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# Mathematical modelling of adsorptive-absorptive processes

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The paper presents results of theoretical studies of sorption processes in submicroporous and microporous elastic materials. The sorption is viewed as consisting of adsorption and absorption. Mathematical formulas describing the processes are derived in a unified way by using a thermodynamic approach. They handle, both absorption-like phenomena in submicropores and constrained multilayer adsorption in micropores. The latter is described by a new BET-type equation (LBET model). Applications of the resultant multiple sorption model (MSM) are discussed. The proposed models are useful tools for interpretation of empirical sorption isotherms in terms of structural and energetic parameters of sorbent-sorbate systems.

## polovab of boundary contracts 1. INTRODUCTION in the second decreases 9 he

A number of important sorbents (polymers in glassy state, crystalline polymers, natural coal), are porous materials exhibiting elastic properties [1]. A characteristic feature of their structure is a noticeable fraction of pores which are of molecular size (sub- and micropores) [2-6]. The sorption process in such materials consists in: penetration of sorbate molecules into elastic phase (absorption); adsorption of the molecules on a surface of large pores; location of sorbate in submicropores (intermediate absorptive-adsorptive processes).

The mathematical description of equilibrium properties of such absorptiveadsorptive systems was derived in ref.[7], in a thermodynamic way. The treatment follows the line of the theory of polymer solutions (Flory [8]), however far generalizations of this theory was necessary, to take into account different size of particles of the sorbent components (polymer chains and quasi crystalline domains).

A simplified approach to this problem is presented in refs.[7, 9], where only adsorption and absorption subprocesses are considered, with entropy modelling being stressed (a so-called dual-sorption model – DSM). A generalization of the polymer solution theory was carried-out, aimed at modelling the sorption equilibria in porous materials exhibiting elastic properties. Formal assumptions required for the theoretical analysis of the thermodynamics of sorbent-sorbate systems were collected, and general formulas for enthalpy and entropy changes in the sorption process (respecting peculiarities of the sorbent structure) are presented. This model was found to be adequate for sorption of small molecules like water and methanol [10]. However, its examination showed that absorption capacity is significantly lower than might be expected from chemical and structural properties of hard coals [10, 11, 12].

To give a formal explanation of such effects and obtain a model satisfactory for larger sorbate molecules, we elaborated an extended mathematical description of sorption equilibrium in submicroporous elastic materials (like glass and crystalline polymers, hard coal), including absorption and a spectrum of adsorption-like subprocesses. It is referred to as the multiple sorption model - MSM. Basic assumptions, formulas and properties of MSM (related to those of DSM) were discussed in refs.[13, 14]. A hypothetical elastic sorbent being a cross-linked chain polymer with randomly distributed sphere-like holes (submicropores) was considered. Effects of submicropore size distribution on the equilibrium sorption capacity were analyzed in details from the energetic side. A distribution function of the hole radius was assumed, and sorption subsystems were defined, each containing holes which require the same energy for the sorption. The model completed with the full entropy terms, respecting the sorbent structure heterogeneity (like in DSM), was presented in refs.[15, 16].

In order to make the approach applicable to gaseous sorptives we elaborated a new state equation enabling us to evaluate thermodynamic parameters of sorbates in sorption systems at near and over-critical temperatures [16, 17]. Further development of the model was directed to improvements of the modelling of the adsorption process with respect to constrained multilayer adsorption [16, 18, 19]. In refs.[16, 18] we showed that MSM can be relatively easy completed with a BET-like formula describing the adsorption process in porous materials with dominant fraction of small micropores (LBET model). The full version of MSM was used in the paper [19] to examine sorption properties of hard coals with methane and carbon dioxide. Heterogeneity of coal structure and multilayer adsorption were taken into account. Applicability of the model to pure adsorption process was also shown (adsorption of  $CH_4$  and  $CO_2$  on activated carbons). The paper [20] develops the theory with certain non-BET effects being taken into account, thus enlarging the model applicability up to the highest pressure range. Possible ways for handling the microporous surface heterogeneity are outlined in refs.[16, 21].

The main idea of our approach to the sorption modelling is to find links between measurable sorption data and physical properties of the sorbent and sorbate viewed separately. These properties, represented by appropriate parameters of DSM and MSM, are assumed to be the same in any sorption system. It enables us to get more information on sorption mechanisms and sorbent structure, by examination of sorption properties of a particular sorbent with different probing sorbates.

This paper presents the multiple sorption model in its recent form, including certain newest concepts. Possible applications of the theory and exemplary results are shown.

### 2. MULTIPLE SORPTION MODEL – THEORETICAL BASIS

Let us consider an equilibrium state of the sorption system corresponding to a pressure P and temperature T. It may be viewed as an effect of the two stage procedure (see Figure 1):

- a) removing of sorptive molecules from their volatile state  $(P, T, V_{\nu})$  into a liquid-like reference state  $(P_s, T, V_s)$ , with appropriate pressure  $P_s$  and molar volume  $V_s$  equal to that occupied by the sorbate molecules in the sorption system
- b) isobaric, isochoric and isothermal mixing of the molecules with the pure adsorbent components

Thus, the mathematical description of the sorption may be derived by considering free energy changes at the above stages. In particular, the polymer solution theory [8] may be applied to describe the mixing stage.

