

DIFFUSIVE BEHAVIOR AND SEPARATION OF ETHANE/ETHYLENE BINARY MIXTURES IN CARBON NANOTUBES

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Abstract

Molecular dynamics simulations were employed for studying both the flow and the adsorption behavior of ethane, ethylene and their mixtures in single walled carbon nanotubes (SWCNT). Large-scale simulations were set up where an open-ended SWCNT was exposed to a bulk fluid in an overall canonical ensemble. The endohedral physical adsorption and non-equilibrium diffusion into the pore was monitored until steady state conditions were attained. Other sets of simulations took into account an infinitely long SWCNT, monitoring mean square displacements and allowing the determination of effective diffusion coefficients for the pure components. Our results for the individual species seem to suggest that different diffusion mechanisms are experienced at different loadings. The possibility of separating the corresponding binary mixtures was addressed by considering the endohedral physical adsorption.

1. Introduction

Separations of close boiling point mixtures, of which the olefin/paraffin mixture is an example, are amongst the most energy-intensive unit operations in chemical and petrochemical industries. For these types of separations, less energy intensive techniques are actively sought, particularly for small scale applications [Noble 2005]. Adsorption could place a role in improving this scenario, however, our molecular-level knowledge of the physical phenomena involved in the diffusion and adsorption of mixtures of fluids in confined nanospaces needs improvement. The co-adsorption of mixtures of ethane and ethylene into carbon slit pores has been previously studied using the Grand Canonical Monte Carlo technique [Curbelo 2005], revealing that, under certain conditions, the pores exhibited a marked selectivity towards the saturated component. This was interpreted not only in terms of structural effects but also due to dispersive energy differences arising from the existence of a double bond in the olefin. A later experimental study of adsorption of mixtures of C_2H_6/C_2H_4 into activated carbons, using a gas-chromatography apparatus [Guo 2007] seemed to point out that the strongly-adsorbed component (ethane) could replace the weakly adsorbed component (ethylene). Recent studies involving the adsorption of propane and propylene into Titanosilicalite Ag-ETS-10 [Tiscornia 2007] and zeolites [Kargol 2005] pointed out that propylene is preferentially adsorbed due to the formation of π -complexation bonds between carbon double bonds in the fluid and the cations in the solid.

Since their discovery in the early 90's [Iijima 1993] carbon nanotubes have attracted much attention towards their particular properties. Their range of potential technological applications is ever expanding [Szeleifer 2005, Sinnott 2001], being suggested as storage materials for hydrogen and methane [Darkrim 2002, Bekyarova 2003, Lee 2006] to separation agents of organic vapors [Mao 2003]. In the present work we will study the adsorption and diffusive behavior of ethane and ethylene, when the fluids are put in direct contact with these carbon nanostructures. Single-walled carbon nanotubes (SWCNT's) of the zig-zag type [Saito 2003, Han 2005] will be used. Our main goal is try to shed some light into the fine details of the fluids behavior by employing classical molecular dynamics (CMD) simulations [Allen 1987, Haile 1997] to study both the diffusion and the adsorption behavior in single walled carbon nanotubes.

2. Theoretical Methods

2.1 Molecular Models and Force Fields

The ethane and ethylene molecules studied in the present work, have been modeled in the framework of the OPLS-AA force field for organic molecules, which gives an account of the total non-bonded interactions through a sum of the coulombic forces with a Lennard-Jones (12,6) potential. The all-atom parameterization with explicit charges for alkanes and alkenes was used [Jorgensen 1996], and the ethylene geometrical model has been adapted from McDonald *et al* [McDonald 1997]. The intramolecular energy contributions arising from bond stretching and angle bending have been calculated according to harmonic potentials. To accurately describe the torsional energy of the dihedrals, a triple cosine function was used. The functional forms to calculate all contributions for the total energy are recorded in Table 1.

Table 1. Force field used in the CMD simulations.^a

Energy	Functional form
Non-bonded	$U(r_{ij}) = \sum_i \sum_j \frac{q_i q_j e^2}{r_{ij}} + 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$
Bonds	$U(r_{ij}) = \sum_{bonds} \frac{1}{2} K_r (r - r^{eq})^2$
Angles	$U(\theta_{ij}) = \sum_{angles} \frac{1}{2} K_\theta (\theta - \theta^{eq})^2$
Torsional	$U(\phi_i) = \sum_i \frac{V_1^i}{2} [1 + \cos(\phi_i)] + \frac{V_2^i}{2} [1 - \cos(2\phi_i)] + \frac{V_3^i}{2} [1 + \cos(3\phi_i)]$

^a r_{ij} is the distance between particles i and j , q_i is the charge on particle i , and r^{eq} and θ^{eq} are the bond equilibrium distance and angle, respectively.

