Surface to volume ratio of carbon nanohorn – A crucial factor in CO₂/CH₄ mixture separation

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A B S T R A C T

Using the first realistic model of single walled carbon nanohorn and molecular simulation data we show the 3D graphs relating the selectivity of CO₂/CH₄ separation with a surface to volume ratio of a nanohorn, the total mixture pressure and the mole fraction of CO₂ in the bulk phase. It is proved that surface to volume ratio is a crucial parameter determining the selectivity. Finally, the equation is proposed, making possible to predict the selectivity of a nanohorn for separation of CO₂/CH₄ mixture.

1. Introduction

Separation of CO₂/CH₄ mixture, especially from biogas, is a very important issue to construct a better sustainable society. Recently Ohba et al. [1] concluded that very promising material for this separation is a Single Walled Carbon Nanohorn (SWCNH). Experimental studies on the possible application of SWCNH for CO₂/CH₄ mixture separation led to conclusion that a high selectivity for CO₂ and a large adsorption capacity can be achieved [1]. This was confirmed by the application of molecular simulations [2]. Namely, it was proved that carbon nanohorn is a very promising material for this mixture separation and simulated equilibrium separation factors (S_{CO₂/CH₄}) were in the range of experimental data [2]. Since the data obtained in [1] were calculated basing on the ideal adsorbed solution theory (IAS), in this manuscript, we checked the applicability of this theory to prediction of CO₂/CH₄ mixture adsorption. We also studied the mechanism of adsorption and separation in details. Moreover, we suggested that values of equilibrium separation factors can be dependent on the internal surface to internal volume ratio (S/V) of a nanocarbon particles (nanotube and/or nanohorn). This information can enable to design a better porous material for highly efficient CO₂/CH₄ separation. However, this interesting suggestion in our opinion needs further studies, because we have not presented the quantitative dependence yet.

Thus, the aim of this Letter is to check the applicability of the IAS theory and to propose a quantitative dependence of the S_{CO₂/CH₄} on S/V the nanocarbons. Moreover, we will present the general formula applicable for rough estimation of separation properties for a nanohorn having arbitrarily chosen S/V ratio.

2. Simulated data

Two series of SWCNH presented in Figure 1 were studied. Model nanohorns were generated via the simple Metropolis Monte Carlo simulations [2,3] employing the carbon EDIP potential proposed by Marks [4,5]. We use the following notation: NH_{ddd.iii.aaa} where ddd, iii, and aaa are the diameter of tubular part (in nm), the length of tubular part (in nm), and the apex angle (in degrees). In this report the influence of the apex angle are not studied since, as it was proved experimentally, for the real SWCNH it is close to 20° [6,7]. Thus, the models with this apex angle value are only considered in this report. Additionally, the reference series i.e. infinite single-walled carbon nanotubes (SWCNTs) having the same diameter as nanohorns in series 1 are studied (Figure 1). For all the models we performed the GCMC simulation of CO₂/CH₄ mixture following the procedure described previously, and the values of separation factor were calculated and reported [2]. However, as mentioned above, the relations between separation factors and surface to volume ratio have not been reported yet.

3. Testing the IAS theory

The ideal adsorbed solution theory proposed by Myers and Prausnitz [8] is a well-known approach used for prediction of multicomponent mixture equilibrium adsorption basing on the
single-component adsorption isotherms. We decided to compare the results obtained from the IAS theory and from direct simulation for CO2/CH4 mixtures adsorption inside the considered model nanohorns. We simulated adsorption of equimolar CO2/CH4 mixture (i.e. mole fractions of both components in bulk phase are equal to 0.5) for different total pressure values from the range 10⁻⁶–1 MPa (we used methodology analogous as previously described [2]). The implementation of the formalism proposed by Myers and Prausnitz [8] was analogous to described in [9] however, to obtain almost perfect approximation of the single-component isotherms three-modal Bradley’s equation was used (we used pure CO2 and CH4 adsorption isotherms simulated previously [2]). Some additional information about applied procedure is available in Supplementary Data.

