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Folding of graphene slit like pore walls—a simple method of improving CO₂ separation from mixtures with CH₄ or N₂

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Abstract
We report for the first time a detailed procedure for creating a simulation model of energetically stable, folded graphene-like pores and simulation results of CO₂/CH₄ and CO₂/N₂ separation using these structures. We show that folding of graphene structures is a very promising method to improve the separation of CO₂ from mixtures with CH₄ and N₂. The separation properties of the analysed materials are compared with carbon nanotubes having similar diameters or S/V ratio. The presented results have potential importance in the field of CO₂ capture and sequestration.

Keywords: graphene folded pores, GCMC simulation, carbon dioxide separation, adsorption

Online supplementary data available from stacks.iop.org/JPhysD/47/485006/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction
It is well known that CO₂ capture from different gas mixtures is an environmentally important problem. It concerns among other things the removal of CO₂ from natural gas or biogas and the CO₂ capture and sequestration from flue gases. We have shown recently, that when choosing the most effective adsorbent for this purpose two parameters should be considered namely: surface to volume ratio, and the energy of adsorption [1]. Both factors should be as large as possible to obtain high CO₂ separation factors.

Among the carbonaceous structures available for this application, the so-called folded graphene structures seem to have particular promise [2–5]. Very interesting results in this field have been published by Liu et al [6] who described the existence of this type of structures in the heat treated graphite. Folded bilayer graphene exhibits AA-stacking of layers. Zhang et al [7] demonstrated that this type of structures can be obtained during the process of graphene ultrasonication, and Ju et al [8] studied theoretically thermal conductivity of folded graphene. Kim et al [9] presented experimental results that folded structures in graphene, termed grafold, exist, and their formations can be controlled by introducing anisotropic surface curvature during graphene synthesis or transfer processes. Moreover, those authors using pseudopotential-density-functional-theory calculations, showed that double folding modifies the electronic band structure of graphene. Lopez-Bezanilla et al [10] compared experimental images of stable closed-edge structures in few-layer graphene samples obtained by high-resolution transmission electron microscopy (HRTEM) with first-principles density functional theory calculations. Dutta et al [11] stated using van-der-Waals-corrected density functional theory calculations that the differential between the adsorption of CO₂ and CH₄ is much higher on folded graphene sheets and at concave curvatures;
this could possibly be leveraged for CH₄/CO₂ flow separation and gas selective sensors.

The discovery of folded graphene shows that the synthesis of carbon membranes containing folded graphene slit-like pores is plausible and it is interesting to investigate adsorption properties of this type of structures. Thus, following our previous findings (adsorption/separation of CH₄/CO₂ mixture on porous carbon models [12] and on carbon nanohorns [1, 13]) the purpose of the current study is to check, using the GCMC simulation method, the influence of slit-like pore walls folding on separation properties. In this study we propose a method of thermodynamically stable folded graphene sheets creation. They are used for slit-like pores construction. Simulated data of adsorption and separation are compared with those calculated for carbon nanotubes. Our results demonstrate that folded graphene structures can very efficiently separate CO₂ from mixtures with CH₄ or N₂.

2. Calculation details

2.1. Folded graphene sheets and simulation boxes

To perform simulation we propose a new procedure to generate folded graphene sheets. All the considered graphene sheets were generated from a flat sheet (presented on figure 1(a)) having a size of 10.2572 × 4.23 nm with periodic boundary conditions in x and z directions. This plane was folded in the y direction according to well-known wave-like equation (see for example [14]):

\[
y(x) = A \times \sin \left( \frac{2\pi nx}{L_{\text{box},x}(A)} \right)
\]

where \(A\) is the amplitude (maximal deviation from the initial position), \(n\) is the integer number (we assumed \(n = 2\)) and \(L_{\text{box},x}(A)\) is the length of the box in x direction after folding for the given \(A\) value. The following amplitude values are considered: \(A = 0.00, 0.25, 0.50, 0.75\) and 1.00 nm. In order to maintain the starting length of the sheet during the folding process (which is necessary to prevent the stretching C–C bond lengths) the length of folded plane should be the same as the initial one (i.e. the length of the box with flat surface for \(A = 0\) (i.e. \(L_{\text{box},x}(A = 0)\))). This condition causes the reduction in the length of the boxes for folded sheets \(L_{\text{box},x}(A \neq 0)\). The length of the curve (defined by equation (1)) may be calculated via the integration. Hence, \(L_{\text{box},x}(A)\) should fulfil the equation:

