

## Microporous Adsorbents for a Selective Separation of Carbon Dioxide from Mixtures with Methane and Nitrogen

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The study describes a theoretical approach of the design of a micro-structure of adsorbents for a selective separation of carbon dioxide from gaseous mixtures at ambient conditions. Adsorption isotherms of carbon dioxide, nitrogen and methane, were experimentally measured on two model carbonaceous surfaces at 293.1 K. Non-local density functional theory was used to predict theoretically the behaviour of these gases as adsorbates in slit-shaped pores for a pore size range of 0.5–5 nm. The gas-solid potential parameters were obtained by fitting the calculated adsorption isotherm of a single model adsorbent surface ( $H^* = 100$ ) to the experimental data. Prediction of behaviour of gas mixtures in adsorption and selectivity calculations were obtained from ideal adsorbed solution theory. It was shown that a set of separation factors evaluated for a particular pore size range give a potential to design completely a microporous structure of a desired carbonaceous adsorbent. To such a surface, macroscopically represented by average selectivity factors, a real adsorbent characterised experimentally by the pore size distribution, could be assigned.

### Keywords:

Density Functional Theory, Ideal Adsorbed Solution theory, separation of gases, adsorption of nitrogen, methane and carbon dioxide

## Introduction

Industrial processes based on adsorption of gases on carbonaceous surfaces play an important role in many fields.<sup>1</sup> Selective adsorption of the main green-house gas, carbon dioxide, from gaseous mixtures is a promising method to limit its volume released to the atmosphere.<sup>2</sup> Some authors<sup>3</sup> claim that combination of adsorption of carbon dioxide from mixtures with other gases and its subsequent catalytic hydrogenation to oxygenates and hydrocarbons can substantially contribute to the suppression of the carbon dioxide level in the atmosphere. It is unlikely that the green-house effect problem could be solved only in this way. Nevertheless, its effective separation is a crucial point of such a technology.

Design of industrial adsorbents is usually based on experimental evaluation of adsorption properties of adsorbents, on mass and energy balance, and scale up calculations. There are many techniques<sup>4</sup> available for evaluation of composition and surface properties of microporous materials, however, hardly any of them can relate an adsorption iso-

therm with a gas uptake in pores of a particular pore size. Even if a material with a very narrow PSD is only necessary for the effective separation, standard experiments cannot simply discover this fact. Repeating of adsorption experiments for a large number of surfaces with variable PSD is an option, however, it is a long and expensive approach providing information of a limited quality. If this intuitive solution is substituted by combination of an experiment and molecular simulations, efficiency of the adsorption process designed could be dramatically increased. Conditions of the separation are much more simple to adjust when the separation properties of individual pores are known. Combination of theoretical calculations and the experiment should lead to the design of a structure and finally in tailor-made microporous carbon for a specific separation.

In this paper we report on a model of a single and multicomponent adsorption equilibria at 293.1 K and pressures up to 1 bar for carbon dioxide, methane and nitrogen. This data is available either from a large number of experiments on mixtures or from theoretical models optimised for the particular adsorbent, and the gas mixture of interest combined with experiments on single component systems. An

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experimental effort was substantially reduced by using the Ideal Adsorbed Solution theory,<sup>5</sup> one of the widely used methods<sup>6–9</sup> for the prediction of the multicomponent behaviour from single component adsorption isotherms.

The single component adsorption equilibria for carbon dioxide, nitrogen and methane were obtained by DFT (Density Functional Theory) calculations,<sup>10–13</sup> and by experiments on microporous and graphitised carbons at 293.1 K. This data was used to predict the behaviour of gas mixtures at ambient temperature (293.1 K) and pressures up to 1 bar. Real industrial adsorbents usually work either at much lower temperature or much higher pressures than systems described in this paper. Such conditions were suggested to simplify the problem to clearly illustrate the design of the microporous structure. This work is an extension of our previous study on separation of methane from a mixture with nitrogen.<sup>14</sup>

## Experimental part

### Experimental

Adsorption equilibria of carbon dioxide, nitrogen and methane were studied at 293.1 K on graphitised carbon Vulcan<sup>15</sup> and activated carbon (AX21)<sup>16</sup> up to a pressure of 1 bar. The volumetric adsorption measurements were carried out<sup>15</sup> in a static regime on a standard Coulter commercial equipment Omnisorp 100.