4. Surface to volume ratio calculation

Basing on simplified geometric structure of a nanohorn [2], presented in Figure 2, the values of surface to volume ratio for considered model nanohorns were calculated according to the formula:

\[
S = \frac{D_{\text{eff}} + 4H_{\text{eff}} + D_{\text{eff}}/\sin(x/2)}{D_{\text{eff}}H_{\text{eff}} + D_{\text{eff}}^2/(6\tan(x/2))}
\]

(1)

where \(D_{\text{eff}}\) and \(H_{\text{eff}}\) are the effective diameter and length of tubular part, respectively, and \(x\) is the apex angle. In the same way the surface to volume ratio for infinite nanotubes may be calculated from:

\[
S = \frac{4}{D_{\text{eff}}}
\]

(2)

5. Results

In Figure 3 we show the comparison of CO2/CH4 equilibrium separation factors (\(S_{\text{CO2/CH4}}\)) inside the selected model nanohorns obtained directly from the mixture simulation and from the IAS approach. One can observe that the agreement between IAS theoretical predications and simulation results is good in the range of small pressures (\(<0.1\) MPa). However, with the rise in pressure the differences increase and the \(S_{\text{CO2/CH4}}\) values obtained from the IAS theory are smaller than simulated ones. The predictions obtained from model and simulation approach one to another with the rise in the diameter and/or length of a nanohorn. Obtained results explain the differences between \(S_{\text{CO2/CH4}}\) values calculated in [1] from experimental single-component isotherms using IAS theory, and simulation.

Figure 4 shows the correlations between separation factors and the surface to volume ratio, for three selected mole fractions of CO2 in the bulk phase (the remaining data are available in Supplementary Data). One can observe that for small and very large SWCNH and nanotubes we observe similar results. However, for the case of very narrow carbon structures to observe the same separation factor, a nanotube should possess higher S/V ratio than a corresponding SWCNH. Contrary, up to S/V equal to c.a. 4 1/nm two opposite effects are seen for the both materials. Namely, the
presence of a tip in a nanohorn leads to concave plot of $S_{\text{CO}_2/\text{CH}_4}$ vs. $S/V$. In nanotubes the same plot is convex to the abscissa. As one can see from this Figure for the same $S/V$ ratio carbon nanohorn shows higher separation factor than corresponding carbon nanotube. This is mainly caused by the larger energy of solid–fluid interactions for CO$_2$ than for CH$_4$ molecule, especially in the conical part of a nanohorn, as it is shown in Figure 5. This figure shows the potential energy map for interaction between nanohorn or nanotube and adsorbed molecules. Summing up, to compensate the rise in energy in a nanohorn tip a corresponding nanotube should be narrower than this forming a nanohorn tubular part. For example, similar energy of solid-CO$_2$ interactions as for NH$_{1.71_03.0_19.2}$ is observed for the nanotube (18,0), while this nanohorn is formed form (22,0) nanotube.

For approximation of equilibrium separation factor ($S_{\text{CO}_2/\text{CH}_4}$) as the function of surface to volume ratio ($S/V$) and CO$_2$ mole fraction ($y_{\text{CO}_2}$) in the bulk phase (each total pressure the effective diameter and length oately) the following empirical function was used:

$$S_{\text{CO}_2/\text{CH}_4} = \frac{A}{1 + B_2 \cdot y_{\text{CO}_2}^2 + B_1 \cdot y_{\text{CO}_2} + C \cdot (\frac{S}{V} U^{-1})^2 \cdot \ln(\frac{S}{V} U^{-1}) + D_2 \cdot \ln^2(\frac{S}{V} U^{-1}) + D_1 \cdot \ln(\frac{S}{V} U^{-1})}$$  \hspace{1cm} (3)

where $A, B_2, B_1, C, D_2, D_1$ are the best-fit parameters and $U^{-1} = 1$ nm is the reciprocal of $S/V$ unit (it was introduced in order to avoid the finding of the logarithm or power from the denominate number).

The relations $S_{\text{CO}_2/\text{CH}_4} = f \left( S/V, y_{\text{CO}_2} \right)$ for each total pressure value were approximated by Eq. (3) using the genetic algorithm proposed by Storn and Price [10] which was previously successfully applied by us for the description of different data sets (see for example [11,12]). The obtained values of best-fit parameters are collected in Table 1.