\[
\frac{1}{2} L_{\text{box},x}(A) = \frac{1}{2} \int_{-\frac{1}{2} L_{\text{box},x}(A)}^{\frac{1}{2} L_{\text{box},x}(A)} \left( 1 + \left( \frac{dy}{dx} \right)^2 \right) dx
\]

\[
\frac{1}{2} L_{\text{box},x}(A) = \frac{1}{2} \int_{-\frac{1}{2} L_{\text{box},x}(A)}^{\frac{1}{2} L_{\text{box},x}(A)} \left( 1 + \frac{4\pi^2 n^2 A^2}{(L_{\text{box},x}(A))^2} \times \cos^2 \left( \frac{2\pi nx}{L_{\text{box},x}(A)} \right) \right) dx.
\]

(2)

For each considered \(A\) value the length of the box \(L_{\text{box},x}(A)\) is find using a bisection procedure and numerical integration. Figure 1(b) shows all the considered folded graphene sheets generated following equation (2) and calculated values of \(L_{\text{box},x}(A)\).

Despite the fact that applied procedure of sheets folding is similar to theoretical generating of nanotubes by graphene folding [16] (and, in consequence, it does not vitaly affect the bonds lengths) we decide to relax the geometrically generated folded sheets. The relaxation is realized using simple Metropolis Monte Carlo simulation in canonical ensemble [17] employing one of the most sophisticated carbon force fields, i.e. carbon EDIP potential proposed by Marks [18, 19]. The computation scheme is similar to one previously described [20]. For each sheet 600 simulation cycles are performed. During each cycle 100 × \(N_C\) (where \(N_C\) is the number of C atoms) attempts of the change of the system state (via the random displacement of randomly chosen atom) are performed. The temperature is changed during the simulation (see figure S1(a) in online supplementary data (stacks.top.org/JPCM/26/485006/mmedia)). It is equal to 1000 K for the first 100 cycles. Next it is linearly reduced down to 100 K during 400 cycles and, finally, the last 100 cycles are performed for a constant temperature equal to 100 K.

Thermodynamically equilibrated sheets generated in this way (figure 1(c)) are used for the preparation of simulation boxes composed of slit-like pores. As in our previous study [21], we consider multiplied slits system in a cubicoid box with periodic boundary conditions in all three directions (see figure 1(d)). For each plane three different values of ‘pore width’ were assumed, i.e. the effective distance between sheets (in y direction)—\(H_{\text{eff}}\) was equal to 0.8 nm, 1.0 nm and 1.2 nm, respectively.

2.2. Geometric characteristics of considered systems

The porosity of the studied carbonaceous adsorbents was characterised by a geometrical method proposed by Bhattacharya and Gubbins (BG) [22]. The implementation of the method was described in detail elsewhere [20, 23]. The accessible volume of pores \((V_{\text{ac}})\) was determined by the combination of Monte Carlo integration and the BG method [20, 23] i.e. only the volume of pores having the diameter above 0.3 nm was integrated. The arbitrarily assumed low limit (0.3 nm) is close to the size of CO₂ molecule.

For each slit-like system, the accessible surface area \((S_{\text{ac}})\) was also determined using VEGA ZZ 3.0.3.18 package [24–27]. We considered so-called van der Waals molecular surface (VdW). The probe radius was equal to 0.15 nm (the sphere analogical as applied during volume integration). During calculations the fast double cubic lattice method was used. For this method, the surface properties are calculated for each dot and its distance from the geometric centre of the molecule (we assumed that the surface dot density is equal to 1000 for Å⁻²). VEGA ZZ can calculate and display some types of molecular surface through its 3D engine and it was successfully used in our previous studies [28, 29].

