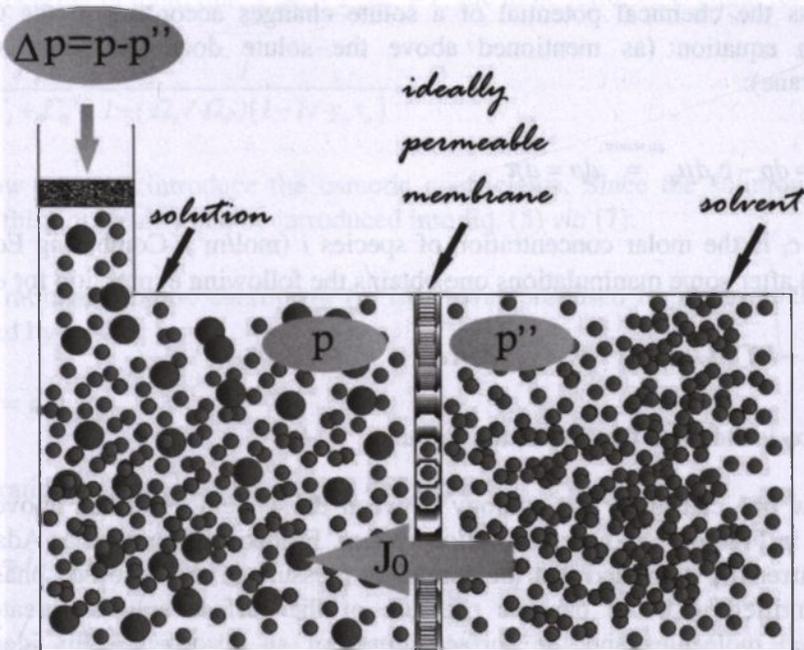
$$\mu_0 = \mu_0''$$ (1)

Fig. 1. Osmotic system; at equilibrium $J_0=0$ and $\Delta p=\pi$ (Eq. (3)).

The part of the system with pure solvent is denoted by ("). The expression for the chemical potential of species i can be written as :

$$\mu_i = \mu_i^o + RT \ln a_i + (p - p^o) \overline{v}_i \qquad\qquad i = 0,1 \qquad\qquad (2)$$

where p^o is the standard pressure, R – the gas constant, T – the absolute temperature, μ_i^o, a_i, and v_i are the standard chemical potential, the activity, and the partial molar volume of species i, respectively. Now re-writing Eq. (2) for a solvent in both parts of the system, and taking into account Eq. (1) the osmotic pressure (π) can be defined as follows:

$$\pi = p - p'' = -\frac{RT}{\overline{v}_0} \ln a_0 \qquad\qquad (3)$$

If some amount of a solute is added to the solution (left side in Figure 1), the new equilibrium establishes. As the right side (pure solvent) does not change, the chemical potential of the solvent on the left side also does not change (Eq. (1)), whereas the chemical potential of a solute changes according to the Gibbs-Duhem equation (as mentioned above the solute does not penetrate the membrane):

$$c_1 d\mu_1 = dp - c_0 d\mu_0 \overset{\mu_0 = const}{=} dp = d\pi \qquad\qquad (4)$$

where c_i is the molar concentration of species i (mol/m^3). Combining Eqs. (4) and (3) after some manipulations one obtains the following expression for $d\mu_1$:

$$d\mu_1 = -RT \left(1/x_1 - 1 + \overline{v}_1 / \overline{v}_0 \right) d \ln a_0 \qquad\qquad (5)$$

where x_1 is the mole fraction of the solute.

Now one can apply the analogy between the system described above (and shown in Figure 1) and the adsorption system. Frumkin [4] as well as Adam [5] and Barrer [6] suggested that the spreading pressure of the adsorbed phase can be identified with the osmotic pressure of the surface solution created by adsorbed molecules and the surface atoms of an adsorbent. This idea was developed by Bering and co-workers [1]. Here an adsorbate plays the role of the dissolved substance (i.e. solute) and the vacancies (i.e. holes) are the solvent (p is the analogue of the surface tension) c_1 is the number of adsorbed moles (per

m^2) of a surface of Γ_1 and c_0 describes the number of moles of vacancies (per m^2) of a surface of Γ_0. Partial molar volumes $\bar{v}_i$ are simply the molar specific surface areas Ω_i (note that here also the adsorption in the porous system can be considered since Ω_i can be assumed as the molar volume of the component i). Assuming that $\Gamma_1 + \Gamma_0$ is constant it is easy to show that $\Omega_0 = \Omega_1$. However, one can consider different approach – it can be assumed that the adsorbed space can be filled incompletely, i.e. for maximum adsorption a_{max} there is the molar ratio of the space filled *via* the vacancies (y_a):

$$y_a = \Gamma_{1,max}\Omega_1 \le 1 \tag{6}$$

Denoting the molar ratio of the adsorbate as x_a:

$$x_a = a / a_{max} = \Gamma_1 / \Gamma_{1,max} \tag{7}$$

where a and a_{max} are the adsorption and the maximum adsorption, respectively. Then, bearing in mind that $\Gamma_1\Omega_1 + \Gamma_0\Omega_0 = 1$, the mole ratio, x_1, is equal to:

$$x_1 = \frac{\Gamma_1}{\Gamma_1 + \Gamma_0} = \frac{1}{1 - (\Omega_1 / \Omega_0)(1 - 1/ y_a x_a)} \tag{8}$$

Now one can introduce the osmotic coefficients. Since the solution is not ideal, this nonideality can be introduced into Eq. (5) *via* [7]:

• the rational osmotic coefficient (g) (as it was proposed in the original OTA) defined by:

$$ln\, a_0 = g\, ln\, x_0 \tag{9}$$

• the rational activity coefficient (γ) defined by:

$$ln\, a_0 = ln(\,\gamma x_0\,) \tag{10}$$

• the molal osmotic coefficient (ϕ) defined by:

$$ln\, a_0 = -\phi x_1 / x_0 \tag{11}$$

• and finally, proposed in this study, the new definition of the osmotic coefficient:

$$ln\, a_0 = -\varphi x_I \tag{12}$$

Here, contrary to Bering et al. [1] one can assume that g and ϕ are the unknown functions of the adsorption.

Introducing Eqs. (9) – (12) into Eq. (5) one obtains, respectively:

$$d\mu_I = \left(\frac{g}{a(1-y_a x_a)(1-(1-1/k_\Omega)y_a x_a)} - \frac{k_\Omega g'}{y_a x_a} ln\left(\frac{1-y_a x_a}{1-(1-1/k_\Omega)y_a x_a} \right) \right) da \tag{13a}$$

$$d\mu_I = \left(\frac{1}{a(1-y_a x_a)(1-(1-1/k_\Omega)y_a x_a)} - \frac{k_\Omega \gamma'}{y_a x_a} \right) da \tag{13b}$$

$$d\mu_I = \left(\frac{\phi}{a(1-y_a x_a)^2} + \frac{\phi'}{1-y_a x_a} \right) da \tag{13c}$$

$$d\mu_I = \left(\frac{\varphi}{a(1-(1-1/k_\Omega)y_a x_a)^2} + \frac{\varphi'}{(1-(1-1/k_\Omega)y_a x_a)} \right) da \tag{13d}$$

where $k_\Omega = \Omega_1/\Omega_0$; g', γ', ϕ', and φ' are the derivative of the osmotic coefficient with respect to a. Obviously, $y_a x_a$ is the fraction of the surface covered (or the fraction of the pore space filled) by an adsorbate. Now if the adsorbate and adsorbent are in the equilibrium:

$$d\mu_I = d\,ln\, p \tag{14}$$

where p is the equilibrium pressure.