### Modeling

In the slit pore model<sup>17–23</sup> used for the adsorbent, the pore consists of two parallel graphitic slabs. The distance between the nuclei of the carbon atoms on each opposing slab is defined as the physical width,  $H_{\text{phys}}$ . The interaction between two adsorbate molecules (single centred spheres)<sup>24–27</sup> was described by the *Lennard-Jones* (12–6) pair potential, and the interaction of the adsorbate with a single graphite slab by the *Steele* (10–4–3) potential.<sup>25–27</sup> The solid-fluid parameters were calculated by combining the graphite parameters with the appropriate fluid parameters using the *Lorentz-Bertelot* mixing rules.<sup>25–27</sup> The potential parameter values for carbon dioxide, nitrogen and methane were estimated by fitting<sup>15</sup> the theoretical adsorption isotherms of a large pore ( $H^* = 100$ ), which represents a flat surface, to the experimental isotherm of graphitised carbon Vulcan.

Non-local density functional theory (NLDFT) was used to predict<sup>10–13,27</sup> the behaviour of carbon dioxide, nitrogen and methane as adsorbates in slit-shaped pores for a pore size range of 0.5–50

nm. On the basis of the single component experimental and DFT generated isotherms the behaviour of binary gas mixtures was predicted by the IAS theory. It is based on assumptions of a perfect mixing of adsorbates and that the adsorbed mixture is an ideal solution at the constant spreading pressure and temperature.<sup>5,28–30</sup> Details on adsorbate and adsorbent models, on the DFT method and the IAS theory, are given elsewhere.<sup>e.g.,14,15,16</sup>

### Selectivity of adsorption

The suitability of the designed adsorption system depends<sup>20</sup> on the selectivity of adsorption (separation factor). For a binary mixture it is defined:

$$S = (x_1 / x_2) / (y_1 / y_2) \quad (1)$$

as the ratio of the amount fractions in the pore divided by the ratio of the amount fractions in the bulk. Values greater than unity imply that component 1 is more strongly adsorbed than the component 2. In all calculations the bulk amount fractions of the binary mixture components were set equal ( $y_1 = y_2 = 0.5$ ).

### Selectivity isotherms

Two types of selectivity isotherms based on DFT adsorption raw data were studied: the dependency of the separation factor on pressure for a particular pore size and the dependency of the separation factor on a pore size at a particular pressure<sup>31</sup>. These isotherms could be indirectly compared with experimental data by using an average selectivity isotherms covering the whole pore size range of the microporous carbon under investigation.

#### Average selectivity isotherms

Average selectivities, based on  $S(i)$  values from IAS for DFT generated single component data, were computed. The average selectivity is defined as:

$$S_{\text{av.}} = (x_1^{\text{av.}} / x_2^{\text{av.}}) / (y_1 / y_2) \quad (2)$$

where  $x_1^{\text{av.}}$ ,  $x_2^{\text{av.}}$  and  $y_1$ ,  $y_2$  are average pore amount fractions and bulk amount fractions of component 1 and 2 in a binary mixture, respectively. For  $x_1^{\text{av.}}$  and  $x_2^{\text{av.}}$  it is valid:

$$x_1^{\text{av.}} = \sum_{\text{pores}} x_{1(i)} (N_{(i)}^{\text{tot.}}) / \sum_{\text{pores}} N_{(i)}^{\text{tot.}} \quad (3)$$