The Lennard-Jones diameter and dispersive energy, σ and ϵ , respectively, are recorded in Table 2 for all atom types considered. To calculate the cross parameters, the Lorentz-Berthelot rules have been employed [Rowlinson 1982]. One of the advantages of the all-atom force field is the fully flexible character it confers to the molecules, therefore accurately reproducing subtle effects arising from the carbon-hydrogen bonds and carbon-carbon double bonds.

As for the carbon nanotubes, we have chosen to study samples of the zig-zag type (n,0) configuration [Saito 2003, Han 2005] of single-walled carbon nanotubes (SWCNT's), with $n = 16$ and a total tube length of *ca.* 52 Å and 208 Å. In most theoretical and simulation works in the literature of confined fluids in nanospaces, the nanotubes are usually modeled with a coarse grained structural description, to avoid large computer processing times. However, in the present work the SWCNT's were described as a collection of explicit and frozen carbon atoms giving rise to fully structured walls; the simulations' results will therefore tend to reflect the tube's corrugation arising from its real structure. A similar approach was used by Kondratyuk *et al* to study the diffusion of n-heptane in CNT's [Kondratyuk 2007]. We have adopted the energetic model for graphite reported by Steele [Steele 1973], widely used in simulation studies of carbon nanotubes [Hung 2005, Kondratyuk 2005, Kondratyuk 2007]. The carbon atoms in the tube walls had σ bonds with a characteristic length of 1.42 Å [Düren 2002, Jiang 2002], slightly different from the usual value of 1.4 Å for a pure sp^2 hybridized carbon; this results from the squeezing of the π orbitals towards the tube exterior [Han 2005].

Table 2. Lennard-Jones and force field parameters.^a

Atom Type	q	$\sigma / \text{Å}$	$\epsilon / 10^3 \text{kJ}\cdot\text{mol}^{-1}$
CRT	-----	3.4	232.805
C3	-0.18	3.5	276.328
H3	0.06	2.5	125.604
C2	-0.23	3.55	318.197
H2	0.115	2.42	125.6040

^a CRT is the carbon atom in a nanotube, C3 and H3 are the sp^3 carbon and hydrogen atoms in ethane, and C2 and H2 are the sp^2 carbon and hydrogen atoms in ethylene.

2.2 Simulation Details

To study the adsorption of the pure fluids and their corresponding mixtures on the SWCNT's, simulation boxes were built as $30 \times 30 \times 302 \text{ Å}$ ($60 \times 60 \times 302 \text{ Å}$) supercells, with the carbon nanotubes occupying a $30 \times 30 \times 52 \text{ Å}$ ($60 \times 60 \times 52 \text{ Å}$) volume (Figure 1). The nanotubes were built up with a total number of 800 graphitic carbon atoms, and the fluids total number of particles ranged from 150 to 800 atoms, according to the corresponding density. Before contact with the tubes, the boxes containing only the fluids of interest were equilibrated at 300 K, during at least 0.1ns. Once the adsorption runs were finished, the upper volume of the simulation cell, containing the nanotube and the adsorbed molecules, was separated from

the bulk fluid and replicated four times along the z -axis to produce a $30 \times 30 \times 206$ Å supercell containing 3104 graphitic carbon atoms (Figure 2). This procedure was employed in all the diffusivity studies.

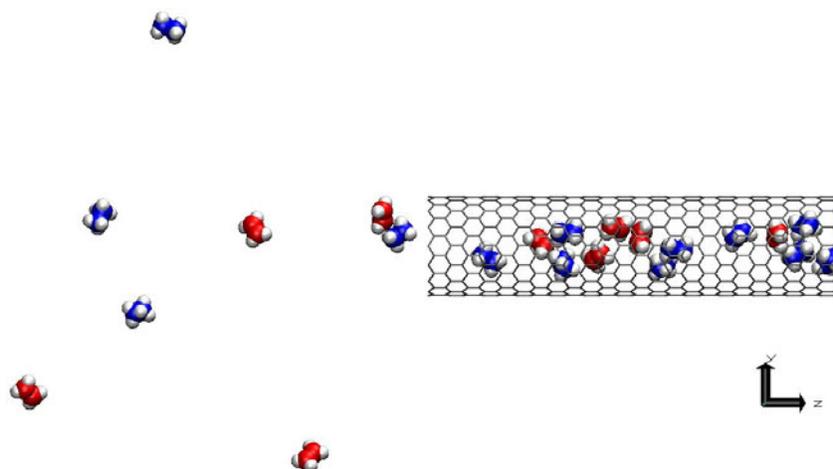


Figure 1. Snapshot of a mixture of ethane (blue) and ethylene (red) with a SWCNT (16,0).