Applying Eq. (13) together with Eq. (14) and integrating under the assumption that osmotic coefficients are constant (similarly to Bering et al. [1]) one can obtain the following adsorption isotherm equations:

$$p = b\left(\frac{x_a}{1-y_ax_a}\left(\frac{1-y_ax_a}{1-(1-1/k_\Omega)y_ax_a}\right)^{1-k_\Omega}\right)^g \tag{15a}$$

$$p = b\frac{x_a}{1-y_ax_a}\left(\frac{1-y_ax_a}{1-(1-1/k_\Omega)y_ax_a}\right)^{1-k_\Omega} \tag{15b}$$

$$p = b\left(\frac{x_a}{1-y_ax_a}\right)^\phi exp\left(\frac{\phi}{1-y_ax_a}\right) \tag{15c}$$

$$p = b\left(\frac{x_a}{1-y_ax_a(1-1/k_\Omega)}\right)^\varphi exp\left(\frac{\varphi}{1-y_ax_a(1-1/k_\Omega)}\right) \tag{15d}$$

where b is the integration constant.

2. SIMPLIFYING THE OTA EQUATIONS

Assuming $y_a = k_\Omega = 1$ Eqs. (15a) - (15d) reduce to:

$$p = b\left(\frac{x_a}{1-x_a}\right)^g \tag{16a}$$

$$p = b\frac{x_a}{1-x_a} \tag{16b}$$

$$p = b\left(\frac{x_a}{1-x_a}\right)^\phi exp\left(\frac{\phi}{1-x_a}\right) \tag{16c}$$

$$p = b(x_a)^\varphi exp(\varphi) = b_1(x_a)^\varphi \tag{16d}$$

Eq. (16a) is in fact the equation proposed by Bering et al. [1] in the original version of the OTA, and it is sometimes called the Bradley isotherm equation. It

is interesting to admit here that the Bradley isotherm was derived by Rudziński and Everett [8] basing on the method proposed by Cerofolini and assuming the Fermi-Dirac distribution of the surface atoms of solid and the condensation approximation method. Eq. (16b) is the Langmuir and Eq. (16d) Freundlich isotherm equation. This leads to the conclusion that the Osmotic Theory of Adsorption is a very powerful concept making possible to derive important and well known adsorption isotherm equations.

3. OTA EQUATION BASING ON THE CONCEPT OF VIRIAL EQUATION OF THE OSMOTIC PRESSURE

Following the presented above methodology one can develop the adsorption isotherm basing on thermodynamics of mixtures, for example applied in description of polymeric solutions. Following Eq.(3):

$$\ln a_0 = -\frac{\overline{v}_0}{RT}\pi \tag{17}$$

The osmotic pressure can be written as:

$$\frac{\pi}{c} = A_1 + A_2 c + A_3 c^3 + \dots \tag{18}$$

and this is simply another way of taking into account the non-ideality of the solution.

By the way, for the ideal solution:

$$\ln a_0 = \ln x_0 = -\frac{\overline{v}_0}{RT}\pi \tag{19}$$

and only in the case of diluted solution:

$$\lim_{c \to 0} \frac{\pi}{c} = A_1 = \frac{RT}{M_{dil.sub.}} \tag{20}$$

where $M_{dil.sub.}$ is the molar mass of the diluted substance. In the case of the solution of polymer this is simply the average molecular mass of the polymer.

Following the Flory – Huggins concept A_2 is given by:

$$A_2 = \frac{RT}{M_0} \frac{\rho_0}{\rho_1} \left(\frac{1}{2} - \chi \right)$$ (21)

where: ρ_0 and ρ_1 are the densities of the solution and polymer, χ – is the parameter describing the interactions between the polymer and solvent.

Taking into account Eqs.(17) and (18):

$$c = \frac{x_1}{x_1 \overline{v}_1 + (1 - x_1) \overline{v}_0}$$ (22)

x_1 is related to x_a (Eq. (7)) by Eq.(8). This makes it possible to calculate the derivative of $\ln a_0$ with respect to x_a. Following the method described above (Eq.(5)) one obtains the adsorption isotherm equation in the form:

$$p = b \cdot x_a^A \exp \left(\frac{2 A_2 y_a}{\Omega_1} x_a + \frac{3 A_3}{2} \left(\frac{y_a}{\Omega_1} x_a \right)^2 + ... \right)$$ (23)

4. HETEROGENEOUS OTA MODEL AND RELATED ENTHALPY FORMULA

In this paragraph we wish to pay attention to Eq. (16a). After simple manipulation and conversion of the symbols accepted in the theory of solutions to symbols applied in the field of adsorption ($x_a = \Theta(h;T,E,g)$, $b = K(T;E)$, $g = g(T)$) this equation can be written in the following form:

$$\Theta \left(h;T;E;g \right) = \frac{K(T;E) h^{\frac{1}{g(T)}}}{1 + K(T;E) h^{\frac{1}{g(T)}}}$$ (24)

where E is the energy of adsorption and h is the relative pressure.
The temperature dependence of K is well known:

$$K(T;E) = K_0 \, exp\left[\frac{E}{RT^i}\right] \quad (25)$$

where K_0 is slightly dependent on the temperature entropic factor.

On the other hand, the temperature dependence of the osmotic coefficient was evaluated from experimental data by Bering et al. [1]:

$$g(T) = 1 - \frac{b}{T} \quad (26)$$

It is obvious that in the adsorption space the regions with different adsorption energy can occur. Moreover, adsorbed molecules can behave non-ideally, and the measure of his behaviour is the value of the osmotic coefficient $g \in (0,1]$ (this assumption should be verified experimentally since in the case of solutions g can be even larger, for example in 7 m NaOH solution g is around 2). Assuming that the lower limit of this coefficient g_{min} is very small and close to zero, and taking this into account the global adsorption isotherm equation one can write:

$$a(h;T) = a_m \int_{E_{min}}^{E_{max}} \int_{g_{min}}^{1} \Theta_L(h;T;E;g) \chi(E;g) \, dEdg = a_m \int_{E_{min}}^{E_{max}} \int_{g_{min}}^{1} \frac{K(T;E)h^{\frac{1}{g(T)}}}{1 + K(T;E)h^{\frac{1}{g(T)}}} \chi(E;g) \, dEdg \quad (27)$$

Here one can introduce a new variable (linearly related to the adsorption energy):

$$E = (1+\delta)Q \quad (28)$$

where Q is the energy median:

$$Q = \frac{E_{min} + E_{max}}{2} \quad (29)$$

Eq. (27) can now be rewritten as:

$$a(h;T) = a_m \int\limits_{\delta=-\lambda}^{\delta=\lambda} \int\limits_{g_{min}}^{1} \frac{K(T;\delta)h^{\frac{1}{g(T)}}}{1 + K(T;\delta)h^{\frac{1}{g(T)}}} \chi(\delta;g) d\delta dg \qquad (30)$$

where the integration limits of the first integral ($-\lambda$ and λ) are connected with the minimal (E_{min}) and maximal adsorption energy (E_{max}) by:

$$\lambda = \frac{E_{max} - E_{min}}{2Q} \qquad (31)$$

and:

$$K(T;\delta) = K_0 \exp\left[\frac{(1+\delta)Q}{RT}\right] \qquad (36)$$

After simple manipulation Eq. (30) can be transformed to the form:

$$a(h;T) = a_m \left(\int\limits_{\delta=-\lambda}^{\delta=\lambda} \int\limits_{g_{min}}^{1} \chi(\delta;g) d\delta dg - \int\limits_{\delta=-\lambda}^{\delta=\lambda} \int\limits_{g_{min}}^{1} \frac{\chi(\delta;g) d\delta dg}{1 + K(T;\delta)h^{\frac{1}{g(T)}}} \right) \qquad (37)$$

Since the distribution function should be normalized, the first integral is equal to 1, and:

$$a(h;T) = a_m \left(1 - \int\limits_{\delta=-\lambda}^{\delta=\lambda} \int\limits_{g_{min}}^{1} \frac{\chi(\delta;g) d\delta dg}{1 + K(T;\delta)h^{\frac{1}{g(T)}}} \right) \qquad (38)$$

and for isothermal conditions:

$$a(h) = a_m \left(1 - \int\limits_{\delta=-\lambda}^{\delta=\lambda} \int\limits_{g_{min}}^{1} \frac{\chi(\delta;g) d\delta dg}{1 + K(\delta)h^{g}} \right) \qquad (39)$$