$$x_2^{\text{av.}} = \sum_{\text{pores}} (1 - x_{1(i)}) (N_{(i)}^{\text{tot.}}) / \sum_{\text{pores}} N_{(i)}^{\text{tot.}} \quad (4)$$

since

$$N_1 = \sum_{\text{pores}} x_{1(i)} (N_{(i)}^{\text{tot.}}) \quad (5)$$

$$N_2 = \sum_{\text{pores}} (1 - x_{1(i)}) (N_{(i)}^{\text{tot.}}) \quad (6)$$

and

$$1 - x_{1(i)} = x_{2(i)} \quad (7)$$

for each pore size.  $N_{(i)}^{\text{tot.}}$  is given by:

$$N_{(i)}^{\text{tot.}} = (\rho_{1(i)}^{\text{pure}} \rho_{2(i)}^{\text{pure}} V_i) / (x_{1(i)} \rho_{2(i)}^{\text{pure}} + (1 - x_{1(i)}) \rho_{1(i)}^{\text{pure}}) \quad (8)$$

where

$$\rho_{1(i)}^{\text{mix}} = x_{1(i)} \rho_{1(i)}^{\text{pure}} \quad (9)$$

$$\rho_{2(i)}^{\text{mix}} = (1 - x_{1(i)}) \rho_{2(i)}^{\text{pure}} \quad (10)$$

and  $V_i$  is a volume of a pore of a particular size. The pore amount fraction in each pore is calculated from selectivity values for each pore size:

$$S_{(i)} = (x_{1(i)} / x_{2(i)}) / (y_1 / y_2) \quad (11)$$

and

$$r_y = (y_1 / y_2) \quad (12)$$

$$x_{1(i)} = (r_y S_{(i)}) / (1 + r_y S_{(i)}) \quad (13)$$

The  $S_{\text{av.}}$  value could be compared with  $S_{\text{exp.}}$  derived from IAS on the basis of the AX21 experimental data. Volumes of individual pores used in calculation of  $S_{\text{av.}}$  were evaluated on the basis of the PSD of AX21 determined<sup>16,32</sup> from adsorption of nitrogen at 77 K. This PSD of AX21 had been extensively tested<sup>16,17,32</sup> and thus was preferably used in this model study to avoid a discussion on PSDs of microporous AX21 evaluated at different temperatures by adsorption of different gases. This topic is treated separately in details elsewhere.<sup>18,26,32,33</sup>

## Results and discussion

Carbon dioxide, nitrogen and methane adsorbed on Vulcan and AX21 do not form a monolayer under studied conditions. Adsorption isotherms of carbon dioxide on Vulcan and AX21 are presented in Figure 1. The „AX21” experimental data were used for prediction of the selectivity of adsorption. This value should be comparable with  $S_{\text{av.}}$  (equation (2)). Figure 2 shows a simulated single component isotherm for carbon dioxide. Uptake of a gas is plotted as a function of pressure up to 1 bar for a group of chosen pore sizes. In very narrow pores (around 0.7 nm) the isotherms are typically of the first type according to the Brunauer classification.<sup>4</sup> These isotherms reflect formation of a monolayer on the surface inside the ultra narrow pores. This phenomenon could be explained in terms of additional attractive forces which are present in very narrow micropores.<sup>18</sup> They have their

