Molecular insight into the high selectivity of double-walled carbon nanotubes†

Piotr Kowalczyk*

Received 1st November 2011, Accepted 16th December 2011
DOI: 10.1039/c2cp23445a

Combining experimental knowledge with molecular simulations, we investigated the adsorption and separation properties of double-walled carbon nanotubes (DWNTs) against flue/synthetic gas mixture components (e.g. CO₂, CO, N₂, H₂, O₂, and CH₄) at 300 K. Except molecular H₂, all studied nonpolar adsorbates assemble into single-file chain structures inside DWNTs at operating pressures below 1 MPa. Molecular wires of adsorbed molecules are stabilized by the strong solid–fluid potential generated from the cylindrical carbon walls. CO₂ assembly is formed at very low operating pressures in comparison to all other studied nonpolar adsorbates. The adsorption lock-and-key mechanism results from perfect fitting of rod-shaped CO₂ molecules into the cylindrical carbon pores. The enthalpy of CO₂ adsorption in DWNTs is very high and reaches 50 kJ mol⁻¹ at 300 K and low pore concentrations. In contrast, adsorption enthalpy at zero coverage is significantly lower for all other studied nonpolar adsorbates, for instance: 35 kJ mol⁻¹ for CH₄, and 14 kJ mol⁻¹ for H₂. Applying the ideal adsorption solution theory, we predicted that the internal pores of DWNTs have unusual ability to differentiate CO₂ molecules from other flue/synthetic gas mixture components (e.g. CO, N₂, H₂, O₂, and CH₄) at ambient operating conditions. Computed equilibrium selectivity for equimolar CO₂–X binary mixtures (where X: CO, N₂, H₂, O₂, and CH₄) is very high at low mixture pressures. With an increase in binary mixture pressure, we predicted a decrease in equilibrium separation factor because of the competitive adsorption of the X binary mixture component. We showed that at 300 K and equimolar mixture pressures up to 1 MPa, the CO₂–X equilibrium separation factor is higher than 10 for all studied binary mixtures, indicating strong preference for CO₂ adsorption. The overall selective properties of DWNTs seem to be superior, which may be beneficial for potential industrial applications of these novel carbon nanostructures.

I. Introduction

Double-walled carbon nanotubes (DWNTs) have recently received a widespread attention due to their unique structure, distinctive nanoporosity, outstanding mechanical, thermal, and optical properties that can be applicable in various areas of nanotechnology.¹–⁹ Current works have been focused on fundamental understanding of adsorption and transport properties of DWNTs in order to develop new applications to future separation devices.¹⁰,¹¹ As in all adsorption separation processes, the essential requirement is a porous material (called adsorbent) that preferentially adsorbs one component (or one family of related components) from a mixed feed.¹²–²⁰ This selectivity may depend on a difference in adsorption equilibrium (i.e., equilibrium selectivity) or on a difference in sorption rates (i.e., kinetic selectivity).¹⁴,¹⁹ As pointed out by Ruthven et al.,²¹ the majority of pressure swing adsorption (PSA) processes are “equilibrium driven” in the sense that the selectivity depends on differences in the equilibrium affinities. In selected equilibrium-controlled industrial PSA processes the adsorbent can be easily selected. For instance, the highly polar adsorbents such as zeolites or activated alumina are suitable for separation of water and methane mixtures.²¹ Although water and methane are characterized by similar molecular weights, their adsorption affinities to polar adsorbents are very different. Water is strongly adsorbed by polar adsorbents because the specific interactions, such as hydrogen bonds, significantly increase its binding energy. Methane is only weakly adsorbed because its interactions with these adsorbents are dominated by weak van der Waals dispersion interactions. However, the selection of an efficient adsorbent for capture of CO₂ from flue/synthesis gas is a nontrivial problem.¹⁴,¹⁹,²¹ This is because these multicomponent fluid mixtures are composed of molecules of similar sizes and polarizabilities (e.g. CO₂, CH₄, N₂, O₂, CO, and H₂). Taking this into
account, one would expect that nonpolar carbonaceous materials show very little equilibrium selectivity between these species (i.e., adsorption isotherms of these molecules on nonpolar carbonaceous materials are very similar).^{21}