To develop the equation describing the isosteric enthalpy of adsorption (q^{st}) related to Eq. (38) we applied the Clausius-Clapeyron formula [9]:

$$q^{st} - L = RT^2 \left(\frac{\partial \ln h}{\partial T} \right)_a \tag{40}$$

where L is the enthalpy of condensation. This leads to:

$$q^{st} - L = \frac{\displaystyle\int_{\delta=-\lambda}^{\delta=\lambda} \int_{g_{min}}^{1} \frac{K(T;\delta)h^{\frac{1}{g(T)}}\left((1+\delta)Q + \frac{Rb}{g^2(T)} \ln h \right)}{\left(1 + K(T;\delta)h^{\frac{1}{g(T)}} \right)^2} \chi(\delta;g)d\delta dg}{\displaystyle\int_{\delta=-\lambda}^{\delta=\lambda} \int_{g_{min}}^{1} \frac{\frac{1}{g(T)}K(T;\delta)h^{\frac{1}{g(T)}}}{\left(1 + K(T;\delta)h^{\frac{1}{g(T)}} \right)^2} \chi(\delta;g)d\delta dg} \tag{41}$$

Taking into account Eq. (26) we have:

$$q^{st} - L = \frac{\displaystyle\int_{\delta=-\lambda}^{\delta=\lambda} \int_{g_{min}}^{1} \frac{K(\delta)h^{\frac{1}{g}}\left((1+\delta)Q + \frac{B(g)}{g^2} \ln h \right)}{\left(1 + K(\delta)h^{\frac{1}{g}} \right)^2} \chi(\delta;g)d\delta dg}{\displaystyle\int_{\delta=-\lambda}^{\delta=\lambda} \int_{g_{min}}^{1} \frac{\frac{1}{g}K(\delta)h^{\frac{1}{g}}}{\left(1 + K(\delta)h^{\frac{1}{g}} \right)^2} \chi(\delta;g)d\delta dg} \tag{42}$$

where:

$$B(g) = RT(1-g) \tag{43}$$

5. DISCUSSION OF SIMULATED RESULTS

To study the behaviour of the heterogeneous version of the OTA equation, and the related enthalpy of adsorption formula we postulate arbitrarily the following distribution function:

$$\chi(\delta;g) = D\sum_{i=1}^{n} \frac{A_i^2}{1 + \left(\dfrac{\delta - \delta_i}{B_i}\right)^2 + \left(\dfrac{g - g_i}{C_i}\right)^2} \tag{44}$$

where D is the normalization factor.

Two cases are studied: one-peak ($n=1$) and two-peak ($n=2$) distribution functions (Figure 2). Obviously here the introduction of A_1 is (due to normalization) redundant and in this case $A_1 = 1$. Figure 3 shows the influence of the parameters (i.e. g_1, δ_1, B_1, and C_1) on contour plots of the one-peak function. The integrals were calculated applying the approximate method from:

$$\int_{\delta=-\lambda}^{\delta=\lambda} \int_{g_{min}}^{1} F(\delta;g)d\delta dg = \frac{1}{4}\sum_{i=2}^{N}\sum_{j=2}^{M}(\delta_i - \delta_{i-1})(g_j - g_{j-1})\left[F(\delta_{i-1};g_{j-1})\right.$$

$$\left. + F(\delta_{i-1};g_j) + F(\delta_i;g_{j-1}) + F(\delta_i;g_j)\right] \tag{45}$$
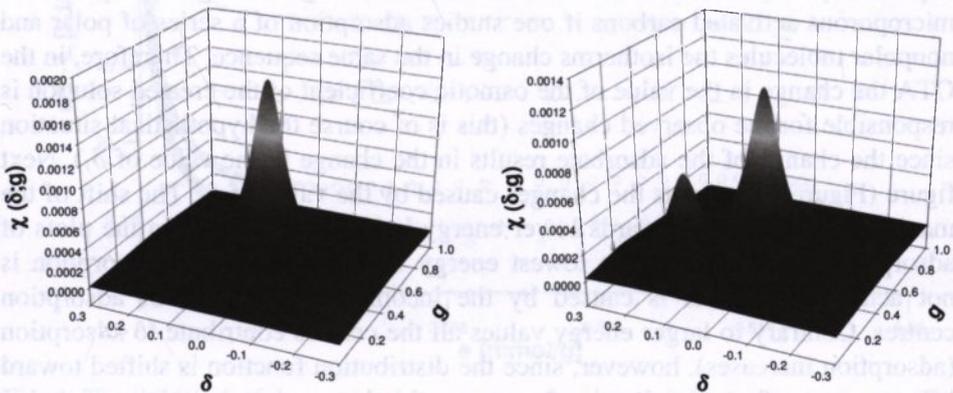
Fig. 2. One- and two-peak distribution functions applied during simulation, and generated from Eq. (33). The values of the parameters: $\lambda=0.3$, $A_1=1$, $B_1= 0.05$, $C_1= 0.05$, $\delta_1=0$, $g_1=0.5$ and $A_2=0.75$, $B_2= 0.05$, $C_2= 0.05$, $\delta_2=0.125$, $g_2=0.25$.
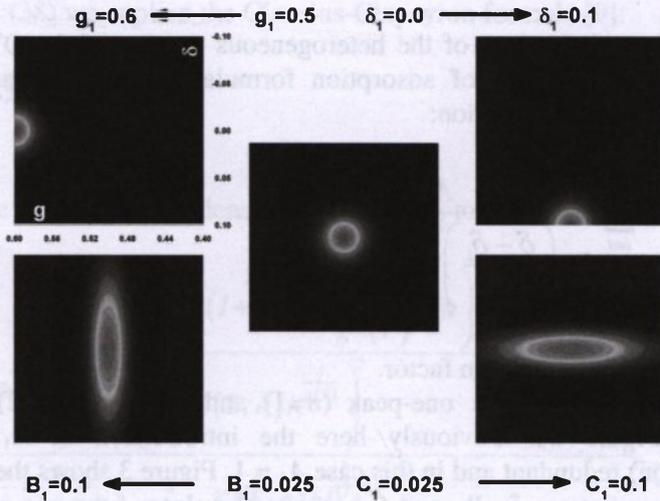
Fig. 3. Contour plots of the one-peak distribution function – the influence of g_1, δ_1, B_1, and C_1. The values of the starting parameters: $\lambda=0.1$, $A_1=1$, $B_1=0.025$, $C_1=0.025$, $\delta_1=0$, and $g_1=0.5$.