2.3. Monte Carlo simulations of gaseous mixtures adsorption

For our studies, we chose two model binary gas mixtures: CO₂/CH₄ and CO₂/N₂. Adsorption at 298 K in the above-described boxes was modelled using the grand canonical
Monte Carlo method (GCMC) [17, 30]. Simulations were performed for the total mixture pressure equal to 0.1 MPa (i.e. atmospheric pressure) and for the following CO$_2$ mole fractions in gaseous phase $y_{CO_2} = 0.0, 0.01, 0.025, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 0.95, 0.975, 0.99$ and 1.0. Additionally, in order to check the separation of the mixtures for other pressures, we simulated adsorption of equimolar mixtures ($y_{CO_2} = 0.5$) at different total pressure values in the range $1.0 \times 10^{-6}$–1.0 MPa. The methodology of calculations was analogous to that described previously [12]. Each GCMC simulation run consisted of $2.5 \times 10^8$ iterations. The first $1.0 \times 10^8$ iterations were discarded to guarantee equilibration. One iteration was an attempt of the system state change by the randomly selected perturbation: (i) displacement and/or rotation of randomly chosen molecule, (ii) creation of new molecule, (iii) annihilation of randomly chosen existing molecule or (iv) swap move with equal probabilities. We used equal probability for each perturbation to guarantee the condition of microscopic reversibility. Both the adsorbent structure and the molecules of adsorbate were modelled as rigid ones. Table 1 collects all applied values of the interaction parameters. Other computations details are given elsewhere [12, 32, 35].

From the GCMC simulation results, we determined the average numbers of each kind of adsorbate molecules in the simulation box ($\langle N_i \rangle$). These values were used for calculation of mole fractions of components in the adsorbed phase ($x_i$). Finally, in order to illustrate the efficiency of mixture separation we also computed the values of equilibrium separation factors:

$$S_{1/2} = \frac{x_1 / x_2}{y_1 / y_2}.$$  

The adsorbed phase is enriched in the first component if $S_{1/2} > 1$. The isosteric enthalpy of adsorption ($q^{st}$) was also calculated (from the theory of fluctuations) to study the energetics of the process.

In addition, the adsorption of both mixtures (at total pressure equal to 0.1 MPa and different mole fractions) was simulated inside the series of 8 single-walled carbon zig-zag type nanotubes ($(14,0)$–$(21,0)$) for comparison. The characteristics of considered nanotubes are collected in table S1 in online supplementary data (stacks.iop.org/JPCM/26/485006/mmedia). Each tube has the length of 6.345 nm. Periodic boundary conditions are applied along the tube axis formally mimicking the infinite nanotubes.

3. Results and discussion

3.1. Carbon structures equilibration process

Figure S1(b) shows the changes in energy and animation 1 in online supplementary data (stacks.iop.org/JPCM/26/485006/mmedia) presents the behaviour of carbon sheets during the equilibration process. As one can see we observe only a slight energy decrease. In the case of structures generated for small $A$ values ($A = 0.25$ and 0.50 nm) geometry is almost unchanged in contrast to the structures generated for $A = 0.75$ and 1.00 nm which become more rounded.

3.2. The influence of pore diameter and folding amplitude on separation

From the data shown in figure 2 one can conclude that generally with the rise in the value of amplitude $A$ adsorbed phase
Table 1. The values of LJ potential parameters and point charges applied in simulations.

<table>
<thead>
<tr>
<th></th>
<th>Geometric parameters</th>
<th>Centre</th>
<th>$\sigma$ (nm)</th>
<th>$\epsilon/k_B$ (K)</th>
<th>$q/e$</th>
<th>References</th>
</tr>
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<td>$l_{C=O} = 0.1162$ nm</td>
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<td>0.2824</td>
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<td>+0.664</td>
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<td></td>
<td></td>
<td>O</td>
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<td>82.000</td>
<td>−0.332</td>
<td></td>
</tr>
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<td>0.3400</td>
<td>55.055</td>
<td>−0.660</td>
<td>[32]</td>
</tr>
<tr>
<td></td>
<td>$\theta_{H-C-H} = 109^\circ$</td>
<td>H</td>
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<td>7.901</td>
<td>+0.165</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C−H$^a$</td>
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<td>30.600</td>
<td>—</td>
<td></td>
</tr>
<tr>
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<td>36.000</td>
<td>−0.482</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>COM$^b$</td>
<td>—</td>
<td>—</td>
<td>+0.964</td>
<td></td>
</tr>
<tr>
<td>Graphene</td>
<td>$l_{C-C} = 0.1410$ nm</td>
<td>C</td>
<td>0.3400</td>
<td>28.000</td>
<td>—</td>
<td>[34]</td>
</tr>
</tbody>
</table>

$^a$ Cross-interaction parameters.

$^b$ Centre of mass.