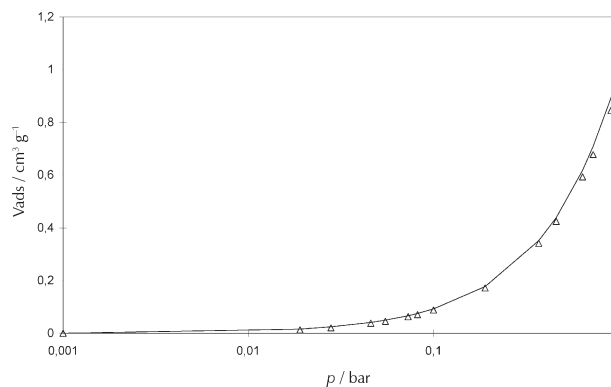


Fig. 1 a – Adsorption of carbon dioxide ( $\Delta$ ) on Vulcan

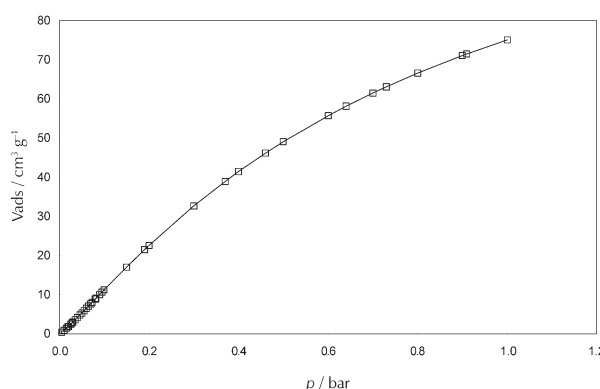


Fig. 1 b – Adsorption of carbon dioxide on AX21 ( $\square$ )

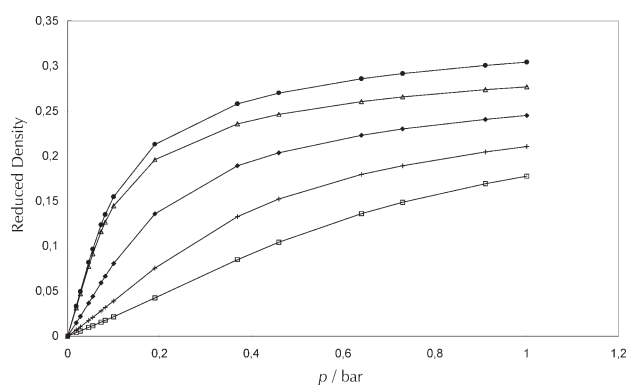


Fig. 2 – A set of DFT generated isotherms for adsorption of carbon dioxide

● 0.7 nm,  $\Delta$  0.8 nm,  $\blacklozenge$  0.85 nm, + 0.9 nm,  $\square$  0.95 nm

origin in the overlap of the potentials of the opposite pore walls. In larger micropores (above 1nm) this effect disappears.

The adsorption isotherm equation that fits the experimental data best must be used in calculation of the spreading pressures<sup>30</sup> in the IAS theory. Several isotherms were tested, however, only three of them fit the data satisfactorily, the Langmuir isotherm (L isotherm), a combination of Langmuir and Freundlich isotherms (LF isotherm) and Dubinin-

-Radushkevich isotherm (DR isotherm). Constants of the adsorption isotherm equations<sup>14</sup> were evaluated by the Levenberg-Marquardt non-linear regression method. The estimated values were compared with those obtained by the random walk algorithm.<sup>34</sup> It appeared that the regression parameters were nearly independent of the regression method if the equation fitted the experimental data well. The quality of the fit was assessed by the  $r^2$  coefficient of determination. This coefficient describes the variability in the response<sup>14,34</sup> due to the variation in the explanatory variable. The  $r^2$  value is used to pick the best curve fit from a group of fitted functions. The closer to 1 the  $r^2$  coefficient is, the better the fit. The DFT generated data for the equilibrium adsorption of carbon dioxide in a pore of size  $H = 0.7$  nm and the three fitted functions (LF, L, DR), are shown in Figure 3. It is seen that the best fit over the whole pressure range was obtained with the Langmuir-Freundlich isotherm ( $r^2 = 0.998978$ ), Dubinin-Radushkevich equation was slightly less accurate ( $r^2 = 0.995349$ ), and the worst accuracy of the fit was obtained by using the Langmuir isotherm ( $r^2 = 0.987038$ ). It was found that despite the incorrect low pressure limit<sup>30</sup>, LF isotherm is able to describe the data well over the whole pressure range and thus it was generally applied.

