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COMMUNICATIONS

Can Chiral Single Walled Carbon Nanotubes Be Used as Enantiospecific Adsorbents?

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Received November 21, 2001

Chromatographic separation of enantiomers relies on the existence of energy differences between analyte enantiomers interacting with a chiral chromatographic phase.[1] One intriguing route toward achieving these energy differences is to create homochiral solids. For example, Evans et al. recently reported the synthesis of a chiral porous solid that was used to enantioenrich an initially racemic mixture of *trans*-1,2-diaminocyclohexane.[2] It is well-known that single-walled carbon nanotubes (SWNTs) exist in chiral forms that arise due to the helical winding of the graphitic rings around the tube axis.[3] Numerous studies have shown that SWNTs can adsorb a range of light gases,[4−8] with excellent size selectivity under appropriate conditions.[9,10] Multiwalled NTs show favorable adsorption properties for NO[11] and dioxins.[12] It is therefore interesting to consider whether chiral SWNTs could be used as enantiospecific adsorbents. Since homochiral samples of SWNTs are not yet available,[13] this issue cannot currently be probed experimentally. Here, we describe atomistic computational modeling of chiral disubstituted cycloalkanes adsorbed in chiral SWNTs that strongly indicates that chiral SWNTs will not act as effective enantiospecific adsorbents.

All SWNTs with indices (n,m) satisfying $n > m > 0$ are chiral.[3] These nanotubes can be characterized by their diameter, d, and chiral angle, $\theta = \arctan(\sqrt{3}m/(2n + m))^3$. We examined a series of 11 SWNTs that span a range of diameters and chiral angles. In each case, we simulated that adsorption of each enantiomer of *trans*-1,2-dimethylcyclopropane (DMCPr) and *trans*-1,2-dimethylcyclohexane (DMCH) using methods adapted from our previous simulations of these species on chiral metal surfaces.[14−19] Briefly, each molecule is represented using a United Atom (UA) model developed by Mondello and Grest[17,20] with the addition of bond stretching.[17] The interaction of the adsorbed molecule with the confining nanotube was described by a pairwise sum of Lennard-Jones (LJ) interactions between each UA in the adsorbate and each C atom in the SWNT. Each SWNT is assumed to be rigid. The LJ parameters for the UA−nanotube interactions were taken from the potential derived by Ayappa[21] for methane in SWNTs. This potential gives similar adsorption energies for methane to the LJ1 potential used by Mao and Sinnott to simulate a range of hydrocarbons in SWNTs.[22,23] We only consider the adsorption of isolated molecules, so interadsorbate interactions do not need to be specified.

For each adsorbed molecule, we use Hybrid Monte Carlo (HMC) at constant T to explore the available configurations.[17] A convenient way to quantify the enantiospecificity of adsorption is to compute $\Delta U = \langle U^R \rangle_T - \langle U^S \rangle_T$, where $\langle \cdots \rangle_T$ is a canonical ensemble average and U^R (U^S) is the potential energy of the R (S) enantiomer of the adsorbate. The isosteric heat of adsorption of a molecule adsorbed in a porous material, $q_{\rm st}$, is[24] $q_{\rm st} = H^{\rm bulk} - \langle U \rangle_T$, where $H^{\rm bulk}$ is the enthalpy of the species of interest in its bulk phase. If the bulk phase in contact with the SWNTs is either an enantiomerically pure phase or a racemic mixture, $H^{\rm bulk}$ is identical for both enantiomers of the adsorbed species. That is, ΔU is the difference between the isosteric heats of adsorption of the two molecular enantiomers in the SWNTs: $\Delta U = \Delta q_{\rm st} = q^R_{\rm st} - q^S_{\rm st}$. In addition to these ensemble average quantities, we have used a standard minimization method to determine the minimum energy state available to each adsorbed molecule.[17] The difference between the minimum energy states for the two adsorbate enantiomers is denoted $\Delta U_0 = U^R_{\rm min} - U^S_{\rm min}$. Step sizes in our HMC simulations were adjusted to give approximately 50% acceptance probabilities.[17] For each adsorbate/SWNT pair, five independent HMC simulations of 10^7 MC steps were performed. Uncertainties in the observed average properties were estimated by the deviation from the mean of the five HMC trajectories.