Figure 2. Comparison of the CO$_2$ mole fractions in adsorbed phase ($x_{CO2}$), the values of equilibrium separation factor ($S_{CO2/CH4}$) and isosteric enthalpy of adsorption ($q^{st}$) for all the considered systems plotted as the function of CO$_2$ mole fraction in gaseous phase ($y_{CO2}$) for adsorption of CO$_2$/CH$_4$ gas mixtures at the total pressure $p_{tot} = 0.1$ MPa. The grey arrows show the direction of changes related to the rise in the values of $A$ parameter (i.e. the amplitude of sheets folding). The dashed lines on upper panels represent the CO$_2$ mole fraction in gaseous phase.
becomes more rich in CO$_2$. It is interesting, that there is a threshold $A$ value (about 0.5 nm) above which a remarkable rise in $S_{CO_2}/CH_4$ occurs. For a given $A$ value the separation efficiency decreases with increasing pore width. Among studied pores, the highest efficiency of separation of CO$_2$ from the mixture with methane is observed for the pore having effective width equal to 0.8 nm. Generally for this smallest studied pore ($H_{eff} = 0.8$ nm) and for the largest $A$ values (and $A = 0.75$ and 1.00 nm) the largest separation factors are recorded (see figure 2). This is accompanied by monotonically increasing enthalpy of adsorption values. One can see however, that around the $y_{CO_2}$ close to about 0.4, the curves for both pores intersect, and due to larger slope, the curve for $A = 1.00$ nm lies above this recorded for $A = 0.75$ nm.

3.3. Separation mechanism

Cracknell et al [36] while discussing the separation of CO$_2$/CH$_4$ mixture in the slit-like pores pointed out that to consider the changes in separation factors one should take into account the energetic and entropic factors, i.e. separation increases if the energy of adsorption increases and at the same time the lost of entropy should be small. As one can observe in figure 2 the enthalpy of adsorption for the considered pore is similar for the both considered $A$ values but only for the $y_{CO_2}$ smaller than about 0.3. Above this value of $y_{CO_2}$, the enthalpy of adsorption in a pore with $A = 1.00$ nm still increases with $y_{CO_2}$, however the enthalpy of adsorption in pore with $A = 0.75$ nm reaches a plateau. The details of the mechanism of this process are shown in animation 2 in online supplementary data (stacks.iop.org/JPCM/26/485006/mmedia) comparing adsorption in both systems. From this movie it is seen that in the both studied systems two major configurations of CO$_2$ in pores are observed, i.e. monolayer in narrower part of pores (observed only in the system having $A = 0.75$ nm; note that in this case a monolayer is mainly created by CO$_2$ molecules) and polymolecular layer (created by the both molecules—CO$_2$ and CH$_4$) in the wider part of pores (observed in both systems i.e.
for $A = 0.75$ and $A = 1.00$ nm). In the monolayer relatively large energy of adsorption is observed due to solid–fluid interactions, but at the same time there are strong restrictions in entropy of rotationally hindered CO$_2$ molecules [36]. Contrary in the polymolecular range molecules have larger entropy, they interact via fluid–fluid interactions, and this leads to progressive rise in the enthalpy of adsorption with the rise in $y_{CO_2}$. Since this monolayer is (due to folding) not observed in pores having $A = 1.00$ nm the progressive rise in energy with pressure, due to strong fluid–fluid interactions occurs. Animation 2 (online supplementary data (stacks.iop.org/JPCM/26/485006/mmedia)) clearly shows that above the intersection level of the both lines adsorption in pores having $A = 0.75$ nm is still mainly monomolecular, while in pores having $A = 1.00$ nm the filling of pores occurs.

The situation for pores with $H_{eff} = 0.8$ nm is similar for CO$_2$/N$_2$ mixture (figure 3, animation 3 in online supplementary data (stacks.iop.org/JPCM/26/485006/mmedia)), but the intersection of selectivity curves for $A = 0.75$ nm and $A = 1.00$ nm occurs at smaller mole fractions of CO$_2$ in the gas phase (around $y_{CO_2} = 0.2$). Also as in the case of CO$_2$/CH$_4$ mixture the enthalpy of adsorption monotonically increases with CO$_2$ mole fraction for $A = 1.00$ nm, and reaches a plateau above $y_{CO_2} = 0.2$. Animation 3 in online supplementary data (stacks.iop.org/JPCM/26/485006/mmedia) shows this situation and the explanation is analogous as for the case of CO$_2$/CH$_4$ mixture. It is worthy to note, that very high separation factors are recorded for this case, especially for $A = 1.00$ nm. This is mainly caused by smaller adsorption of nitrogen, comparing to methane.