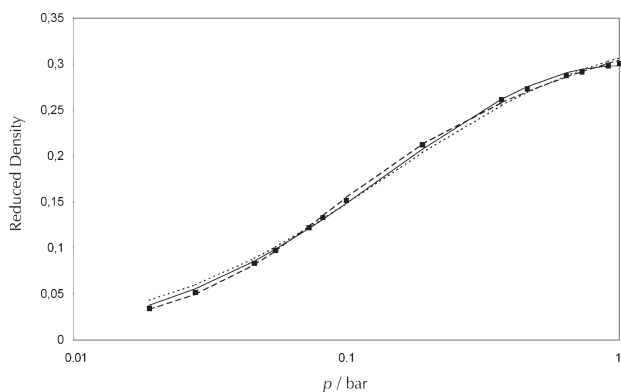


Fig. 3 – Adsorption equilibria of carbon dioxide generated by DFT for the pore size  $H = 0.7$  nm and different fitted functions; LF equation – solid line, DR equation – dashed line, L equation – dotted line

A set of selectivity isotherms (for the mixture carbon dioxide – nitrogen) in slit micropores of different radius are given in 3D geometry in Figure 4 as a 3D surface map. It exhibits a variation of the separation factor (selectivity) with the pressure and the pore size. In all inspected pores and over the whole pressure range  $S(i)$  is much greater than unity which indicates the preferential adsorption of carbon dioxide. It shows that  $S(i)$  is not very sensitive to pressure in pores with a radius above 1.3 nm, reaching almost a constant value above 1.5 nm.

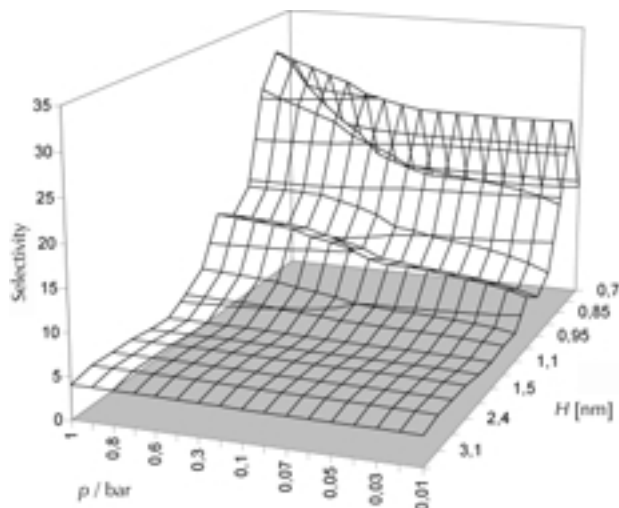


Fig. 4 – 3D surface map for dependency of selectivity on pressure and pore size for the binary mixture carbon dioxide – nitrogen

This general trend could also be expected at much higher pressures at which majority of industrial adsorbents are operated. The selectivity surface below  $H = 1.3$  nm is corrugated and reaches its maximum at the pore size of 0.8 nm. The 3D image clearly illustrates that for efficient separation of carbon dioxide from a mixture with nitrogen a material with only a very narrow PSD is necessary (0.7 nm to 1.1 nm). If this fact is omitted (molecular simulation methods are not used) it is reflected directly in much higher material and operational costs of the separation step (pressure drop over the adsorption bed, cost of an adsorbent, etc.).

