Quasi-One-Dimensional Adsorption of Alkanes on Carbon Nanotubes Observed from Experiments and Simulations

(Extended Abstract)

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We present a combined experimental and simulational study of the adsorption of five linear alkanes, n-pentane to n-nonane, and a branched alkane molecule, 2,2,4-trimethylpentane, on SWNT adsorption sites. Temperature programmed desorption (TPD) is the experimental tool used to characterize the adsorption of these six alkanes. Hybrid Monte Carlo (HMC) simulations were used to theoretically probe the molecular-level details of alkanes adsorbed on different sites on the SWNT bundles.

Figure 1 shows the representative TPD traces from three alkanes – pentane, n-nonane and 2,2,4-trimethylpentane. Alkane molecules can be adsorbed in four distinct environments on single wall carbon nanotubes, resulting in four resolved features (labeled as A, B, C and D) in temperature desorption spectra. These four peakes (A to D) are identified as interior, groove site, exterior, and multilayer adsorption respectively.

Figure 2 shows the simulated "pseudo-TPD" profile for n-Pentane. N-pentane molecules on the exterior sites desorb more readily than molecules on the groove and interior sites. Moreover, n-pentane is completely depleted on the external sites at the lowest temperature (~175 K), the groove site is depleted at the next lowest temperature (~220 K) and the internal sites are depleted at the highest temperature (~270 K). These temperature trends are in qualitative agreement with the TPD data and corroborate that peak A corresponds to the internal sites, peak B to the groove sites, and peak C to the external sites of the nanotube bundles.

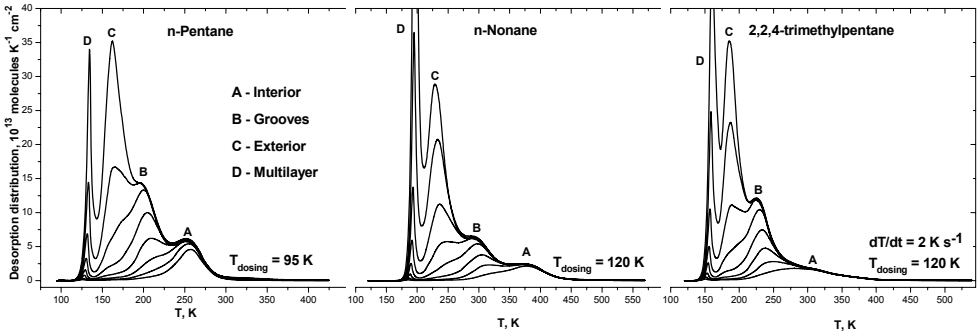


Figure 1. Temperature Programmed Desorption Spectra of n-Pentane, n-Nonane and 2,2,4-trimethylpentane from SWNTs.

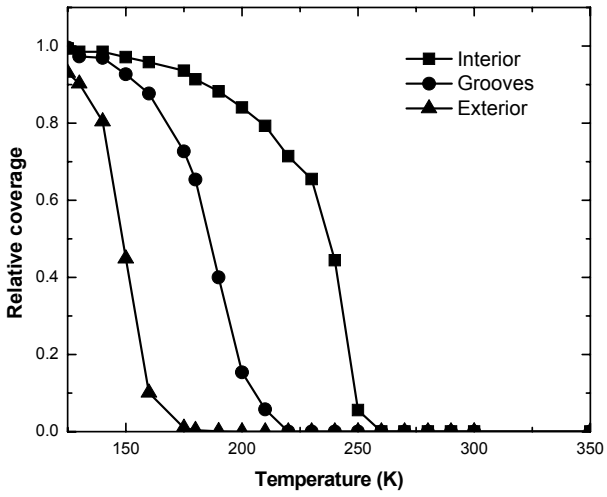
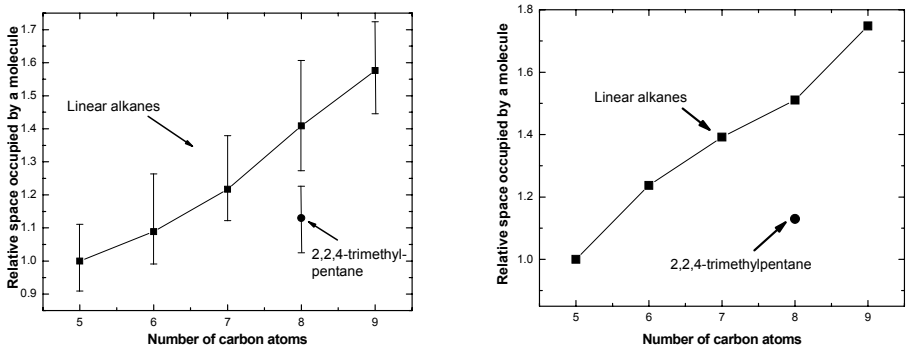


Figure 2. Simulated Desorption of n-Pentane.

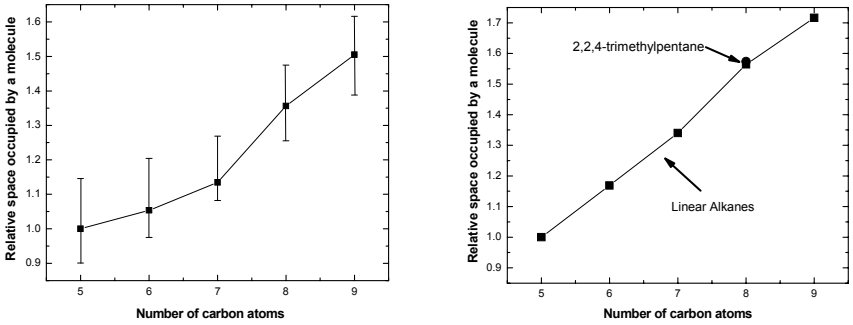
Figure 3 shows experimental and simulated results of the groove site (site B) capacities for various alkanes. It is evident that an approximately linear relationship is observed for n-alkanes from C_5 to C_9, while the 2,2,4-trimethylpentane point clearly does not follow the trend expected for a C_8 molecule. A 2,2,4-trimethylpentane molecule occupies much less space on site B than a C_8 molecule, in accordance with its shorter carbon skeleton. These results demonstrate the one-dimensional nature of the groove site for adsorption, since the space occupied by a molecule is proportional to the chain length, not to the number of carbons in the molecule.



(a) Experiments (b) Simulations

Figure 3. Linear Alkanes and 2,2,4-trimethylpentane in Groove Sites (B).

Figure 4 shows experimental and simulated results of the internal site (site A) capacities for various alkanes. We again observe a roughly linear relationship between the inverse capacity of the interior site and the number of carbon atoms in a molecule. However, the experimental data for 2,2,4-trimethylpentane cannot be interpreted, due to peak overlap. Simulation data show that the branched alkane falls on the same line as the linear alkanes for interior site adsorption. The interior site, therefore, is quasi-one-dimensional, since the volume occupied by a molecule is proportional to the number of segments, not to the length of the molecule.



(a) Experiments (b) Simulations

Figure 4. Linear Alkanes and 2,2,4-trimethylpentane in the Internal Site (A).