As a first example of our results, we consider the adsorption of DMCPr in a (10,5) SWNT. This tube has $d = 10.35$ Å. The minimum energy state for the adsorbed R enantiomer has $U_{\rm min} = 23.61$ kcal/mol lower than the isolated gas-phase molecule, confirming the expectation that it is highly energetically favorable for the molecules to be adsorbed inside SWNTs of this type. More significantly, the difference between the isosteric heat of adsorption for the two enantiomers is practically zero. At $T = 290$ K, our HMC results yield $\Delta q_{\rm st} = -0.002 \pm 0.007$ kcal/mol. Calculating the minimum energy configurations of the adsorbed molecules confirms that the two molecular enantiomers interact slightly differently with this SWNT, giving $\Delta U_0 = 0.0053$ kcal/mol. For comparison, similar modeling of the same molecules adsorbing on chiral Pt surfaces yields values of $|\Delta U_0|$ in the range 0−0.6 kcal/mol.[17] Similar enantiospecific energy differences are seen in experimental measurements of desorption barriers for small chiral molecules from chiral Cu surfaces.[25] Numerous other examples of enantiospecific binding energy differences exceeding 0.1 kcal/mol are known,[17,26,27] and these energy differences are sufficient to allow effective chromatographic separations.[26]

We conclude from the results above that (10,5) SWNTs do show enantiospecific interactions with adsorbed DMCP, but the energy differences associated with these interactions are far too small for these SWNTs to be an effective enantiospecific adsorbent for this species. Even for the chiral surfaces cited above that show energy differences up to 0.6 kcal/mol, however, a small number of adsorbate/surface pairs are known where $|\Delta U_0| \cong 0$.[14,17,19] On the basis of this observation, we cannot use the single example above to rule out the possibility that some SWNTs may act as effective enantiospecific adsorbents from the single system discussed above. To further explore this issue, we performed analogous calculations for DMCP and DMCH in a series of 11 SWNTs chosen to span a range of tube diameters and chiral angles. Our results are summarized in Table 1, ordered by tube diameter. To determine an appropriate range of tube diameters, we first examined adsorption

10.1021/ja017585x CCC: $22.00 © 2002 American Chemical Society

Table 1. Δq_{st} at 290 K for DMCP and DMCH Adsorbed in 11 SWNTs as Computed from HMC Simulations[a]

tube indices	d (Å)	θ (deg)	Δq_{st}, DMCP	Δq_{st}, DMCH
(8,6)	9.52	34.7	-0.0005 ± 0.0033	-0.0015 ± 0.0040
(10,5)	10.35	40.9	0.0022 ± 0.0070	0.0039 ± 0.0100
(12,3)	10.76	49.1	0.0017 ± 0.0124	-0.0140 ± 0.0067
(12,9)	14.29	34.7	-0.0041 ± 0.0127	0.0152 ± 0.0248
(18,2)	14.94	54.8	-0.0024 ± 0.0148	0.0129 ± 0.0095
(16,8)	16.57	40.9	0.0077 ± 0.0108	0.0028 ± 0.0183
(20,5)	17.94	49.1	-0.0059 ± 0.0130	-0.0122 ± 0.0251
(27,3)	22.40	54.8	0.0067 ± 0.0156	0.0070 ± 0.0208
(20,15)	23.81	34.7	-0.0008 ± 0.0100	-0.0175 ± 0.0225
(26,13)	26.90	40.9	0.0046 ± 0.0150	-0.0066 ± 0.0130
(32,8)	28.71	49.1	-0.0059 ± 0.0106	0.0102 ± 0.0148