DWNTs, a relatively new form of carbon nanotubes, have a coaxial structure containing two concentric graphene cylinders.\(^1\) The outer and inner diameter of DWNTs extracted from Raman spectra (RS) and high-resolution transmission electron microscopy (HRTEM) is equal to 1.46 nm and 0.77 nm, respectively.\(^3\) The effective diameter of internal carbon pores is comparable with collision diameters of flue and synthesis gas mixture components, which indicate potential applications for CO\(_2\) capture. A strong adsorption field in narrow DWNTs (i.e., confinement in quasi-one dimensional carbon pores) can significantly differentiate the adsorption affinities of similar nonpolar molecules. However, we need to obtain deep understanding on the molecular assembly structures inside DWNTs and other exotic carbonaceous nanomaterials in order to attain the industrial applications.

The aim of the present paper is to study the microscopic mechanism of CO\(_2\), CO, N\(_2\), H\(_2\), O\(_2\), and CH\(_4\) adsorption and separation in DWNTs at 300 K and pressures up to 1 MPa. We want to answer the following questions: Are DWNTs potential adsorbent for CO\(_2\) capture from flue/synthesis gas? What is the magnitude of the equilibrium selectivity of CO\(_2\) over other small molecules adsorbed in DWNTs? What are the optimal operating conditions for CO\(_2\) capture from flue/synthesis gas? To answer these questions, we combined recent experimental knowledge about the internal structure of DWNTs\(^1,4\) with molecular simulation techniques. We employed Grand Canonical Monte Carlo simulations to compute the enthalpy and adsorption isotherm of CO\(_2\), CO, N\(_2\), H\(_2\), O\(_2\), and CH\(_4\) in DWNTs at 300 K and pressures up to 1 MPa. Next, we used well-established Myers and Prausnitz phenomenological ideal adsorbed solution theory to predict the equilibrium selectivity of CO\(_2\) against all studied mixture components. Finally, we presented the final results and discussion with the special attention to the potential application of DWNTs in separation processes, including separation and capture of CO\(_2\) from flue/synthesis gas of power plants, removal of CO\(_2\) from natural gas, separation of CO\(_2\) and H\(_2\) from gasified coal.

II. Theory and simulation details

II.1. Simulation methodology

In the current work we used a fully atomistic representation for each investigated adsorbate and DWNT. As have been shown recently,\(^22\)\(^-\)\(^25\) the detailed shapes of adsorbed molecules as well as electrostatic interactions in the adsorbed phase are crucial when the sizes of pores are of molecular dimensions.

In the atomistic simulations, we expressed the intermolecular potential between two molecules A and B as a sum of site-site terms,
\[ U^{A,B}(q) = \sum_i \sum_j u_{ij}(r_{ij}^{A,B}) \]  
where the sum is taken over all sites i of the molecule A and the sites j of the molecule B, \(q \equiv \{r_{ij}^A - r_{ij}^B\}_{ij}\) is the set of separations between each atom in the molecule A and each atom in the molecule B, \(r_{ij}^{A,B} = \|r_i^A - r_j^B\|\) is the distance between two sites i and j on the molecule A and B, respectively, and \(u_{ij}(r)\) denotes distance dependent site-site interaction potential. Depending on the type of the site, \(u_{ij}(r)\) is given by a pairwise dispersion or electrostatic interaction energy. We assumed that the dispersion energy of interaction is given by the (12,6) Lennard-Jones equation.\(^{26,27}\)

\[
u_{ij}^{A,B} = 4e^{A,B} \left[ \frac{\sigma^{A,B}}{r_{ij}^{A,B}} \right]^{12} - \left[ \frac{\sigma^{A,B}}{r_{ij}^{A,B}} \right]^{6} \]  