In elastic-porous material the mixing process is significantly dependent on amount of micropores and submicropores [2, 3, 5, 7, 12-14]. In the theoretical treatment such pores may be viewed as irregular holes of molecular and submolecular size, randomly distributed within the elastic phase [13, 14]. Meso- and macropores affect sorption properties to a much smaller extent [2, 3] as their surface area is practically negligible while compared to that of submicro- and micropores. In such materials the sorption process may proceed by penetration of sorbate molecules among elastic chains (pure absorption), and by placing of molecules in holes (pores) properly enlarged to the molecule size. In the latter case we may distinguish larger holes (micropores), which may hold one or more sorbate molecules with no changes in size. The corresponding process will be referred to as pure adsorption, while that in smaller holes (submicropores) is of an adsorptive-absorptive nature. Differences in original hole size (and in corresponding expansion ratios) imply energetic heterogeneity of the absorption-like processes. In turn, the adsorption heterogeneity is due to diversity of geometric and chemical properties of particular sites placed on the surface of micropores.



#### Fig.1. Virtual creation of the sorption system

Let us consider the sorption system as consisting of a number of subsystems a, each containing  $m_{pa}$  moles of sorbate molecules with the same molar energy  $Q_a$  and the molar volume  $V_s$  [14]. In the equilibrium state of such a system the following general formula is valid [7, 8]:

$$\mathbf{R}T \cdot ln\left(\frac{f(P,T)}{f(P_s,T)}\right) \cdot \sum_{a} m_{pa} = \Delta H - T\Delta S \tag{1}$$

where  $\Delta H$  and  $\Delta S$  denote total enthalpy and entropy change due to the mixing; R – gas constant, f(P, T) – sorbate fugacity. In case of vaporous sorptives  $(T << T_c; T_c - \text{critical temperature of the sorptive})$  one takes  $f(P,T) \cong P$ ,  $f(P_s,T) \cong P_0$ ,  $U_c = U_E$  and  $V_s \cong V_m$  ( $V_m$ ,  $P_0$ ,  $U_E$  – molar volume of sorbate in liquid state, its saturated vapor pressure and evaporation energy, respectively, at temperature T). For sorption at near and above critical temperatures (e.g. methane and carbon dioxide in room temperature) the quantities  $P_s(V_s)$ , f(P,T)and cohesion energy  $U_c(V_s)$  are proposed to be determined by using the fluid state equation derived in the paper [17], with  $V_s$  treated as a fitting parameter of the model.

The enthalpy change  $\Delta H$  may by expressed in the following concise form

$$\Delta H = \sum m_{pa} \cdot Q_a + \delta H_0 \tag{2}$$

where  $Q_a$  denotes the main component of the molar sorption energy contributed to the system by *a*-th subprocess, and  $\delta H_0$  is a component of relatively small magnitude representing effects of sorbate-sorbate interactions and of sorbent surface expansion (see ref.[14]).

In our approach the energy  $Q_a$  is viewed as the effect of combination of cohesion energies of the sorbent and sorbate according to the Berthelot rule. It may be expressed as [7, 13, 14]:

$$Q_{a} = V_{s} \{ \varphi_{c}^{o} [ \omega_{a} \delta_{c}^{2} - \zeta_{a} \cdot 2\delta_{c} \delta_{p} ] + \delta_{p}^{2} \}, \qquad \delta_{p} = \sqrt{U_{p} / V_{s}}$$
(3)

 $\phi_c^0$  – fraction of surface of sorbent molecules in total surface of dry sorbent and pores;

 $\delta_c$ ,  $\delta_p$  – solubility parameter of sorbent and of sorbate, respectively;

 $U_p$  – molar cohesion energy of pure sorbate with the molar volume  $V_s$ ;

 $\omega_a$  – surface expansion ratio of holes attributed to a-th subsystem

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$$\omega_a = 1 - \left(\frac{R_{ha}}{R_p}\right) \quad \text{for } R_{ha} < R_p; \quad \omega_a = 0 \quad \text{for } R_{ha} \ge R_p \tag{4}$$

 $R_{ha}, R_p$  – the radius of a-th type hole and of sorbate molecule, respectively  $\zeta_a$  – a factor correcting the adhesion energy due to non perfect sorbent--sorbate contacts (geometric factor) and effects of specific interactions (chemical factor):

$$\zeta_{a} = \zeta \left( R_{ha} / R_{p} \right) = \begin{cases}
1 & \text{for } R_{ha} = 0 \text{ (pure absorption)} \\
Z_{B} \cdot R_{ha} / R_{B} & \text{for } 0 < R_{p} < R_{B} \\
Z_{B} + \left( Z_{A} \cdot C_{p} - Z_{B} \right) \frac{R_{ha} - R_{B}}{R_{p} - R_{B}} & \text{for } R_{B} < R_{ha} < R_{p} \\
Z_{A} \cdot C_{p} = \zeta_{A} & \text{for } R_{ha} \ge \text{(pure adsorption)}
\end{cases}$$
(5)

where: Z<sub>B</sub> is an empirical parameter determining a fraction of effective sorbent sorbate contact area (like that occuring among molecules absorbed in polymers) for the given hole radius R<sub>B</sub>:

 $Z_A$  – value of  $\zeta_a$  averaged over holes larger than sorbate molecule;  $C_p$  – polarity factor expressing effects of specific interactions of polar sorbates with active groups on the surface.