[a] Δq_{st} is shown in kcal/mol.

of DMCH in (n,1) SWNTs with $2 \leq n \leq 13$. We find that DMCH cannot adsorb inside these tubes for $n \leq 11$. That is, the potential energy of adsorbed molecules is much larger than its gas-phase value in these pores. DMCH adsorbs very favorably in (n,1) tubes with $n > 11$. The (11,1) and (12,1) nanotubes have $d = 9.03$ and 9.81 Å, respectively. From these results, we conclude that the smallest SWNT listed in Table 1 is close to being the narrowest nanotube that can adsorb DMCH. Thus, the SWNTs listed in Table 1 span the range from nanotubes that tightly confine the adsorbed molecules to nanotubes that are substantially larger than the two adsorbates we have considered.

The results in Table 1 show that differences in isosteric heats of adsorption for molecular enantiomers adsorbed in SWNTs are extremely small. Only one system, DMCH in the (12,3) tube, yields a value for Δq_{st} at 290 K that is statistically distinguishable from zero, despite the small uncertainties. Our calculations yield very similar results at other temperatures we have sampled (data not shown). These results are consistent with our calculations of $|\Delta U_0|$, the binding energy difference between the minimum energy states. The largest value of $|\Delta U_0|$ we observed was 0.030 kcal/mol for DMCH in the (20,5) tube. Only four of the remaining systems we examined gave $|\Delta U_0|$ greater than 0.01 kcal/mol. Thus, the observation above that interactions of molecular enantiomers with chiral SWNTs leads to nonzero energy differences between adsorbed enantiomers appears to be quite general, but so does the observation that these energy differences are far too small for these materials to act as effective enantiospecific adsorbents for the species we have simulated.

The inability of chiral SWNTs to differentiate between enantiomers of DMCP or DMCH can be understood in terms of the smoothness of the potential energy surface for these molecules when they are adsorbed in SWNTs. Small molecules such as H_2 and CH_4 have extremely small energy barriers to diffusion inside SWNTs, resulting in diffusivities for these species that are several orders of magnitude higher than those in noncationic zeolites with similar pore sizes.[28] This smoothness applies individually to each atom in the adsorbed molecules we have considered, leading to the miniscule energy differences that exist between adsorbed molecular enantiomers. This suggests that the only strategy for observing adsorption enantiospecificity in SWNTs would be to adsorb chiral species that bind to the graphitic carbon making up the nanotubes in a highly spatially specific manner. Spatially specific binding of ethane and ethylene in SWNTs has been observed in molecular dynamics simulations,[22] leading to helical diffusion paths for these molecules. This specificity is due to the preferential alignment of carbon−carbon bonds in the adsorbate and adsorbent,[22] and this effect is evidently lost with the more structurally complex adsorbates we have examined here.

In conclusion, we have used atomistic simulations to examine adsorption of chiral hydrocarbons inside chiral SWNTs with a range of pore diameters and chiral angles. The differences between the isosteric heats of adsorption for pairs of molecular enantiomers are negligible in all cases we have studied. We suggest that this result stems from the inherent smoothness of the potential energy surface for molecules physisorbed in SWNTs. While our results cannot exclude the possibility that specific classes of chiral molecules will show significant enantiospecific adsorption in SWNTs, they do suggest that chiral SWNTs will not be effective as general-purpose enantiospecific adsorbents.

Acknowledgment. This work was supported by a National Science Foundation CAREER award (CTS-9983647) to D.S.S. T.D.P. received a graduate fellowship from Air Products and Chemicals Inc. A.I.S. received a scholarship from the Alexander S. Onassis Public Benefit Foundation. D.S.S. is an Alfred P. Sloan fellow. Computing resources were provided by the Pittsburgh Supercomputer Center and through a computer cluster in our department supported by the NSF (CTS-0094407) and Intel. We thank Prof. J. Karl Johnson for helpful discussions.

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JA017585X