Figure 4 presents the results considering the influence of g_1 on adsorption isotherms and related enthalpy data for the one-peak distribution function. The rise in the value of the osmotic coefficient leads to the conversion of the adsorption isotherms from type IV up to I. Simultaneous rise in the adsorption enthalpy value is observed. This result shows the tendency often observed in experimental systems. It is well known that e.g. during adsorption on microporous activated carbons if one studies adsorption of a series of polar and nonpolar molecules the isotherms change in the same sequence. Therefore, in the OTA the change in the value of the osmotic coefficient of the created solution is responsible for the observed changes (this is of course the hypothetical situation since the change of the adsorbate results in the change in the value of δ_1). Next figure (Figure 5) presents the changes caused by the value of δ_1. The shift of the maximum of the peak towards lower energy leads to the change in the plots of adsorption isotherms. For the lowest energy value the maximum adsorption is not achieved and this is caused by the incomplete saturation of adsorption centres. Contrary to larger energy values all the centres contribute to adsorption (adsorption increases), however, since the distribution function is shifted toward larger energy (but simultaneously up to the lower g values) the enthalpy decreases.
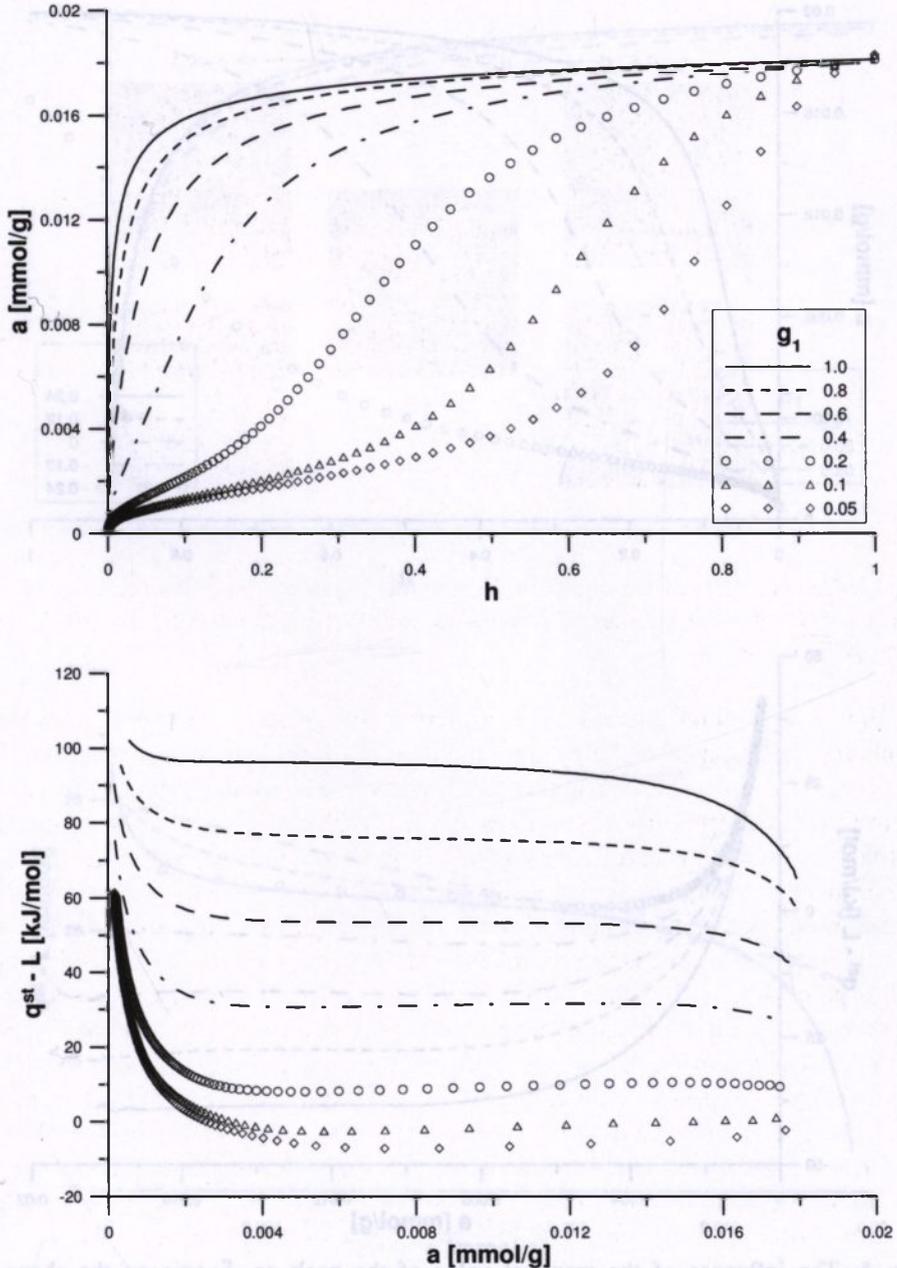
Fig. 4. The influence of the maximal g_1 value on the shape of adsorption isotherms (Eq. (27)) and related enthalpy (Eq. (30)) data. One-peak distribution function was assumed (Eq. (33) and Figure 3). The values of the parameters: a_m=0.02 mol/g, K_0=5 10^{-16}, Q=100 kJ/mol, λ=0.3, T=298 K, A_1=1, B_1=0.01, C_1=0.01, δ_1=0, and g_{min}=0.01.
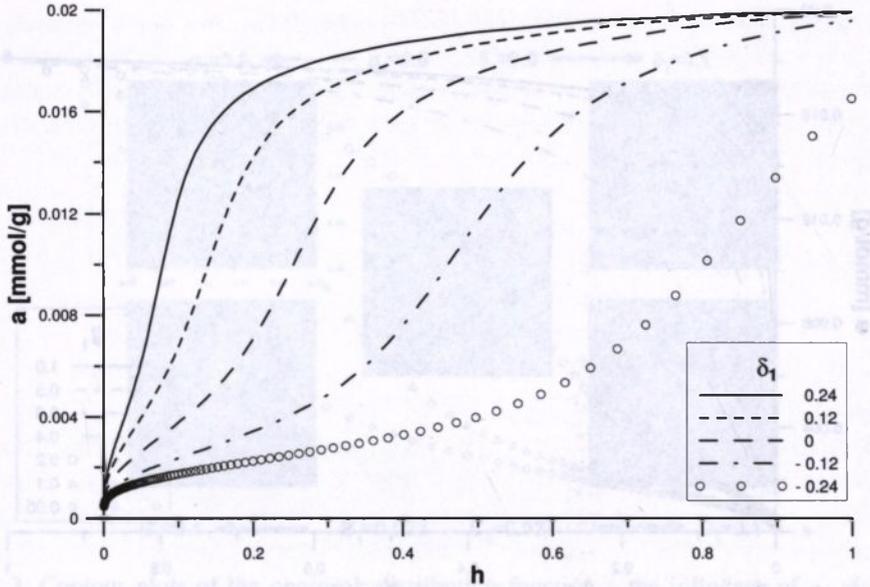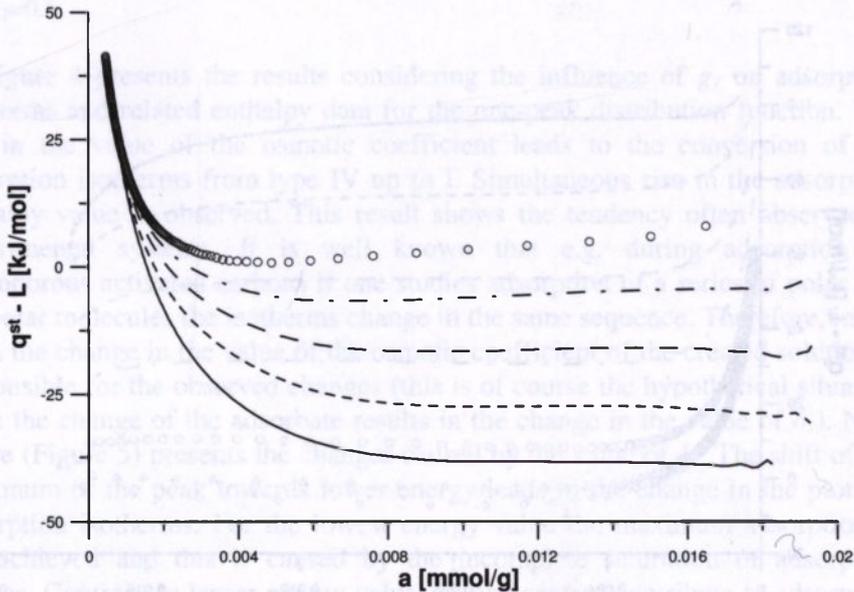
Fig. 5. The influence of the maximal value of the peak on δ_l axis on the shape of adsorption isotherms (Eq. (27)) and related enthalpy (Eq. (30)) data. One-peak distribution function was assumed (Eq. (33) and Figure 3). The values of the parameters: a_m=0.02 mol/g, K_0=5 10^{-16}, Q=100 kJ/mol, λ=0.3, T=298 K, A_l=1, B_l=0.01, C_l=0.01, g_l=0.1, and g_{min}=0.01.
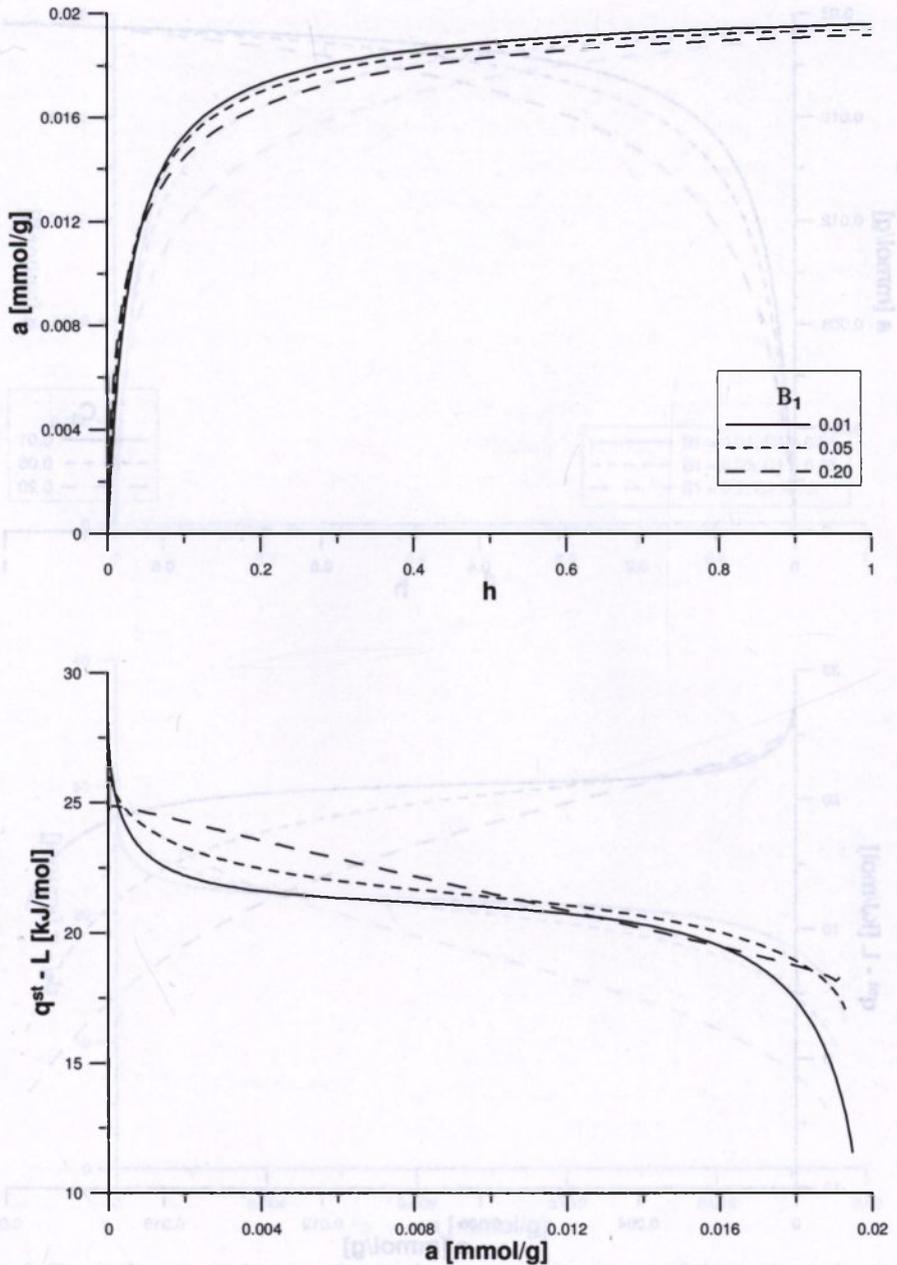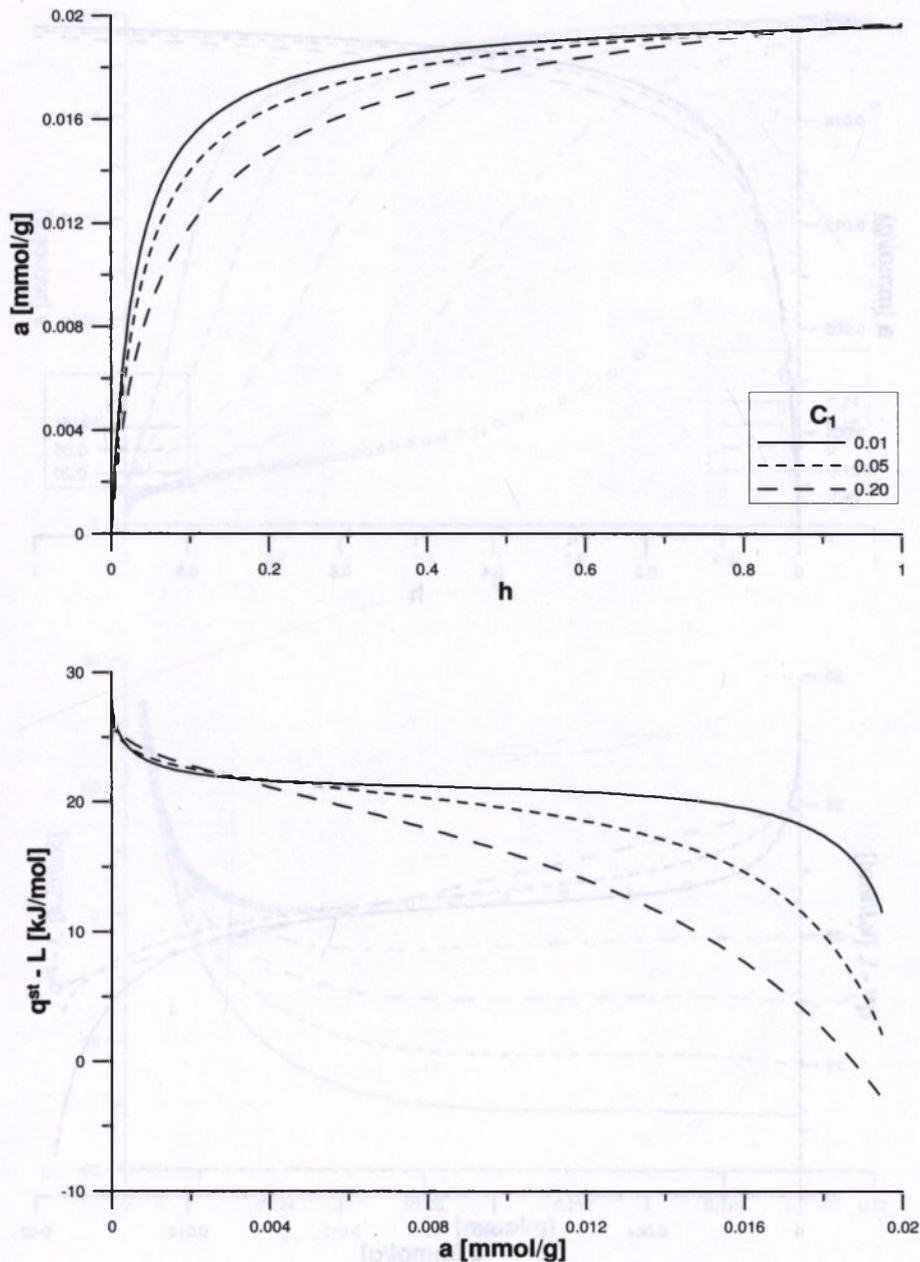
Fig. 6. The influence of the B_1 value on the shape of adsorption isotherms (Eq. (27)) and related enthalpy (Eq. (30)) data. One-peak distribution function was assumed (Eq. (33) and Figure 3). The values of the parameters: a_m=0.02 mol/g, K_0=5 10^{-4}, Q=30 kJ/mol, λ=0.3, T=298 K, C_1=0.01, δ_1=0, g_1=0.8, and g_{min}=0.01.