For nonpolar sorbates  $C_p=1$ , so as  $\zeta_a$  is equal to the fraction of the hole wall surface viewed as being in full contact with the sorbate molecule (like in polymer solutions), while the remaining part of the surface is treated as being in contact with vacuum.

For the pure adsorption (pointed to with the subscript A)  $(R_{hA} \ge R_p)$  we have  $\omega_{A}=0$ ; and

$$Q_{A} = \left(\delta_{p}^{2} - Z_{A} \cdot C_{p} \cdot 2\delta_{c}\delta_{p}\varphi_{c}^{o}\right) \cdot \mathbf{V}_{s}$$

$$\tag{6}$$

As it can be seen, the adsorption is mostly probable on local niches and cavities where  $Z_A$  is appropriately large, and – in case of polar sorbates – on active groups, where  $C_p$  is high. According to (6) the surface magnitude affects the adsorption capacity in two opposite directions. The larger surface, the greater number of adsorption sites, but they become less attractive due to decrease in  $\varphi_c^0$ .

In turn, energetic interactions in pure absorption may be characterized by the Flory-Huggins parameter  $\chi_{pc}$ , calculated by using the equation (1) with  $\zeta_a=1$ ,  $\omega_{a}=1$  and  $\varphi_{c}^{0}=1$  (as for polymers [8]):

$$\chi_{pc} = \frac{V_s}{RT} \cdot \left(\delta_c^2 - 2\delta_c \delta_p + \delta_p^2\right) = \frac{V_s}{RT} \cdot \left(\delta_c - \delta_p\right)^2$$
(7)

It should be emphasized that sorption energy in the above model is expressed by cohesion energies of sorbate  $(U_p \text{ or } \delta_p)$  and of sorbent  $(\delta_c)$  – see the formula (3) for  $Q_a$  – those are treated as being independent on the particular sorption system ( $\delta_c$  can be taken from the van Krevelen formulas [1]). Moreover, in case of gaseous sorbates,  $U_p$  and  $V_s$  are strictly intercorrelated by the pure sorbate state equation (ref.[17]). For the pure adsorption and absorptive-adsorptive subprocesses the parameter  $Q_a$  is corrected by the fitting parameters  $Z_A$ ,  $R_B$ ,  $Z_B$  (with respect to constraints:  $Z_A < 1$ ,  $Z_B < 1$ ), but for the pure absorption  $\zeta_a = 1$  is assumed (see Eq.5), so the absorption capacity is closely

correlated with that of remaining subprocesses. This specific feature of the model tightens considerably an area of acceptable values for its parameters, which allows us to draw more reliable conclusions on sorption mechanisms in submicroporous materials [19].

In classical adsorption models  $Q_A$  is often treated as an empirical parameter characterizing the sorption system. The Eq.(3) shows that this quantity is very sensitive to changes in the surface properties (represented by  $\varphi_c^\circ$  and  $Z_A$ ), hence  $Q_A$  is not appropriate to characterize the system, if prediction of sorption properties is required. The proposed model seems to be more appropriate for such purposes.

The entropy term  $\Delta S$  may be derived with a modified Flory method [7, 8, 10, 15, 16], based on a lattice model of the mixture containing empty holes. Finally, the formula for the sorption isotherm in *a*-th subsystem attributed to the holes of  $R_{ha}$  size may be derived by differentiation (with respect to  $m_{pa}$ ) of the formula (1) including equations for  $\Delta H$  and  $\Delta S$ .

In this paper the recent version of MSM is presented, respecting the heterogeneous structure of the sorbent. In particular, effects of quasi-crystalline domains on both  $\Delta S$  and  $\Delta H$  are taken into account as depending on their volume and surface fraction in the system.

The isotherm equation has the form:

$$\ln \Pi = w_{a} \cdot \left\{ \ln v_{pa} - \left[ 1 - \frac{1}{x_{d}} \right] \frac{1}{\beta_{dd}} \cdot \ln(1 - v_{d} \cdot \beta_{dd}) - \frac{z}{2} \cdot \ln \left[ 1 - \frac{2}{z} \cdot \frac{v_{e1} + v_{e2} \left( 1 - \frac{1}{x_{e2}} \right)}{1 - v_{d} + v_{d} \cdot a_{d}} \right] + \frac{1}{x_{e1}} \cdot u_{e1} \cdot \left[ \left( 1 - \sum_{b} v_{pb} \cdot w_{b} \right)^{\frac{1}{3}} - L_{e1} \left( 1 - \sum_{b} v_{pb} \cdot w_{b} \right) \right] \right\} + \left( 1 - w_{a} \right) \cdot \ln \frac{v_{pa}}{(v_{ha} - v_{pa}) \cdot (1 - w_{a})} + \frac{Q_{a}}{RT} - \omega_{a} \left( 1 - \sum_{b} \varphi_{pb} \cdot \omega_{b} \right) \cdot \varphi_{h} \cdot \varphi_{e}^{0} \cdot \frac{\delta_{c}^{2} \cdot V_{s}}{RT} + \frac{\Sigma}{p_{b}} \varphi_{pb} \left[ E_{ab} + E_{ba} - \omega_{a} \sum_{b} \varphi_{pb} \cdot E_{bb} \right] \frac{1}{RT} + \frac{\partial}{\partial} \frac{\delta}{R_{pa}} \left\{ (1 - \delta \varphi_{h}) \cdot \left[ \varphi_{e} \varphi_{e}^{0} \delta_{c}^{2} \cdot V_{s} + \sum_{b} \varphi_{pb} (Q_{b} - U_{p}) \right] + \varphi_{n} \cdot \varphi_{e}^{0} \cdot \delta_{c}^{2} \cdot V_{s} \sum_{b} \varphi_{pb} \cdot \omega_{b} + \sum_{b} \sum_{b} \varphi_{pb} \cdot \varphi_{pb} \cdot E_{bb} \right\} \frac{1}{RT} + \frac{\partial}{\partial} \varphi_{pb} \left\{ \omega_{a} \left[ \varphi_{e} \cdot \varphi_{e}^{0} \cdot \delta_{c}^{2} \cdot V_{s} - \sum_{b} \varphi_{pb} (Q_{b} - U_{p}) \right] + Q_{a} - U_{p} \right\} \frac{1}{PT}$$