The data presented in figures S2 and S3 in online supplementary data (stacks.iop.org/JPCM/26/485006/mmedia) show a progressive rise in the separation factor with the rise in total mixture pressure, and as high values as around 50 for the mixture of CO$_2$ with nitrogen are recorded.

To discuss in detail the mechanisms of separation/adsorption the pore size histograms (calculated using the BG method) presented in figure 4 should be analysed. Since for a perfect slit-like pore only one pore diameter can be recorded, the BG method detects this diameter perfectly for all three analysed pores (see figure 4). However, with the rise in $A$ value two effects are recorded, namely narrowing of the major pore and the appearance of smaller pores between graphene sheets (figure 4). Since the structural heterogeneity caused by folding is strictly related to the energetic heterogeneity this effect appears also in figure 5 presenting the potential energy of solid–fluid interactions maps. They are calculated for all three studied adsorbates in all studied pores. The data collected in figures 4 and 5 make it possible to explain relatively high $S_{ij}$ factors observed in figures 2 and 3 (as well as figures S2 and S3 in online supplementary data (stacks.iop.org/JPCM/26/485006/mmedia)), especially for high $A$ values. One can see that for the smallest and the most folded studied nanopore ($H_{eff} = 0.8$ nm, $A = 1.00$ nm) all three molecules cannot access the narrowest part of the pore, due to repulsion (see also animations 2 and 3 in online supplementary data (stacks.iop.org/JPCM/26/485006/mmedia)). Therefore they can be adsorbed only in the wider part of pores. Since the value of potential energy of CO$_2$ interaction with this part of pore is much higher than for CH$_4$ and N$_2$ separation factor is also high. As mentioned above, for small CO$_2$ mole fractions in the gas phase the highest separation factors are recorded for the pore with $H_{eff} = 0.8$ nm, and $A = 0.75$ nm (see figure 2). The potential energy profiles of solid–fluid interactions calculated for interaction of gases with studied pores explain observed situation (figure 5). As was mentioned above, in the monolayer region formed in the narrowest part of pore the highest energy of solid–fluid interactions is observed (see red places in figure 5). However the formation of a monolayer enables the appearance of strong fluid–fluid interactions, and this
Figure 5. Comparison of solid–fluid interaction energy ($U_{sf}$) for three adsorbates in pores of all considered carbonaceous structures. For a molecule in a given location of its centre of mass, its angular orientation corresponding to the energy minimum was found in an iterative way. It is why the enthalpy for adsorption in this system (see figure 2) is smaller than the enthalpy for the pore having $A = 1.00$ nm (here only polymolecular adsorption is observed—see above). By the way, high energy sites are also observed in the corners of pore having $A = 1.0$ nm (see figure 5). It is obvious that the decrease in pore width leads to decrease in the value of potential energy of solid–fluid interactions as it is shown in figure 5.

Finally a confirmation of the proposed regularities can be obtained from an analysis of selected snapshots collected on figure 6 and figures S4 and S5 in online supplementary data (stacks.iop.org/JPCM/26/485006/mmedia). The first two figures show the influence of $A$ values (three arbitrarily chosen) on CO$_2$/CH$_4$ adsorption mechanism at constant total pressure (figure 6) and for equimolar mixture at different $p_{tot}$ (figure S4). One can easily observe how the adsorbed phase enriches with CO$_2$ with the rise in $A$ and pressure values. The changes in mechanism of adsorption caused by the increase in pore width (as an example equimolar CO$_2$/CH$_4$ mixture at $p_{tot} = 0.10$ and 1.00 MPa is shown) are presented in figure S5.
Figure 6. Selected equilibrium snapshots showing the configurations of molecules adsorbed inside the selected system (having the slit width $H_{\text{eff}} = 0.8$ nm) from the CO$_2$/CH$_4$ mixtures at the total pressure equal to 0.1 MPa for the selected mole fractions. The views on the whole box along the slits and from the top on the middle slit are shown.