The 3D projection of the Figure 4 to 2D dimensional space at two chosen pressures is shown in Figure 5. Selectivity isotherms (separation factor vs. pore size) display two maxima<sup>30</sup> before decaying with additional pressure. The first sharp peak is located at the pore size  $H = 0.8$  nm, the second one at  $H = 1$  nm and its appearance is more pronounced at higher pressure. In the model used the adsorbate molecules

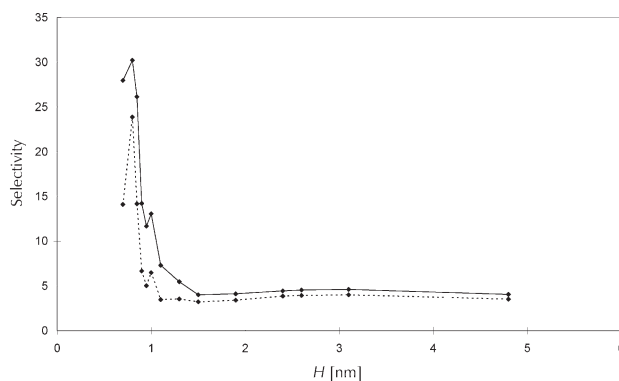


Fig. 5 – Selectivity vs. pore size for the mixture carbon dioxide – nitrogen;  $p = 0.01$  bar (dotted line),  $p = 1$  bar (solid line), ◆ selected pores



are treated as hard spheres with different molecular diameters. In ultra-narrow pores preferential adsorption of larger carbon dioxide molecule<sup>18,32</sup> is already negatively affected as seen in Figure 5 ( $H = 0.7$  nm and less). However, at  $H = 0.8$  nm the peak appears, likely due to the overlap of the potential walls. It seems that carbon dioxide molecules are particularly attracted by these additional forces. As they disappear with the increased pore size, a selectivity minimum followed by the second maximum, are observed.

Figures 6 and 7 are analogies of Figures 4 and 5 for the mixture carbon dioxide – methane. This system reveals two sharp maxima separated by a pore size interval with much lower selectivity. These extremes are located at approximately same pore sizes as they were found for the mixture carbon dioxide – nitrogen. When Figures 4 and 6 are compared it arises that nitrogen is always less strongly adsorbed than methane under studied con-

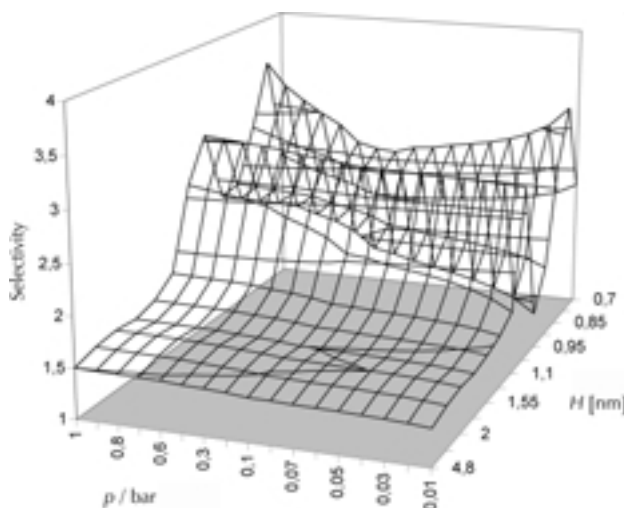


Fig. 6 – 3D surface map for dependency of selectivity on pressure and pore size for the binary mixture carbon dioxide – methane

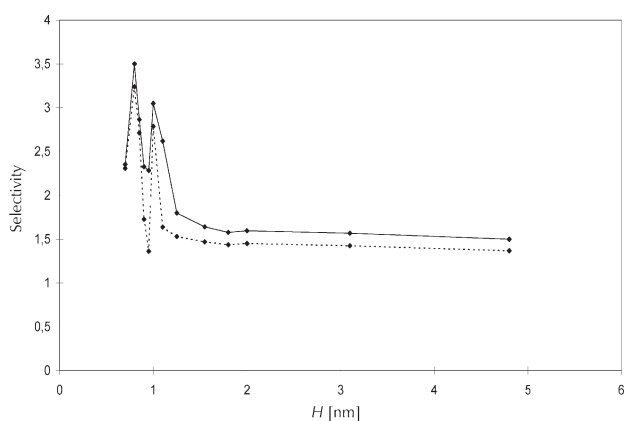


Fig. 7 – Selectivity vs. pore size for the mixture carbon dioxide – methane;  $p = 0.01$  bar (dotted line),  $p = 1$  bar (solid line), ● selected pores