$$(8)$$

where indices *a*, *b* point to different subsystems, and  $\Pi = f/f_s \cong P/P_0$  denotes the relative fugacity of the sorbate (relative pressure for vapours),

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 $v_{pa}$ ,  $v_{pb}$  – volume fraction of sorbate molecules sorbed in a-th, b-th subsystem, respectively

 $v_{ha}$  – volume fraction of original size holes attributed to a-th subsystem;  $v_d$ ,  $v_{el}$ ,  $v_{e2}$  – volume fraction of quasi-crystalline domains, crosslinked chains and noncrosslinked chains, respectively, in sorption system;  $w_a w_b$  – volume expansion ratio of holes attributed to a-th, b-th subsystem:

$$w_a = 1 - \left(\frac{R_{ha}}{R_p}\right) \quad for \ R_{ha} < R_p; \quad w_a = 0 \quad for \ R_{ha} \ge R_p$$

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 $u_{el}$  – volume fraction of crosslinked chains in sorbent;  $x_d$ ,  $x_{el}$ ,  $x_{e2}$ -, average size of quasi-crystalline domains, crosslinked chains and non-crosslinked chains, respectively, related to volume of sorbate molecule;  $\beta_{dd}$  – geometrical parameter representing an effect of shape of paired {d,d} quasi-crystalline domains on the configurational entropy, calculated as:

$$\beta_{dd} = \frac{z_{wd}}{z} \left( 3 - \frac{2}{x_d} \right) - \frac{1}{z}$$
(9)

where  $z_{wd}$  characterizes a compactness of quasi-crystalline domains  $(z_{wd} \in [1, z/2])$  – see Eq.(18) given in paper [10]; z – lattice coordination number;  $a_d$  – "specific surface area" of quasi-crystalline domains related to that of sorbate molecule;

$$\mathbf{a}_{d} = 1 - \frac{2}{z} \cdot z_{wd} \cdot \left(1 - \frac{1}{x_{d}}\right) \tag{10}$$

 $L_{el}$  – number of typical crosslinkages per crosslinked chain;  $Q_a$ ,  $Q_a$  – the main energetic parameter defined in Eq.(3) for subsystems *a* and *b*,  $\varphi_{pb}$ ,  $\varphi_{pB}$  – surface fraction of sorbate molecules placed in b-th, B-th, subsystem of holes, respectively;  $\varphi_h$ ,  $\varphi_e$  – surface fraction of holes, elastic chains, respectively, in the sorption system;  $\varphi_e^0$  – surface fraction of elastic chains in dry sorbent;  $\varphi_d^0$  – surface fraction of quasi-crystalline domains in dry sorbent;  $\omega_a$ ,  $\omega_b$  – surface expansion ratio of holes of a-th, b-th subsystem (see Eq.1);  $E_{ab}$ ,  $E_{ba}$ ,  $E_{Bb}$  – energetic constant defined for each pair of molecules {a,b}, {b,a}, {B,b} by equation (15) in ref. [7];

$$\mathbf{E}_{ab} = \boldsymbol{\omega}_{a} \cdot \boldsymbol{Q}_{b} + \left[ \boldsymbol{\xi}_{a} \cdot \boldsymbol{\xi}_{b} \cdot \left( 1 - \boldsymbol{\varphi}_{d}^{0} \right)^{2} \cdot \left( 1 - \frac{\left( \boldsymbol{R}_{ha} \cdot \boldsymbol{R}_{hb} \right)^{2}}{\boldsymbol{R}_{p}^{4}} \right) - \boldsymbol{\omega}_{a} \right] \cdot \boldsymbol{U}_{p}$$
(11)

 $\xi_a$ ,  $\xi_b$  are expressed by equation (2) with  $C_p=1$ ;  $A_h$  – total surface area of pores related to that of the sorbate molecule (in moles);  $\delta \varphi_h$  – changes in free surface area of coal due to swelling of coal matter, computed like for isotropic expansion of spheres, i.e.:

$$\delta A_h = \frac{2}{3} [A_h - \sum_b (1 - \omega_b) \cdot m_{pb} \cdot \xi_b] \cdot \sum_b \frac{v_{pb} \cdot \omega_b}{v_c}$$
(12)

and the derivative of  $\delta A_h$  in Eq.6 is:

$$\frac{\partial \delta A_{h}}{\partial m_{pa}} = \frac{2}{3} \cdot \frac{W_{a}}{\varphi_{c}} \left[ \varphi_{h} - \sum_{b} (1 - \omega_{b}) \varphi_{pb} \xi_{b} \right] - \frac{2}{3} (1 - \omega_{a}) \xi_{a} \sum_{b} \frac{V_{pb} W_{b}}{V_{c}}$$
(13)

 $m_p$  – total sorption capacity;  $m_{pa}$  – amount of sorbate in the a-th subsystem of a sorption system (in moles);  $v_c$  – volume fraction of coal molecules in the sorption system.