3.4. Comparison with carbon nanotubes

Finally, figure 7 compares the separation factors of both mixtures for, studied in this paper, folded pores and for single-walled carbon nanotubes. As was concluded in our previous study [1] there are two major factors important to reach high separation factor values, namely $S/V$ ratio and the energy of solid–fluid interactions. The rise in the values of the both factors leads to the rise in $S_{ij}$ value. Table 2 collects the geometric parameters for studied folded graphene
structures. One can observe the progressive rise in $S/V$ ratio with the rise in $A$ value (the system $H_{eff} = 0.8$ nm and $A = 1.00$ nm is an exception—this is due to the fact that folding in this case leads to elimination of some parts of pore space at the places of pore walls contacts). With the rise in pore diameter the ratio $S/V$ decreases. Also in this case the rise in tube diameters one can observe the progressive decrease in $S/V$ ratio (table S1 in online supplementary data (stacks.iop.org/JPCM/26/485006/mmedia)). The efficiency of folded graphene slit-like pores and nanotubes in separation of the both studied mixtures is shown in figure 7. One can see that for CO$_2$/CH$_4$ mixture folded graphene structures with comparable diameters to nanotubes show similar separation coefficients but have, at the same time, smaller $S/V$ ratios.

Thus for example tubes (15,0) and (16,0) having diameters 0.826 nm and 0.904 nm, respectively, have $S/V$ equal to 4.842 nm$^{-1}$ and 4.426 nm$^{-1}$. Folded graphene structures with width $H_{eff} = 0.8$ nm have $S/V$ values equal to 3.649 nm$^{-1}$ and 3.237 nm$^{-1}$ for $A = 0.75$ nm and 1.00 nm, respectively. In the case of separation of CO$_2$/N$_2$ mixture similar separation factors are observed for folded graphene systems as for nanotubes having very close $S/V$ ratios, however in this case nanotubes have larger diameters. The reason of this (neglecting the differences in energy of adsorption) is that in the case of folded graphene structures and CO$_2$/CH$_4$ mixture linear CO$_2$ molecules are effectively adsorbed in corners and heterogeneous places created by the folding of a pore, and this is no so simple for spherical CH$_4$ molecules. Since such heterogeneous places are not present inside infinite nanotubes similar separation factors are observed for folded pores having smaller $S/V$ ratios than nanotubes. However, in the case of CO$_2$/N$_2$ mixture both molecules are linear and have similar possibility to adsorb in corners, since the enhancement of separation as in the case of CO$_2$/CH$_4$ mixture does not occur.

3.5. Comparison with other carbonaceous adsorbents

In figure 8 we present the comparison of equilibrium separation factors obtained from our simulations for two slit systems having the best separation efficiency, and the values calculated basing on experimental data published by Dreisbach et al [37] for adsorption of considered mixtures on commercial activated carbon Norit R1 Extra. This carbon was chosen since it is widely applied and commercially available. One can observe that adsorbents studied in this paper work better. Moreover, also better results than for carbon nanohorns [38] are observed for studied in this manuscript structures. Summing up, pore folding is a very promising method to improve separation efficiency.

Table 2. Geometric characteristics of all the considered simulation boxes constructed from the folded graphene sheets.

<table>
<thead>
<tr>
<th>$H_{eff}$ (nm)</th>
<th>$A$ (nm)</th>
<th>$V_{acc}$ (cm$^3$ g$^{-1}$)</th>
<th>$S_{acc}$ (m$^2$ g$^{-1}$)</th>
<th>$S/V$ $^b$ (nm$^{-1}$)</th>
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<td>2.356</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.680</td>
<td>1885</td>
<td>2.773</td>
</tr>
</tbody>
</table>

$^a$ Effective distance between parallel sheets (see figure 1(d)).

$^b$ Surface to volume ratio.
Figure 8. Comparison of equilibrium separation factors (adsorption of CO2/CH4 and CO2/N2 mixtures) obtained from our simulations for two slit systems constructed from folded graphene sheets (both for $H_{eff} = 0.8$ nm and Aequal to 0.75 or 1.00 nm) and experimentally observed values for adsorption of these mixtures on commercial activated carbon Norit R1 Extra [37]. All the data for $T = 298$ K.

4. Conclusions

In conclusion we show that folding of graphene pores (independent of pore width) is a promising method of increasing CO2 separation from the mixtures with methane and nitrogen. Our results suggest that the among studied systems, the best separation properties are observed for pores having an effective pore width 0.8 nm, and folding amplitude close to 1 nm. We explain the mechanism of separation showing, that for the most effective pores mono and polymolecular layers are formed in nanopores. The comparison with nanotubes shows that folded graphene pores are very promising, especially for separation of CO2/CH4 mixture since the same separation factor values are reached for smaller S/V ratios. However, this situation does not occur for the second studied mixture (CO2/N2) where folding leads to similar separation factors as for nanotubes with comparable diameters and S/V ratios.

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