Fig. 7. The influence of the C_1 value on the shape of adsorption isotherms (Eq. (27)) and related enthalpy (Eq. (30)) data. One-peak distribution function was assumed (Eq. (33) and Figure 3). The values of the parameters: $a_m=0.02$ mol/g, $K_0=5 \ 10^{-4}$, $Q=30$ kJ/mol, $\lambda=0.3$, $T=298$ K, $A_1=1$, $B_1=0.01$, $\delta_1=0$, $g_1=0.8$, and $g_{min}=0.01$.
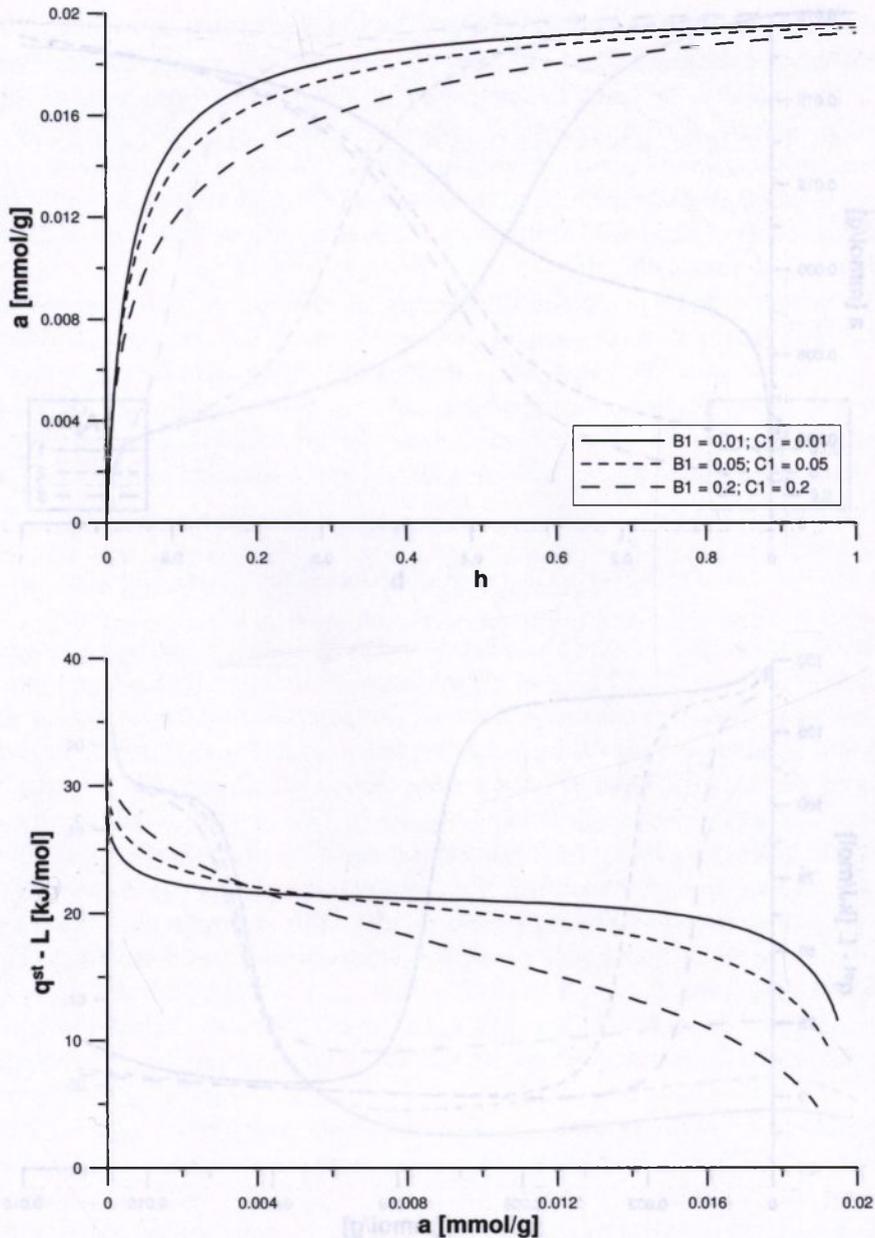
Fig. 8. The influence of the changing in the cross-sectional area of the peak on the shape of adsorption isotherms (Eq. (27)) and related enthalpy (Eq. (30)) data. One-peak distribution function was assumed (Eq. (33) and Figure 3). The values of the parameters: $a_m=0.02$ mol/g, $K_0=5 \ 10^{-4}$, $Q=30$ kJ/mol, $\lambda=0.3$, $T=298$ K, $A_1=1$, $\delta_1=0$, $g_1=0.8$, and $g_{min}=0.01$.
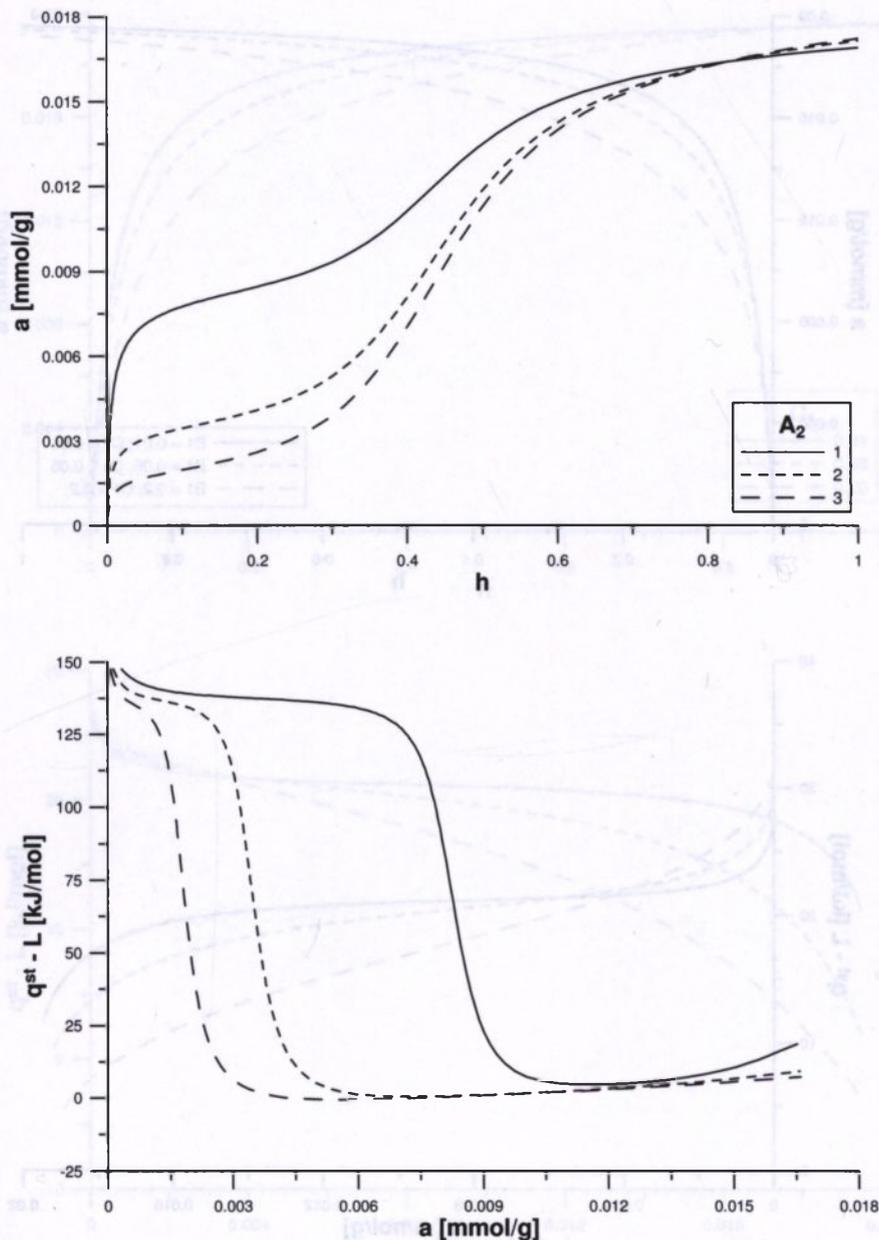
Fig. 9. The influence of the ratio of the heights of two peaks on the shape of adsorption isotherms (Eq. (27)) and related enthalpy (Eq. (30)) data. Two-peak distribution function was assumed (Eq. (33) and Figure 2). The values of the parameters: a_m=0.02 mol/g, K_0=5 10^{-29}, Q=150 kJ/mol, λ=0.3, T=298 K, A_1=1, B_1=0.01, C_1=0.005, δ_1=0.18, g_1=0.8, B_2=0.01, C_2=0.005, δ_2=0.21, g_2=0.1, and g_{min}=0.01.
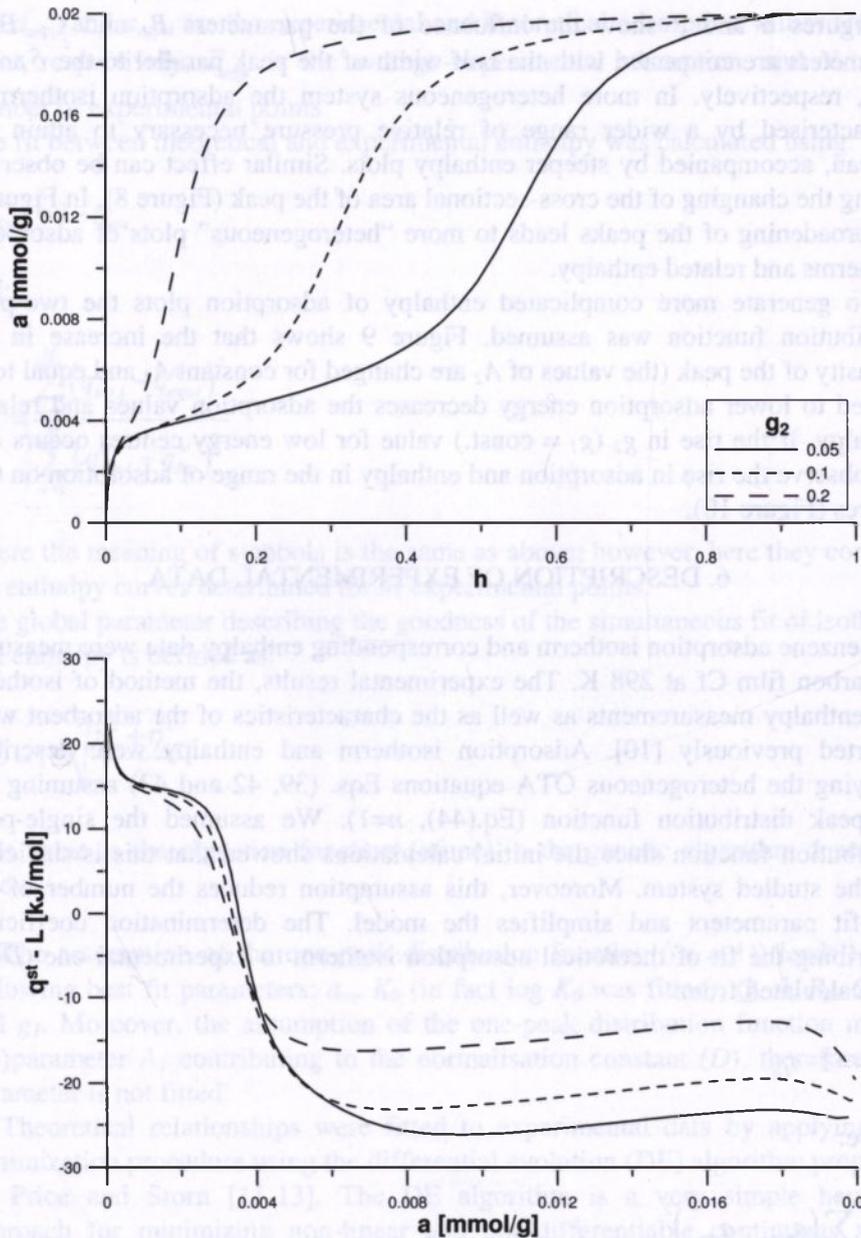
Fig. 10. The influence of the g value related to the second peak on the shape of adsorption isotherms (Eq. (27)) and related enthalpy (Eq. (30)) data. Two-peak distribution function was assumed (Eq. (33) and Figure 2). The values of the parameters: $a_m=0.02$ mol/g, $K_0=0.05$, $Q=30$ kJ/mol, $\lambda=0.3$, $T=298$ K, $A_1=1$, $B_1=0.01$, $C_1=0.005$, $\delta_1=0.21$, $g_1=0.8$, $B_2=0.01$, $C_2=0.005$, $\delta_2=0.21$, and $g_{min}=0.01$.