ditions. The initial sharp peak in  $S(i)$  is found at a pore size that is sufficient to accommodate a single layer of carbon dioxide molecules attracted by additional wall forces. As the pore size increases a second peak appears again. Relatively, lower selectivity to carbon dioxide in ultra-narrow pores (less than  $H = 0.7$  nm) is likely due to the molecular sieving, that occurs because of the carbon dioxide molecular size (applies only for a model used in this study).

The design of the most suitable microporous structure for the preferential adsorption of carbon dioxide from a ternary mixture (or higher mixtures) with methane and nitrogen could also be based on the prediction of behaviour of binary mixtures in adsorption. Generally, it is possible to evaluate the  $S(\text{ternary})$ ; however, information value of such a parameter is more general than that from combined  $S(i)$  values for binaries.

The straightforward way to design the structure of the microporous material is based on the knowledge of the variation of the binary mixtures' separation factors with the pore size at different pressures. A combination of pore size locations of the selectivity maxima for each of the mixtures shows a desirable microstructure profile. To maximise the efficiency of the adsorption the selectivity maxima should be located at different, well separated, pore sizes. If the maxima overlap, competitive adsorption could take place and the process efficiency is lower. If this is successfully achieved the proposed material is composed of regions selectively adsorbing a gas of interest from ternary or higher components mixtures. Each of the region is responsible for separation of the gas from a particular mixture. In the process of the microstructure design several pressures are usually worthy of inspection to find peaks with the best location.

Despite the different absolute values the selectivity curves in Figures 5 and 7 are very similar including maxima positions. It could be concluded that the PSD of microporous material, suitable for the separation of carbon dioxide from a mixture with nitrogen and methane, should cover the region from 0.8 nm to 1.1 nm at the working pressure of the process  $P = 1$  bar. Although, due to the overlap of the most selective regions, competitive adsorption is likely to take place. This conclusion is, however, limited only to the presented model system which is in many respects very simplified.

The  $S_{\text{av}}$  values were evaluated from local selectivity isotherms, DFT database, and by using PSD (volumes of relevant pores) of AX21 computed from 77 K nitrogen experimental data, and 77 K local isotherm database.<sup>16–18,32</sup> PSD of AX21 (Figure 8) displays bi-modal structure with two well separated peaks. The first sharp maximum is located at 1.3 nm, the second, more diffuse band, peaks at

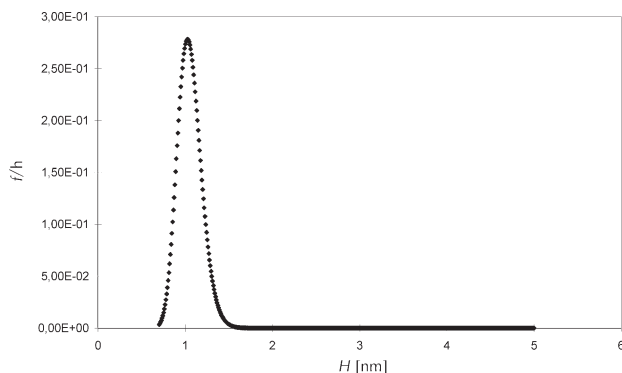


Fig. 8 – PSD of AX21 evaluated from adsorption of carbon dioxide at 293.1 K

about 2.2 nm. Average selectivity ( $S_{av}$ ) isotherms for the mixtures carbon dioxide – nitrogen and carbon dioxide – methane are shown in Figure 9 together with curves for  $S_{exp}$ , representing behaviour of a real adsorbent AX21, evaluated by IAS from the experimental data. It is seen that the agreement achieved between these two parameters (a theory based selectivity approximation of the AX21 and its real behaviour in adsorption) is very good. The  $S_{av}$  values are, however, in general, slightly underestimated for both of the mixtures. The reason of this phenomenon might be sought in terms of the AX21 PSD used, (evaluated at 77 K) which does not sufficiently cover the very selective regions below 1 nm.