In order to evaluate the surface and volume fractions ( $\varphi$  and v) of the system components, the model has to be completed with a quantitative description of the pore structure. The submicropores can be treated as sphere-like holes of left-truncated normal size distribution with the mean value  $R_{hav}$ , minimal radius  $R_{hmin}$  and dispersion  $\sigma_{Rh}$  [13]. Thus, if the total volume of the submicropores  $V_{hsub}$  is known, their specific surface area  $a_h$  may be evaluated. It was stated in our earlier research that  $a_h$  is usually larger then that of water molecule (refs [6, 7, 9-12]). The micropores are of more irregular shape, therefore there is no simple and reliable relation between their volume and surface area. However, the following assumptions seem to be acceptable:

- a) placing of a sorbate molecule at a site on a micropore surface disables a part of the micropore space for further independent first layer adsorption, and the volume excluded in this way depends on the sorbate molecule volume (micropore volume filling, rather than surface coverage);
- b) the surface of micropores may be roughly calculated by treating the first layer adsorption space (described above) as consisting of randomly placed spheres of the same radius, referred to as the micropore radius  $R_{hm}$ ;
- c) next molecules can be adsorbed in a direct neighbourhood of the site occupied by a molecule, provided that there is a space large enough, and the consecutive molecules are in direct contact with previously adsorbed ones (it may be treated as a multilayer adsorption of BET type).

The assumption (a) is valid if a typical micropore wall distance is of range of double diameter of small molecule sorbates (ca  $12 \cdot 10^{-10}$  m) that is fulfilled for hard coals (refs [1-3]). It allows us to assume that the volume of the first layer adsorption space  $V_{hm}$  is a property of the microporous structure, which does not depend on the sorbate molecule size (like  $V_{hsub}$  for submicropores). Therefore, by virtue of the assumption (b), the surface of submicropores may be roughly evaluated, if  $V_{hm}$  and  $R_{hm}$  are given. In case of hard coals the radius of micropores  $R_{hm}$  is of less importance, as the main contribution to the coal surface is due to submicropores (refs [1-3]). However, for microporous sorbents this parameter may be of consideration. On the basis of our computations made

for an active carbon the value  $R_{hm}$ =8.5·10<sup>-10</sup> m (ca five times larger then water molecule radius) was found as appropriate [19].

The equation (8) describes also the pure adsorption (a=A;  $\omega_A=0$ ;  $w_A=0$ ), but under assumption that only Langmuir type monolayer adsorption occurs. To handle possible multilayer adsorption in microporous sorbents – see assumption (c) – we assumed ([16, 18]) that there is a spectrum of adsorption sites in micropores, each being capable to contain the number of 1, 2, ... k, ...  $\infty$  sorbate layers. Hence, creation of stack-like clusters (as in BET theory) is possible, but only for the limited number of k layers. In the paper [20] this concept was developed by admitting more compact clusters, in which the *n*-th layer of the clusters started from k-th type sites (containing  $m_{pkn}$  molecules) provides  $m_{pkn} \cdot \beta_{kn}$ sites for the next layer ( $\beta_{kn} \ge 1$ ). In effect, we derived the following general equation describing the local adsorption equilibrium for the k-th type sites (constrained nonBET adsorption):

$$-\Pi \cdot \beta_{kn} \cdot m_{pkn-1} + (\Pi + B_{kn}^*) \cdot m_{pkn} - \frac{B_{kn}^*}{\beta_{kn+1}} \cdot m_{pkn+1} = 0 ; (14)$$

where: n=1,...k;  $m_{pk0} \equiv m_{hk}$  ( $m_{hk}$  stands for the number of k-th type sites);  $m_{pkk+1} \equiv 0$ , and

$$B_{kn}^{*} = B_{kn} \cdot \left( 1 - \frac{1}{\beta_{kn+1}} \cdot \frac{m_{pkn+1}}{m_{pkn}} \right)^{\beta_{kn+1}-1}; \quad B_{kn} = \exp(Q_{kn}^{*} / RT)$$
(15)

In the model (14, 15) proper representation of changes in configurational entropy is stressed [20], although side energetic interactions may be also taken ino account in the quantity  $Q_{kn}^*$ . The set of eq.(14) has to be solved numerically (eg. by direct iterations) for specified sites (k).

This approach seems to be useful for examination of adsorbents of regular porous structures (like zeolites), for which parameters  $m_{hk}$ ,  $\beta_{kn}$  and  $Q^*_{kn}$  can be specified. Thus, it offers an alternative way (not exploited yet) to the concepts presented in refs [22-24] for analysis of such adsorption systems.