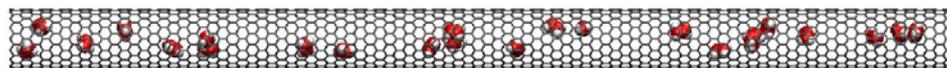


Figure 2. A CMD box used in the diffusivity studies, containing ethylene and a SWCNT (16,0) with total length of 206 Å.

Molecular dynamics simulations were performed using the DL_POLY package [Smith 1999]. The Verlet algorithm was used to integrate the equations of motion with a timestep of $t = 1$ fs [Verlet 1967, van Gunsteren 1990]. In order to verify the adequacy of such a timestep, some test simulations were conducted at $t = 0.5$ fs; no significant differences could be observed. The Ewald summation method [Woodcock 1971, Woodcock 1974, Lewis 1975, van Gunsteren 1990] was employed to calculate the long-range electrostatic interactions together with a potential cut-off distance of 15 Å, and the Nosé-Hoover thermostat was used to control the temperature with a relaxation constant of 0.1 ps [Nosé 1984]. The production runs at $T = 300$ K, spanning a total time length of up to 1.8 ns (0.2 ns in the diffusivity studies), were performed using the canonical ensemble (NVT), resulting in a temperature precision always better than 0.5%.

3. Results

3.1 Adsorption Isotherms

The results obtained are recorded in Figure 3, where the surface area was determined for an effective tube radius, representing an accurate picture of the volume available for adsorption. In the high-pressure region, ethylene is slightly more adsorbed than its saturated counterpart; as pressure decreases, both components present a similar endohedral adsorption behavior towards the nanotube. The overall adsorption curves seem to belong to the type-I isotherms, although further work in the low-pressure region will be needed to validate this assumption.

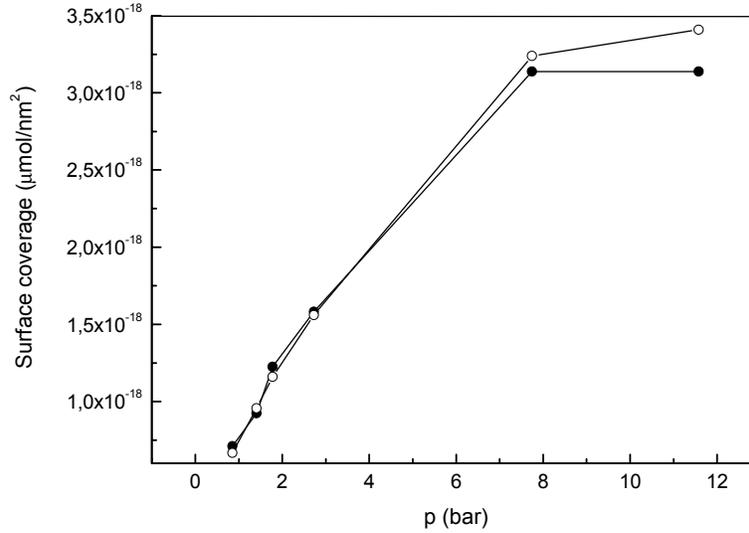


Figure 3. Adsorption isotherms for ethane (closed circles) and ethylene (open circles) at $T = 300$ K (lines are just a guide to the eye).

To study the effect of feedstock composition on the separation process, simulations were run for mixtures of different ethylene partial pressure. As the pressure in this kind of systems is ill defined, we have chosen to approximate this value to the corresponding pressure in the bulk fluid CMD box. The total pressure was thus calculated as a sum of two ideal contributions from C_2H_6 and C_2H_4 (please note that this is a reasonable assumption under the PVT conditions of the present work [Reid 1988]); these partial pressures in the bulk fluid box, were obtained from interpolation of NIST data for the pure components at $T = 300$ K [Lemmon 2005]. The preliminary results were interpreted in terms of the selectivity coefficient, defined in equation 1 for ethane.

$$S = \frac{(x_{ethane} / x_{ethylene})_{nanotube}}{(x_{ethane} / x_{ethylene})_{bulk}} \quad (1)$$

As indicated in Figure 4, ethane selectivity increases with increasing ethylene partial pressure; the lowest value for the adsorption at $T = 200$ K still needs further confirmation to access its reliability. A previous simulation study with a mixture containing 10% molar fraction of ethane in a 10 \AA carbon slit pore presents a different trend for the selectivity behavior with temperature [Curbelo 2005]. Nevertheless, the absolute selectivity values are of the same order of magnitude as ours.