The parameters of the potential, i.e. \(\sigma^{A,B}\) and \(\epsilon^{A,B}\), were taken from the following force fields: He (1-side Hirschfelder et al.),\(^22\) CO\(_2\) (3-site Nguyen et al.),\(^23,24\) CH\(_4\) (5-site Terzyk et al.),\(^35\) H\(_2\) (5-site Belof et al.),\(^36\) O\(_2\) (3-site Vrabec et al.),\(^37\) N\(_2\) (3-site Potoff and Siepmann),\(^38\) and CO (3-site Vrabec et al.).\(^37\)

We modeled electrostatic force via the Coulomb law of electrostatic potential,\(^{26,27}\)

\[ \nu_{ij}^{A,B} = \frac{1}{4\pi\varepsilon_0} \frac{q_i^A q_j^B}{r_{ij}^{A,B}} \]  

where \(\varepsilon_0\) is the permittivity of free space (\(\varepsilon_0 = 8.85419 \times 10^{-12}\) C\(^2\) N\(^-1\) m\(^-3\)), \(q_i^A\) denotes the value of the point charge i on the molecule A, \(q_j^B\) denotes the value of the point charge j on the molecule B, \(r_{ij}^{A,B}\) is the distance between two charges i and j on the molecule A and B, respectively. The values of the point charges were taken from the force fields given above.\(^{32-38}\)

Because our model DWNT is not charged, the solid–fluid interactions were computed from eqn (2) by summing all dispersion interactions between carbon atoms and Lennard-Jones interaction sites of adsorbate molecules. The solid-fluid Lennard-Jones parameters were computed from Lorentz-Berthelot mixing rule.\(^{26,27}\)

We performed all adsorption experiments in the grand canonical ensemble by the Monte Carlo method (GCMC)\(^{26,27}\) at 300 K and pressures up to 1 MPa. A 12.3 nm long DWNT (outer and inner diameter equal to 1.49 nm and 0.75 nm, respectively; equivalent chiral vector (16, 5) and (6, 5), respectively) was constructed using the Nanotube Modeler program.\(^39\) Next, we optimized the geometry of this DWNT using the conjugate gradients method implemented in the General Utility Lattice Program (GULP).\(^30\)\(^-\)\(^42\) Carbon–carbon interactions were computed from Brenner potential.\(^43\) As mentioned previously, optimized DWNTs were kept rigid during all computer experiments in the grand canonical ensemble.\(^34\) This simplification is reasonable because we investigated the equilibrium properties of adsorbed molecules. Due to cylindrical geometry of DWNTs, we imposed periodic boundary conditions in the longitudinal direction. Note that in doing so we neglected any effects related to the ‘entrance’ and ‘exit’ or ‘closing’ of a pore, which is a relatively good approximation if the pore length is significantly greater than its radius.\(^1,44\) Moreover, the operating temperature is relatively high that promotes diffusion of molecules from the bulk phase to pores. Similarly, we kept all studied adsorbates rigid during computer experiments. Note that in all applied force fields the molecules were kept rigid during the adjustment of potential parameters. The Monte Carlo steps (in our simulations) consist of a grand canonical (Widom) insertion/deletion move,
and of a translational/rotation move. The details of these moves can be found elsewhere.\textsuperscript{26,27} To attain microscopic reversibility and detailed balance, the translation/insertion/deletion move was selected with equal probability of 1/3. In all GCMC simulations, 10\textsuperscript{0} configurations were used, of which we discarded the first \(5 \times 10^{3}\) to guarantee equilibration. The stability of the simulation results was confirmed by additional longer runs of \(5 \times 10^{5}\) configurations. Absolute values and enthalpy of adsorption were computed using energy/particle fluctuations in the grand canonical ensemble.\textsuperscript{55,66}