Figures 6 and 7 show the influence of the parameters B_1 and C_1. Both parameters are connected with the half-width of the peak parallel to the δ and g axes, respectively. In more heterogeneous system the adsorption isotherm is characterised by a wider range of relative pressure necessary to attain the plateau, accompanied by steeper enthalpy plots. Similar effect can be observed during the changing of the cross-sectional area of the peak (Figure 8). In Figure 8 the broadening of the peaks leads to more "heterogeneous" plots of adsorption isotherms and related enthalpy.

To generate more complicated enthalpy of adsorption plots the two-peak distribution function was assumed. Figure 9 shows that the increase in the intensity of the peak (the values of A_2 are changed for constant A_1 and equal to 1) related to lower adsorption energy decreases the adsorption values and related enthalpy. If the rise in g_2 (g_1 = const.) value for low energy centres occurs one can observe the rise in adsorption and enthalpy in the range of adsorption on this centres (Figure 10).

6. DESCRIPTION OF EXPERIMENTAL DATA

Benzene adsorption isotherm and corresponding enthalpy data were measured on carbon film Cf at 298 K. The experimental results, the method of isotherm and enthalpy measurements as well as the characteristics of the adsorbent were reported previously [10]. Adsorption isotherm and enthalpy were described applying the heterogeneous OTA equations Eqs. (39, 42 and 43) assuming the one-peak distribution function (Eq.(44), $n=1$). We assumed the single-peak distribution function since the initial calculations showed that this is sufficient for the studied system. Moreover, this assumption reduces the number of the best-fit parameters and simplifies the model. The determination coefficient describing the fit of theoretical adsorption isotherm to experimental one (DC_{iz}) was calculated from:

$$DC_{iz} = 1 - \eta_{iz} \tag{46}$$

where:

$$\eta_{iz} = \frac{\sum\limits_{i=1}^{N}\left(a_{teo,i} - a_{exp,i}\right)^2}{\sum\limits_{i=1}^{N}\left(a_{exp,i} - \bar{a}_{exp}\right)^2} \tag{47}$$

and $a_{exp,i}$ and $a_{exp,i}$ are the experimental and theoretical adsorption values for i-th point, respectively, $\overline{a}_{exp}$ is the average experimental adsorption, and N is the number of experimental points.

The fit between theoretical and experimental enthalpy was calculated using:

$$DC_{qst} = 1 - \eta_{qst} \tag{48}$$

and:

$$\eta_{qst} = \frac{\sum_{i=1}^{M} \left(q_{teo,i}^{st} - q_{exp,i}^{st} \right)^2}{\sum_{i=1}^{M} \left(q_{exp,i}^{st} - \overline{q}_{exp}^{st} \right)^2} \tag{49}$$

where the meaning of symbols is the same as above; however, here they concern the enthalpy curves determined for M experimental points.

The global parameter describing the goodness of the simultaneous fit of isotherm and enthalpy is defined as:

$$DC = 1 - \sqrt{\frac{\eta_{iz}^2 + \eta_{qst}^2}{2}} \tag{50}$$

This value is the objective function (ofunc) in the genetic algorithm described below.