What concerns sorbents of irregular porous structures (like glassy polymers or hard coals), which are of our main interest, the model (14, 15) is not effective because of large number of parameters involved in, faced with highly uncertain parametrization of the sobent. Hence, in refs. [16, 18, 20] we assumed that the number of sites for consecutive k- layers adsorption may be roughly expressed by the following exponential function:

$$m_{hk} = m_{hA} \cdot (1 - \alpha) \cdot \alpha^{k-1} \tag{16}$$

where  $\alpha$  is an empirical parameter,  $m_{hA}$  - the number of sites for the first layer adsorption.

The above assumptions and certain simplifications (see refs [18, 20] bring the model (14, 15) to the following concise formula, referred to as LgBET equation (see ref.[20]):

$$\frac{m_{pA}}{m_{hA}} = \frac{(1-\alpha)\cdot\Pi^*}{B_L^* + \Pi^*} + \frac{\Pi^*\cdot\alpha\cdot\left[1+\Pi^*\cdot\beta\cdot(1-\alpha)\cdot\right]}{\left[B_L^* + \Pi^*\cdot\left(1-B_L^*\right)\right]\cdot\left(1-\alpha\cdot\beta\cdot\Pi^*\right)}$$
(17)

where:  $\beta = \beta_{kn} = \text{const for } n=1, ...k; \ k=1,... \infty; \ B_L^* = B_A/B_C; \ B_A = B_{kl} = \text{const}, B_C = B_{kn} = \text{const for } n>1 \text{ (see eq.(15) with } Q_{kl}^* = Q_A \text{ and } Q_{kn}^* = Q_C = \text{const for } n>1, \text{ respectively), and:}$ 

$$\Pi^* = \Pi / B_C; \ \Pi^{**} = \Pi^* \cdot \left( 1 - \Pi^{**} \right)^{1 - \beta}$$
(18)

Nevertheless, we stated that the eq.(14) with  $\beta \equiv 1$  is good enough to describe the constrained nonBET adsorption over relative pressures ranging to ca.0.85, and it is well applicable to typical adsorption systems with wide range of adsorption energies. In this pressure range effects of  $\alpha$  and  $B_C$  on  $m_{pA}$  are hardly separable (isotherm is affected rather by  $\alpha/B_C$ ). Hence, to complete MSM for sorption systems, we recommend application of the formula derived before in [16, 18], (referred to as LBET model), assuming that  $\beta \equiv 1$  and  $B_C \equiv 1$  (notice that  $B_C = 1$  is commonly accepted in BET theory – see ref.[25]). The model LBET has the form:

$$m_{pa} = m_{hA} \left[ \frac{(1-\alpha) \cdot \Pi}{B_A + \Pi} + \alpha \cdot \left( \frac{1+\Pi - \alpha \cdot \Pi}{1-\alpha \cdot \Pi} \right) \cdot \frac{\Pi}{B_A (1-\Pi) + \Pi} \right]$$
(19)

 $B_{\star} = \exp(Q_{\star}^{\star} / RT) \tag{20}$ 

where  $Q_A^*/RT$  is the sum of the all energetic terms in equation (8) applied to the A-th subsystem  $(Q_A^* \cong Q_A)$ .

In spite of serious simplifications involved in the above formula, it seems to be advantageous, when compared to other constrained BET formulas (see e.g.[26]), as it represents clearly and relatively well effects of geometrical and energetic constraints on adsorption capacity. In turn, the model LgBET (eqs.1 7, 19) may be useful to explain singular properties of some adsorption systems. A convincing example is shown in Figure 2 [20], where LgBET and LBET formulas were applied to adsorption data measured and discussed by Choma & Jaroniec [27].

The same approach may be used to describe local adsorption isotherms on heterogeneous surfaces. In order to derive a heterogeneous adsorption formula based on LBET equation one may consider the parameter  $Z_A$  in eq.(6) as uniformly distributed over the first layer adsorption sites. In the ref.[16] such a model was derived assuming that the distribution is the same for all sites (hLBET formula). It can be also done with a class of different distributions.

Let us take that the distribution function ranges from  $Z_A$  (the same for all sites) to  $Z_{Ak}$ , which is correlated with the number k of layers possible to be kept on the site:

$$Z_{A1} = Z_A; \quad Z_{Ak} = Z_A \cdot \left(\frac{C}{k} + (1 - C)\right)$$
 (21)

 $C \in (0,1)$  is a constant factor specifying the width of the energy spectrum.



Fig. 2. Sorption of  $N_2$  on synthetic carbon Ambersorb 563 (circles – Choma & Jaroniec [27]) and isotherms obtained with LgBET (eq.17) and LBET equations [19], compared to BET and Langmuir (L) isotherms fitted to the initial adsorption data