Finally, in Figure 6 we present a three dimensional representation of obtained results. The extrapolation of surfaces leads to conclusion that for very large $S/V$ values one should observe rapid increase in $S_{\text{CO}_2/\text{CH}_4}$, for all range of CO$_2$ mole fractions in the bulk phase. This effect should be observed especially in the range of pressures up to ca. 0.5 MPa. However, obtained results show that at larger total pressures higher separation factors are available only at larger CO$_2$ mole fractions in the bulk phase. This is caused by the filling of the whole pore volume by CO$_2$ (which is subcritical at studied conditions), while methane (which is supercritical) is mainly adsorbed in the monolayer by solid–fluid interactions.

6. Conclusions

It seems to be very interesting that surface to volume ratio determines the effectiveness of CO$_2$/CH$_4$ mixture separation. In
Figure 4. The correlations between CO₂/CH₄ equilibrium separation factor (S_{CO₂/CH₄}) and surface to volume ratio (S/V) for all the considered systems and the arbitrary chosen values of CO₂ mole fractions in bulk phase (y_{CO₂}), i.e. 0.10, 0.50 and 0.90.

Figure 5. Profiles of solid–fluid interaction energy for CH₄ and CO₂ molecules inside nanohorns (the axial plane is shown) and single walled carbon nanotubes having the same diameter like nanohorn tubular part (the plane perpendicular to the tube axis is shown). For the molecule in given location of its centre of mass its angular orientation corresponding to the energy minimum was found in an iterative way. All the profiles are presented in the same scale.
this study we show that this is the major reason of SWCNH better separation properties comparing to carbon nanotubes. Table 2 shows the comparison of $S/V$ ratios for different carbon structures having the same effective diameter and/or length. In fact one can see that carbon nanohorn has larger $S/V$ ratio than the corresponding nanotube. Moreover, among considered in this table carbon structures spherical and conical pores seem to be ever more promising than carbon nanohorn for CO$_2$/CH$_4$ mixture separation. It seems probable, that using molecular simulations we will be able to propose a general relationship between separation factor ($S_{CO_2/CH_4}$) and $S/V$ for different carbon geometries. However, this conclusion needs further calculations and experimental verification.

Since the differences between the IAS theory predictions and simulation results can be large in the high pressure range, proposed by us relationship (Eq. (3)) can be very useful for prediction of realistic $S_{CO_2/CH_4}$ values for the real SWCNH synthesised and characterised in laboratories.
Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2014.01.031.

Table 2
The comparison of geometric properties of different carbon structures.

<table>
<thead>
<tr>
<th>Pore geometry</th>
<th>S/V formula</th>
<th>S/V value for fixed geometrical parameters [1/nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infinite nanotube</td>
<td>$S = \frac{4}{\sqrt{V}} \cdot D_{eff}$</td>
<td>2.000</td>
</tr>
<tr>
<td>Nanohorn</td>
<td>$S = \frac{D_{eff} + 4H_{eff} + D_{eff} / \sin(\pi/2)}{D_{eff} H_{eff} + D_{eff}^2/\sin(\pi/2)}$</td>
<td>2.615</td>
</tr>
<tr>
<td>Slit-like</td>
<td>$S = \frac{2}{\sqrt{V}} \cdot D_{eff}$</td>
<td>1.000</td>
</tr>
<tr>
<td>Spherical</td>
<td>$S = \frac{6}{\sqrt{V}} \cdot D_{eff}$</td>
<td>3.000</td>
</tr>
<tr>
<td>Cylindrical</td>
<td>$S = \frac{2D_{eff} + 4H_{eff}}{D_{eff} H_{eff}}$</td>
<td>2.667</td>
</tr>
<tr>
<td>Conical</td>
<td>$S = \frac{1 + 1/\sin(\pi/2)}{\sqrt{V} \cdot D_{eff}/(6 \pi/\sqrt{3})}$</td>
<td>3.550</td>
</tr>
</tbody>
</table>

* i.e. $D_{eff} = 2$ nm; $H_{eff} = 3$ nm; $\alpha = 19.2^\circ$.

References