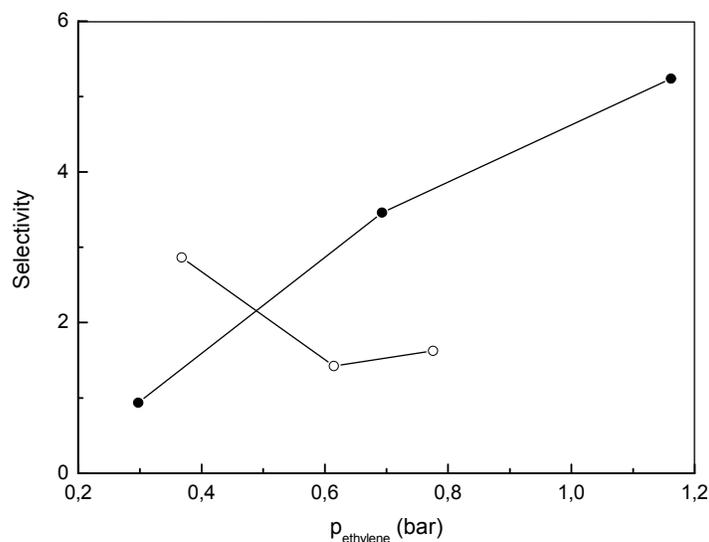


Figure 4. Selectivity profiles for mixtures of $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$ at $T = 300$ K (closed circles) and $T = 200$ K (open circles) (lines are just a guide to the eye)^a. Results for simulations containing a total of 40 molecules. ^a See text for calculation of pressure (Sect. 3.1).

3.2 Diffusion

As previously mentioned (*cf.* 2.2), the final state of each adsorption run was used to generate the initial configuration for the diffusivity studies. As no concentration (or pressure) gradients were present in the system, the displacement of particles, as simulations evolved in time, resulted from an effective transport diffusion of molecules along the nanotube. The mean square displacement (MSD) was monitored and plotted as a function of time, producing a reasonable linear behavior for most systems; this indicated a Fickian-type diffusion process [Lee 2004, Striolo 2006]. Naturally, as the number of molecules inside the tube decreased, the corresponding diffusion coefficients increased proportionally. An exception for this trend was the ethylene system at $p = 0.85$ bar (Figure 2). In this kind of systems, characterized by a low density, molecules have enough free space between them to “jump” over one another: the MSD thus exhibits a quadratic behavior with simulation time, evidencing a ballistic-type diffusion mechanism (Figure 5).

An earlier reported simulation study on the diffusion of ethane and ethylene molecules inside carbon nanotubes, revealed that the first molecules entering the confined space followed a spiraling diffusive path, oriented according to the carbon bonds on the walls [Mao 2002]. This same behavior was confirmed visually in the present work, by inspection of the movies generated from the configuration files (Supplementary material).

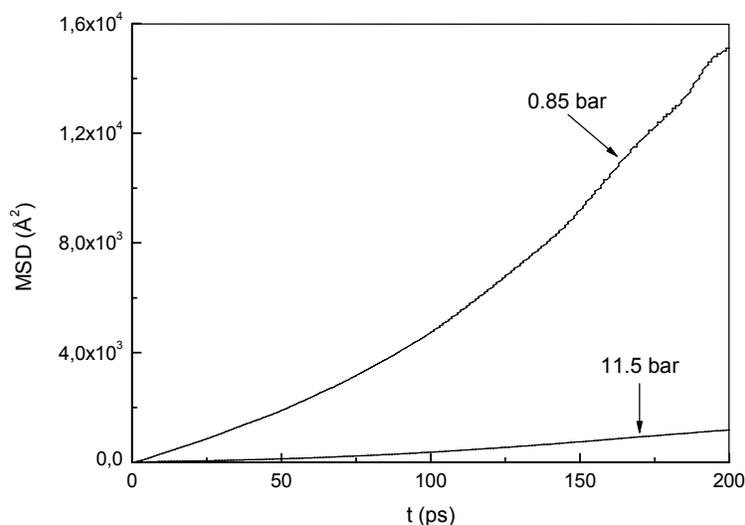


Figure 5. MSD functions for ethylene confined in a SWCNT with length 206 Å.

4. Conclusions and perspectives

Our preliminary results seem to show that both the adsorption and transport behavior is dependent on the nature of the SWCNT's. Apparently little important details such as the nanotube chirality (zig-zag or armchair symmetry) can result in significant differences in terms of diffusive transport. Likewise, relatively small changes in the nanotube diameter can have a marked effect on the transport and adsorption properties and, consequently, on the separation selectivity of mixtures. Further work will be needed to establish the results now being presented, in a larger pore with/temperature range. The mixture propane/propylene will be addressed in a near future, namely its similar helical diffusive path inside the nanotubes.

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