In effect, a specific distribution of the surface energy is obtained, depending on the site capacity distribution  $m_{hk}(k)$ . Such a representation of the surface heterogeneity makes possible to integrate analytically the local LBET adsorption isotherms over the set of sites, provided that an approximation to the eq.(19) for local isotherms is taken. Possible approximating formulas are discussed in ref.[21]. Finally, the adsorption isotherm  $m_{pa}/m_{hA}$  is expressed in the following form:

$$\frac{m_{pa}}{m_{hA}} = \frac{(1-\alpha)\cdot\Pi}{B_A + \Pi} + \alpha \cdot \left(\frac{1+\Pi - \alpha\cdot\Pi}{1-\alpha\cdot\Pi}\right) \cdot \left\{1 - \frac{1}{\ln(B_A/B_K)} \cdot \ln\left(\frac{B_A\cdot(1-\Pi) + \Pi}{B_K\cdot(1-\Pi) + \Pi}\right)\right\} (22)$$
  
where:  $B_K = B_A \cdot (B_p/B_A/B_C)^{C\cdotW}$ ;  $B_p = \exp(U_p/RT)$ ;  $Q_A(Z_A, U_p)$  is the energy of

adsorption on the most adsorptive first layer sites (k=1),  $U_p$  – cohesion energy

of adsorbate,  $Q_c$  – adsorption energy on the second and further layers, and  $W(\alpha, \Pi)$  is the following correcting function:

$$W(\alpha,\Pi) = \frac{\alpha \cdot (1 + \Pi - \alpha \cdot \Pi) \cdot (1 - \Pi)}{\alpha \cdot (1 + \Pi - \alpha \cdot \Pi) \cdot (1 - \Pi) - (1 - \alpha) \cdot (1 - \alpha \cdot \Pi) \cdot [\ln(1 - \alpha) - \Pi \cdot \ln(1 - \alpha \cdot \Pi)]}$$
(23)

The above model may be used to determine the number  $m_{hA}$  of the first layer sites in porous structures, including the sites of very low adsortpivity. Such a parameter is a measure of a porous structure geometry, slightly affected by the adsorbate properties. Moreover, the model may be useful to examine energetic properties of adsorbents.

## 3. MSM BASED INTERPRETATION OF SORPTION PROPERTIES OF MATERIALS

The model (8) and (19 or 22) makes possible to calculate the theoretical isotherms of adsorption in submicropores, absorption in elastic regions of the sorbent matter, and the sorbent expansion ratio due to absorption and sorption in submicropores. It needs the system parameters to be assumed, i.e.: energetic parameters  $U_p$ ,  $\delta_c$ ; polarity factor  $C_p$  and correcting function parameters  $Z_A$ ,  $Z_B$ ,  $R_B$ , (see eq.3); the number  $m_{ha}$  of holes of particular size  $R_{ha}$ ; parameters describing the structure of the sorbent matter: volume fraction and average size of crosslinked chains, quasi-crystalline domains, and non-crosslinked chains  $u_{el}$ ,  $x_{el}$ ,  $u_{db}$   $x_{db}$   $u_{e2}$ ,  $x_{e2}$ ;  $x_d$ ,  $x_{el}$ ,  $x_{e2}$ , compactness parameter  $z_{wd}$  for quasi-crystalline domains (see eq.9), number of typical crosslinkages per crosslinked chain  $L_{el}$ . Moreover, the molar volume  $V_s$  of sorbate in the reference state has to be known.

The pore structure may be specified in the form of pore size distribution  $m_{ha}=f(R_{ha})$  that enables us to compute the values for  $m_{ha}$ . It was stated [14, 16], that the left truncated normal distribution may be applied to express distribution of submicropores, and one point distribution expresses adequately the amount of micropores. Therefore, data characterizing the pore structure are: volume of submicropores  $V_{hsub}$ , their average radius  $R_{hav}$ , minimal radius  $R_{hmin}$  and dispersion  $\sigma_{Rh}$ , volume of the first layer adsorption space in micropores  $V_{hm}$ , and micropore capacity distribution parameter  $\alpha$  (see eq.16).

Total volume  $V_{hls}$  of the "large" submicropores (determined by the normal distribution for  $R_h \ge R_p$ ) is viewed as providing a room only for the first layer adsorption, like the volume  $V_{hm}$  of micropores – see assumption (a). Therefore, the number of sites  $m_{hA}$  for the first layer adsorption is calculated as:

$$m_{hA} = (V_{hls} + V_{hm})/V_s$$
(24)

Let  $V_h$  denote the total pore volume available for the monolayer adsorption:

$$V_h = V_{hsub} + V_{hm} \tag{25}$$

The volumetric adsorptivity of the micropores  $V_{mic}$ , viewed by the above models is

$$V_{mic} = (V_{hls} + V_{hm})/(1-\alpha);$$
(26)

and the total volume of pores  $V_{pores}$  available for sorption, may be evaluated as:

$$V_{pores} = V_{hsub} - V_{hls} + V_{mic} = V_{hsub} + V_{hls} \cdot \alpha / (1 - \alpha) + V_{hm} / (1 - \alpha);$$

$$(27)$$

Let us notice that all the parameters listed above are of direct physical or geometrical meaning, hence their values provide information on more general properties of the sorbent and sorbate (molecular and porous structure, intermolecular interactions, cohesion forces etc.) that may be used for different purposes.

The equations (8, 19) have to be solved together for all subsystems, with an assigned pressure P. In this way one obtains values of  $m_{pa}(P/P_s)$  for a sequence of P, i.e. the set of theoretical sorption isotherms for the specified subprocesses, in particular, the absorption and volumetric expansion isotherms. Then by summing up the sorption capacities  $m_{pa}$  for all the subsystems, one may obtain the theoretical sorption isotherm  $m_p(P/P_s)$ .