II.2. Ideal adsorbed solution theory

The ideal adsorbed solution theory (IAST) due to Myers and Prausnitz is a well-known phenomenological approach used for prediction of multicomponent adsorption isotherms in microporous materials from experimental or simulated single-component adsorption data.\textsuperscript{47,48} It has been shown that IAST provides an accurate and thermodynamically consistent method for predicting multicomponent adsorption equilibria.\textsuperscript{49–54} According to IAST theory, the following equation holds for each component of the studied mixture,\textsuperscript{47}

\[ p_x y_i = p_i^0 \Pi(x_i) \] (4)

where \( p_i \) is the total pressure of mixture, \( y_i \) and \( x_i \) denote the molar fraction of \( i \)-th mixture component in the bulk and the pore phase, respectively, and \( p_i^0 \Pi(x_i) \) is the pure adsorbed gas pressure for the \( i \)-th mixture component.

For each mixture component, the value of the spreading pressure, \( \Pi \) in eqn (4), is given by the following equation,\textsuperscript{47,48}

\[ \Pi^*(p^0) = \frac{\Pi(p^0) A}{RT} = \int_0^{p^0} \frac{1}{\theta} d\theta \] (5)

where \( A \) is the surface area of the adsorbent, \( R \) is the universal gas constant, \( T \) denotes temperature, and \( a \) is the single-component absolute adsorption. To compute \( \Pi^*(p^0) \), we described the single-component absolute adsorption isotherm by the following Toth equation,\textsuperscript{55}

\[ p = \left( \frac{b}{a_m (a/a_m)^{t - 1}} \right)^{1/t} \] (6)

where \( a_m \) is the monolayer capacity, \( b \) and \( t \) are the Toth’s model parameters.\textsuperscript{55} Integration of eqn (2) gives the following expression for the spreading pressure,\textsuperscript{48}

\[ \Pi^*(p^0) = a_m \left[ \theta - \frac{\theta}{t} \ln(1 - \theta^t) - \sum_{j=1}^{\infty} \frac{\theta^{t+1}}{j(t+1)} \right] \] (7)

where \( \theta = (a/a_m) \).

If we consider a binary mixture composed of species 1 and 2, the equality of the spreading pressure of each component in the adsorbed phase implies that,

\[ \Pi^*_1 \left( \frac{p_x y_i}{x_i} \right) = \Pi^*_2 \left( \frac{p_x y_2}{1 - x_1} \right) \] (8)

This identity can be solved by standard numerical methods.\textsuperscript{56} Thus, for a given composition of the binary mixture in the bulk phase \((p_x, y_1, \text{and} y_2)\), we can predict the molar fractions of both mixture components in the adsorbed phase \((x_1 \text{and} x_2 = 1 - x_1)\). The correct description of single-component absolute adsorption isotherms is crucial for accurate prediction of mixture equilibria.\textsuperscript{47,48} When the single-component adsorption data cannot be correctly described by the three-parametric Toth adsorption model, we suggest to consider the following expansion for the absolute adsorption isotherm and spreading pressure, respectively,

\[ p = \sum_{k=1}^{M} \frac{b}{(a/a_m)^{ak} - 1} \] (9)

\[ \Pi^*(p^0) = \sum_{k=1}^{M} \frac{b}{(a/a_m)^{ak} - 1} \] (10)

where the number of terms, \( M \), is adjusted to ensure the good representation of single-component adsorption data. Following Valenzuela and Myers,\textsuperscript{48} the equilibrium selectivity of the adsorbent for component 1 relative to component 2 is given by,

\[ S_{1/2} = \frac{x_1}{y_1} \frac{x_2}{y_2} \] (11)

Values greater than unity imply that component 1 is preferentially adsorbed from 1–2 binary mixture compared to component 2.