The assumption of the one-peak distribution function $((n = 1))$ leads to the following best fit parameters: a_m, K_0 (in fact log K_0 was fitted), Q, λ, B_1, C_1, δ_1 and g_1. Moreover, the assumption of the one-peak distribution function makes the parameter A_1 contributing to the normalisation constant (D), therefore this parameter is not fitted.

Theoretical relationships were fitted to experimental data by applying the minimization procedure using the differential evolution (DE) algorithm proposed by Price and Storn [11-13]. The DE algorithm is a very simple heuristic approach for minimizing non-linear and non-differentiable continuous space functions. Moreover, it was successfully used [14-20] to verify different theoretical models. In other words, to optimize the objective function (ofunc: $(1-DC_i)$, where DC_i is the determination coefficient with DE the following settings for the input file are taken into account: 'DE/best/2/bin' method is chosen (this time, the new vector to be perturbed is the best performing vector of

the current generation); the number of parents (i.e. number of population members), NP is 10 times greater than the number of parameters of the objective function, N_D; weighting factor, F is equal to 0.8 and crossover probability constant CR=0.5; the value to reach, VTR is equal to $1 \cdot 10^{-25}$ (the procedure stops when ofunc < VTR, if either the maximum number of iterations (generations) "itermax" is reached, or the best parameter vector "bestmem" has found a value f(bestmem)≤VTR). The algorithm seems to work well only if [XV_{min}, XV_{max}] covers the region where the global minimum is expected. Therefore, we have taken into account the very wide ranges of XV. Moreover, the calculations were repeated at least five times in order to check the reproducibility.

7. RESULTS

Figure 11 shows the algorithm at work. For the assumed single-peak distribution function the algorithm reproduces the isotherm and related enthalpy very well. The parameters are practically the same as assumed after few thousands of iterations. In this figure we also show the changes in the value of DC calculated from Eq.(50). The fit of theoretical model to experimental data is shown in Figure 12 together with the distribution function obtained from the best fit parameters. The results of the fit are good. Obtained distribution function has maximum at the g value around 0.4. This suggests strong deviation of the system from ideality. The maximum value on the energy is shifted towards large values (the maximum of the peak is located behind the integration limit) suggesting relatively high energy of solid-fluid interactions.
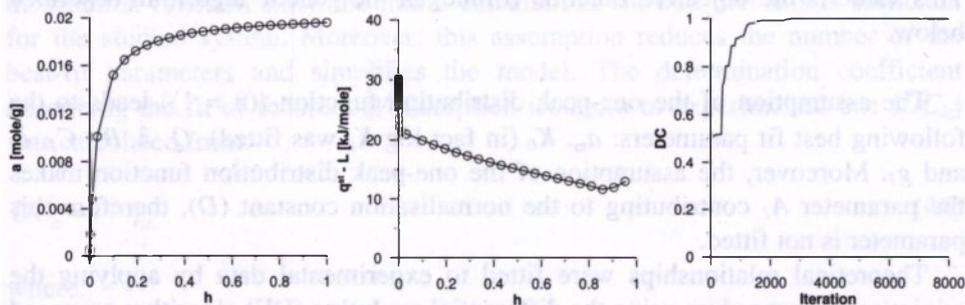

Fig. 11. The results showing reproducibility of the adsorption isotherm and related enthalpy by the genetic algorithm. Points – starting data, lines – recovered data. Third figure shows the changes in the value of the global DC (Eq.(50)) with the number of iterations. Starting parameters (Eqs.(39), (42) – (44), $n=1$): $a_m=0.02$ mol/g, $K_0=5 \ 10^{-4}$, $Q=30$ kJ/mol, $\lambda=0.3$, $B_l=0.01$, $C_l=0.01$, $\delta_l=0$, and $g_l = 0.8$ ($T=298$ K, $g_{min}=0.01$).
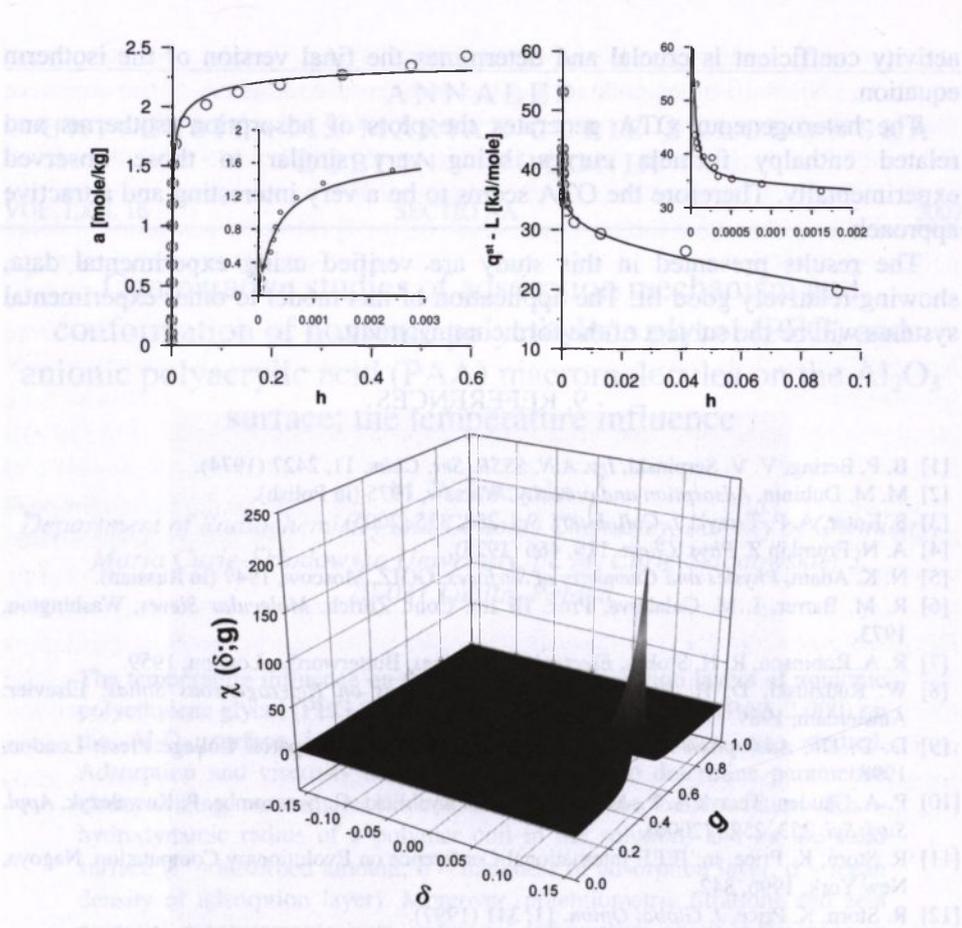
Fig. 12. Applicability of the heterogeneous OTA model for description of experimental data of benzene adsorption and enthalpy of adsorption measured on carbon film Cf at 298 K. Points – experimental data, lines – Eqs.(39), (42) – (44), $n=1$ ($DC_{iz}=0.9858$, $DC_{qst}=0.9243$). The best fit parameters: $a_m=2.333$ mol/kg, $K_0=1.904 \times 10^{-20}$, $Q=145.3$ kJ/mol, $\lambda=0.1612$, $B_l=1.556 \times 10^{-4}$, $C_l=1.006 \times 10^{-4}$, $\delta_l=0.1931$, and $g_l=0.3855$. Bottom figure shows the distribution function obtained from the fitting of the model to experimental data.

8. CONCLUSIONS

The proposed procedure of derivation of the Osmotic Theory of Adsorption related isotherms leads to adsorption equations that can be reduced to the most popular, sometimes empirical (e.g. Bradley) equations. Therefore, the assumption of the form of the relation between the osmotic coefficient and the

activity coefficient is crucial and determines the final version of the isotherm equation.

The heterogeneous OTA generates the plots of adsorption isotherms and related enthalpy formula curves being very similar to those observed experimentally. Therefore the OTA seems to be a very interesting and attractive approach.

The results presented in this study are verified using experimental data, showing relatively good fit. The application of this model to other experimental systems will be the subject of the forthcoming study.

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