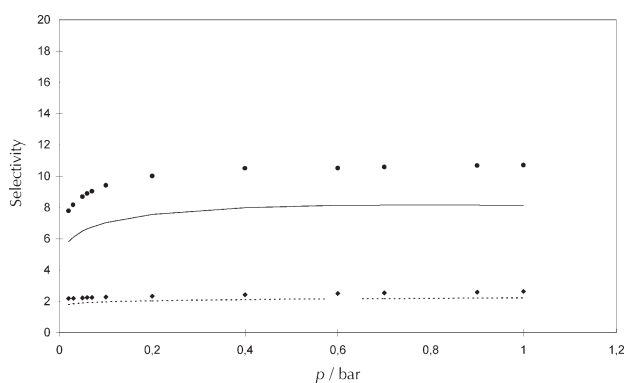


Fig. 9 –  $\blacklozenge$   $S_{av}(CO_2/CH_4)$ ;  $\bullet$   $S_{av}(CO_2/N_2)$ ; dotted line –  $S_{exp}(CO_2/CH_4)$ ; solid line –  $S_{exp}(CO_2/N_2)$

## Conclusion

A set of isotherms was generated by NLDFT for adsorption of carbon dioxide, nitrogen and methane on the model surface of the microporous carbon with graphite slit-like pore geometry at 293.1 K and pressures up to 1 bar. Adsorbing molecules were modelled as one-centred hard spheres without quadrupole or partial charges. Fluid-fluid and solid-solid interactions were described by Lennard-Jones (12–6) potential, for description of interactions of solid gas mole-

cules with the graphite surface Steele (12–4–3) potential was chosen. Adsorption of the three gases was also measured experimentally at the same conditions on two model surfaces. AX21 microporous carbon represented a real adsorbent in this study. Experimental isotherms measured on non-porous graphitised carbon (Vulcan) were fitted by the large pore ( $H = 40$  nm) DFT generated data to evaluate potential parameters. A variation of the shape of the DFT adsorption equilibrium curves with a pore size, was observed. In ultra-narrow pores a monolayer formation appeared due to the additional attractive forces having their origin in the overlap of potentials of opposite pore walls. The IAS theory was used then to predict the multicomponent adsorption equilibria from DFT and experimentally measured adsorption isotherms. The IAS theory is not restricted to any particular type of a semi-empirical fitting function. The best fits were obtained by using Langmuir-Freundlich isotherm, which despite an incorrect low pressure limit, described accurately the data over the whole pressure region. Separation factors obtained were discussed as functions of the pressure and the pore size. Adsorption of carbon dioxide was preferred to those of nitrogen or methane from binary mixtures under studied conditions. Design/selection scheme of the microstructure of the most suitable carbonaceous material was also based on separation factors of binary mixtures. The micropore size interval of a carbonaceous adsorbent for selective adsorption of carbon dioxide from a mixture with nitrogen and methane should preferentially cover the region from 0.8 to 1.1 nm. Average selectivities evaluated from a set of DFT based local selectivity isotherms macroscopically represent a desirable real adsorbent. The agreement between experimental based selectivities and  $S_{av}$  was very good.

The present knowledge on separation of carbon dioxide from carbon dioxide – methane and carbon dioxide – nitrogen binary mixtures on microporous carbonaceous adsorbents constitutes a good basis for further research. Especially, promising is to treat nitrogen and carbon dioxide molecules as two-centred L-J spheres with quadrupole (or partial charges). Such a more realistic adsorption model have a potential to give further details (geometrical constrains, energetic aspects of optimal packing in pores, etc.) on preferential adsorption of carbon dioxide.

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