III. Results and discussion

To validate our methodology and used force fields we computed the pressure variation of the CO\textsubscript{2}, CO, N\textsubscript{2}, H\textsubscript{2}, O\textsubscript{2}, and CH\textsubscript{4} density at 300 K. As shown in Fig. 1, a qualitative reproduction of the experimental measurements in the bulk phase is achieved for each studied adsorbate. Therefore, we are confident that equilibrium properties of studied adsorbates confined in DWNTs can be accurately predicted from our computer experiments.

All adsorption experimental data are based on \(^{4}\text{He}\) as a non-adsorbing gas.\textsuperscript{58} To be consistent with the experiment, we determined the pore volume of studied DWNTs from the \(^{4}\text{He}\) absolute adsorption isotherm simulated at 300 K. It is interesting to note that the simulated isotherm follows Henry’s law up to 1 MPa (see Fig. 2 and Table 1). We noticed that the pore density of \(^{4}\text{He}\) is not greater than its bulk density up to 1 MPa.
Moreover, due to geometric restriction imposed by DWNTs, the density ratio at higher pressures is lower than one, as is displayed in Fig. 2. A ratio of unity would be expected for pores of macroscopic sizes. Taking into account the small value of Henry’s law constant and the variation in density ratio we concluded that the use of $^4$He at 300 K as a non-adsorbing gas for determination of DWNT pore volume seems to be fully justified.

![Fig. 2](image1.png)

**Fig. 2** Upper panel: Absolute adsorption of $^4$He in DWNTs at 300 K computed from GCMC simulation (circles) and fitted to Henry’s law (line). Lower panel: Ratio of absolute density of $^4$He adsorbed in DWNTs to its bulk density at 300 K.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Henry’s law constant/kg mol$^{-1}$ MPa$^{-1}$</td>
<td>0.11</td>
</tr>
<tr>
<td>Pore volume/cm$^3$ g$^{-1}$</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Table 1 Basic properties of studied DWNTs computed from simulated $^4$He absolute adsorption isotherm at 300 K

Fig. 3 shows the CO$_2$, CO, N$_2$, H$_2$, O$_2$, and CH$_4$ absolute adsorption isotherms in DWNTs at 300 K and pressures up to 1 MPa. All adsorption isotherms exhibit type I behavior according to IUPAC classification. As pointed out by Ruthven et al., type I is characteristic for “favorable” adsorption equilibria, where the adsorbed phase density is greater than the bulk one. Due to weak dispersion interactions of H$_2$ molecules with DWNTs at 300 K, the curvature of its adsorption isotherm is lower in comparison to all other studied nonpolar molecules. Fast saturation of DWNTs by CO$_2$, CO, N$_2$, O$_2$, and CH$_4$ results from the strong solid-fluid potential generated from narrow cylindrical carbon pores. Indeed, the computed enthalpy for these adsorbates is very high and dominated by the contribution from the solid-fluid potential, as shown in Fig. 4. We noticed that for CO$_2$ the heat transfer accompanying the adsorption process in DWNTs is the highest and reaches 50 kJ mol$^{-1}$ at low pore concentrations. As would be expected, the enthalpy of CH$_4$ adsorption at zero coverage, 35 kJ mol$^{-1}$, is lower than that corresponding to CO$_2$. Due to weak dispersion

![Fig. 3](image2.png)

**Fig. 3** Absolute adsorption isotherm of CO$_2$, CO, N$_2$, H$_2$, O$_2$, and CH$_4$ at 300 K in DWNTs computed from the GCMC method (symbols). Bottom panel corresponds to the region of low pressures. Solid lines present the fitting of the three-parametric Toth adsorption model to simulated isotherms.

![Fig. 4](image3.png)

**Fig. 4** Enthalpy of CO$_2$, CO, N$_2$, H$_2$, O$_2$, and CH$_4$ adsorption at 300 K in DWNTs (open symbols) computed from the GCMC method. The solid-fluid contribution to the total enthalpy of adsorption is displayed by solid lines.