The multiple sorption equation (8) has no analytical solution with respect to  $m_{ha}$ . Hence, it should be solved numerically for a finite number of sorption subsystems specified according to the radius  $R_h$  of pores. For this aim the range  $R_h \in [R_{hmin} - R_p]$  may be divided into a number of sections with an average value  $R_{ha}$  (in our calculations we specify 10 sections, i.e. we consider 11 subsystems including the pure absorption  $- R_{h0}=0$ ). The number of sorption sites  $m_{ha}$  in the *a*-th subsystem is calculated by dividing the volume of *a*-th subsystem holes (evaluated according to the normal distribution of  $R_h$  within *a*-th section), by the volume  $V_s$  of sorbate molecule. The last section, corresponding to the average radius equal to that of sorbate molecule ( $R_{ha}=R_p$ ), is attributed to the pure adsorption subsystem (pointed with the subscript A). To this subsystem one also includes the first layer adsorption at remaining "large" submicropores and micropores.

The model parameters are to be determined by fitting the theoretical isotherm to empirical sorption data for the examined system. In spite of a large number of the parameters the fitting is usually rather difficult. The quantities  $u_{el}$ ,  $x_{el}$ ,  $u_{db}$ ,  $x_{db}$ ,  $u_{e2}$ ,  $x_{e2}$ ;  $x_d$  and  $z_{wd}$  describing the sorbent molecular structure and the solubility parameters  $\delta_c$  may be tightly bounded on the basis of literature data (see ref.[1]). MSM isotherms are strongly affected by the parameters of quasi-crystalline domains ( $u_{db}$ ,  $x_{dc}$ ,  $z_{wd}$ ), average size of submicropores (and

volume of micropores, and by energetic parameters  $(U_p, \delta_c; C_p, Z_A, Z_B, R_B)$ . Therefore, these parameters are well determinable. In particular sorption capacity is considerably affected (in energetic way) by the specific surface area of submicropores, which makes possible to detect a fraction of porous structure unavailable for sorbate molecules. Accurate description of elastic chains  $(u_{el}, x_{el}, L_{el}, x_{e2})$  is of less importance

In general, the examination of a system does not provide precise values for the model parameters, but rather shows an area in the parameters space, in which the sorption data may be fitted. Nevertheless, this area may be highly tightened by examination of the sorbent with a number of different probing sorbates. Notice that the sorbent structure parameters ( $V_{hsub}$ ,  $V_{hm}$ ,  $R_{hav}$ ,  $\sigma_{Rh}$ ,  $u_{el}$ ,  $x_{el}$ ,  $u_{d}$ ,  $x_{d}$ ,  $u_{e2}$ ,  $x_{e2}$ ;  $x_{d}$ ,  $z_{wd}$ ) and  $\delta_c$  should not depend on the probing sorbate. The remaining ones may be bounded in such a way to force consistency of the examined systems parameters. Moreover, the results obtained with MSM may be confronted with data obtained in another way, especially, with sorption induced expansion of the sorbent (see refs.[12, 15]).



Fig. 3. Sorption of CH<sub>3</sub>OH in a hard coal type 42 (92.4%C) (Wójcik [28]) and MSM isotherm calculated with eqs.(8, 19)

Numerous examples of such multilateral studies of hard coals of different rank and type are shown in refs. [6, 7, 9, 10, 12, 15, 19, 28]. They give evidence that sorption capacity of coal is affected by, both molecular and porous structure, and confirm significant role of submicropores in sorption processes. We showed that sorption induced swelling of coals may my well explained as an effect of absorption in elastic regions of coal and in submicropores.

A representative example of MSM fitting results is given in Figures 3, 4 (taken from [28]).



Fig. 4. Sorption of  $H_2O$  in a hard coal type 42 (92.4%C) (Wójcik [28]) and MSM isotherm calculated with eqs.(8, 19)

The figures show that sorption mechanisms of  $H_2O$  and  $CH_3OH$  in coals are essentially different. The sorption of  $H_2O$  is mainly by multilayer adsorption in microposes, although absorption is large enough to explain measurable coal swelling. In turn,  $CH_3OH$  is sorbed mainly by penetration among elastic chains and filling of submicropores.

#### 4. CONCLUDING REMARKS

The multiple sorption model may be viewed as a research instrument, supporting analysis of structures of elastic-porous materials. It yields a quantitative description of the material structure and intermolecular interactions in sorption systems. Such a description may be used to answer the questions concerning the material structure, surface properties and mechanisms of sorption. The model needs more advanced computation tools, then commonly applied adsorption formulas (BET, DR). Nowadays it seems to be of no importance.

Fitting of MSM to empirical data does not provide precise values for the model parameters, but shows an area, in which the sorption data may be explained with MSM mechanisms. Hence, the examination of a sorbent needs different probing sorbates to be used. Moreover, the results should be critically analyzed and confronted with data obtained in other ways. Nevertheless, the parameter determined in such a multilateral analysis may be used for prediction of the sorption system properties in pressure conditions unachievable in laboratories (e.g. analysis of hard coal sorption capacity and swelling in coal beds [15]).

Apart from MSM we propose a set of formulas applicable to examination of adsorption systems. In particular LBET and LgBET models were found to be promising alternative for commonly accepted BET and DR equations.

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