---

This journal is © the Owner Societies 2012

interactions, the lowest value of the adsorption enthalpy, 14 kJ mol\(^{-1}\), corresponds to H\(_2\) adsorbed in DWNTs. In the low-concentration limit, we found that DWNTs significantly differentiate CO\(_2\) from all other small molecules. When we reduce the pressure below 0.01 kPa, the CO\(_2\) molecules are strongly adsorbed by DWNTs, whereas all other studied nonpolar molecules are in the bulk phase (see Fig. 3). This result is consistent with the high value of CO\(_2\) enthalpy at low pore concentrations. To gain insight into molecular assembly of CO\(_2\) adsorbed in DWNTs, we present selected snapshots from our computer experiments. Fig. 5 shows that adsorbed rod-shaped CO\(_2\) molecules form single-file chain structures stabilized by the strong solid–fluid potential. Observed bending of CO\(_2\) molecules in the quasi-one dimensional assemblies results from the minimization of electrostatic interactions between adsorbed molecules and relatively high thermal energy. Except H\(_2\), all other studied small molecules form single-file chain assemblies inside DWNTs (see Fig. 6). However, the key prediction is that the pore filling of DWNTs by CO, N\(_2\), H\(_2\), O\(_2\), and CH\(_4\) is significantly shifted to higher pressures in comparison to CO\(_2\). Thus from single-component adsorption data, we expected that in certain operation pressure regions, DWNTs act as highly selective potential adsorbents being able to selectively adsorb CO\(_2\) molecules leaving the other components of the flue/synthesis gas mixtures in the bulk phase.

We used IAST theory to predict the equilibrium selectivity and the composition of CO\(_2\)–X (where X: CO, N\(_2\), H\(_2\), O\(_2\), and CH\(_4\)) binary mixtures in DWNTs at studied operating conditions. For all studied binary mixtures we assumed the equimolar composition in the bulk phase (molar ratio of both components is equal to 0.5). Fig. 3 presents the fitting of single-component absolute adsorption isotherms by the three-parametric Toth theoretical adsorption isotherm. Good agreements between simulated data and theoretical model have been achieved for all studied adsorbates. A plot comparing the composition of CO\(_2\)–X binary mixtures in DWNTs is displayed in Fig. 7. It is important to note that the CO\(_2\) fraction in the DWNT ultramicropore is very high for all studied CO\(_2\)–X binary mixtures. With an increase in mixture pressures, the CO\(_2\) fraction in DWNTs is decreasing because the competitive adsorption of the X binary mixture component. As would be expected, H\(_2\) is excluded from the internal pore of DWNTs because its binding energy is very weak. Under the same operating conditions, the CH\(_4\) fraction in pores is the highest from all studied binary mixtures, however, it is still much lower than CO\(_2\). The equilibrium CO\(_2\)–X selectivity is decreasing with an increase in bulk mixture pressure, as is displayed in Fig. 7. At low pressures, CO\(_2\) molecules are only adsorbed in

![Fig. 5](https://example.com) A snapshot of single-file chain of CO\(_2\) molecules in DWNTs. At ambient operating conditions, the carbon pore is completely filled by CO\(_2\) molecules.

![Fig. 6](https://example.com) A snapshot of single-file chain of CO molecules in DWNTs. At ambient operating conditions, the carbon pore is completely filled by CO molecules. However, CO molecules filled DWNTs at higher operating pressures than CO\(_2\) (see Fig. 3).

![Fig. 7](https://example.com) Upper panel: CO\(_2\) mole fraction in DWNTs computed for equimolar composition of studied CO\(_2\)–X binary mixtures at 300 K (where X: H\(_2\), CO, CH\(_4\), N\(_2\), and O\(_2\)). Bottom panel: Equilibrium selectivity of CO\(_2\) over X at 300 K computed from the IAST method.
DWNTs as can be interfered from single-component isotherms. Interestingly, CO$_2$ molecules perfectly fit to the narrow cylindrical pore of DWNTs. The adsorption lock-and-key mechanism of CO$_2$ binding to DWNTs explains the infinite equilibrium separation factor at zero coverage predicted for all studied CO$_2$-X binary mixtures (see Fig. 7). However, what is more important, we showed that at 300 K and equimolar mixture pressures up to 1 MPa, the CO$_2$-X equilibrium separation factor is higher than 10 for all studied binary mixtures, indicating strong preference for CO$_2$ adsorption. We believe that this knowledge is important because CO$_2$, CO, N$_2$, H$_2$, O$_2$, and CH$_4$ are components of exhaust industrial gases (e.g. flue and synthetic gas). Thus, the overall selective properties of DWNTs seem to be superior, which may be beneficial for potential industrial applications of these novel carbon nanostructures. It is worth to point that in our calculations the effect of additional polarization of carbon atoms due to adsorption of guest molecules was neglected. It is theoretically justified that in small DWNTs the solid-fluid potential can be further enhanced with pore loading. This is because adsorbed molecules can enhance the local density of electrons on carbon atoms. Any charge transfer between adsorbed molecules and DWNTs is not expected because of weak interactions. However, to account for the effect of additional polarization of solid atoms, the empirical fitting of solid-fluid parameters is necessary.

So far, there have not been experimental studies of CO$_2$ adsorption on DWNTs. Moreover, we speculate that additional polarization of studied adsorbates increases the computed equilibrium separation factor. This is simply because the polarization due to adsorption of CO$_2$ is higher than all remaining adsorbates (see quadrupole moment of all studied adsorbates). It would be interesting to verify this prediction experimentally. It is beyond the scope of the current work, but it will be the topic of our future studies.

IV. Conclusions

We investigated the adsorption and separation properties of double-walled carbon nanotubes against flue/synthetic gas mixture components (e.g. CO$_2$, CO, N$_2$, H$_2$, O$_2$, and CH$_4$) at 300 K. At thermodynamics equilibrium, narrow cylindrical pores of DWNTs efficiently differentiate CO$_2$ molecules from other studied nonpolar adsorbates. We showed that except H$_2$, all studied adsorbates self-assemble into single-file chain like structures at 300 K and pressures below 1 MPa. The strong adsorption field generated from DWNT pore walls stabilizes these assemblies of adsorbed molecules. However, what is more spectacular, we found that a CO$_2$ molecule rod-shaped adsorbed wire in DWNTs is formed at very low operating pressures. Highest values of adsorption enthalpy (i.e., 50 kJ mol$^{-1}$ at 300 K and low pore concentrations) result from perfect fitting of CO$_2$ molecules into the structure of the adsorbent and strong solid-fluid interactions (so-called adsorption lock-and-key mechanism). In contrast, adsorption enthalpy for all other studied nonpolar adsorbates is significantly lower than CO$_2$ (for instance 35 kJ mol$^{-1}$ for CH$_4$, and 14 kJ mol$^{-1}$ for H$_2$). Computed equilibrium selectivity for equimolar CO$_2$-X binary mixtures (where X: CO, N$_2$, H$_2$, O$_2$, and CH$_4$) is very high at low mixture pressures, and it is decreasing with pore loading due to competitive adsorption of the X binary mixture component. Nevertheless, we showed that at 300 K and equimolar mixture pressures up to 1 MPa, the CO$_2$-X equilibrium separation factor is higher than 10 for all studied binary mixtures, indicating strong preference for CO$_2$ adsorption.

Acknowledgements

P.K. acknowledges partial support by the Office of Research & Development, Curtin University of Technology, Grant CRF100084. P.K. acknowledges partial support by the Australian Academy of Science, Scientific Visits to Japan 2011–12 Grant. P.K. Acknowledges the Pawsey Centre and iVEC for computing facilities. P.K. also acknowledges Prof. J. Gale (Curtin University) for fruitful discussions and comments.

References