

Study of Argon Adsorbed on Open-Ended Carbon Nanotube Bundles

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The adsorption of Ar on open-ended single-walled carbon nanotube bundles was studied. The amount of argon, which corresponds to the first coverage adsorbed on open-ended carbon nanotube bundles, was about 3 mmol/g. The isosteric heat of adsorption was obtained from the isothermal adsorption measurement in the low coverage region performed at temperatures ranging from 120 to 135 K. The estimated heat of adsorption of argon in the low-coverage region was 182 meV and was comparable to that of nitrogen.

I. Introduction

Carbon nanostructures have attracted a great deal of interest,¹ due to the discovery of fullerenes.² Numerous novel and exceptional physical properties have been observed or predicted for these carbon systems. Recently, among the large variety of members in the fullerene family, carbon nanotubes (CNTs) have received the focused attention³ of the scientific and technological community. The basic structural unit of CNT is a graphitic sheet rolled into a cylinder, with the tube tips closed by hemispherical or polyhedral graphitic domes. These tubes have impressive aspect ratios from 100 to 1000, with diameters as small as 1 nm and lengths ranging from microns to millimeters.⁴

In addition to chemical or physical properties, a fascinating aspect of fullerene materials is their central empty space, where particles can be enclosed. The very long cavities of CNTs have special potential due to their aspect ratio, and they can be used as templates to fabricate elongated nanostructures. Ajayan et al.⁵ studied the physical mechanisms of filling CNT cavities that could exploit the capillary properties. Subsequent studies by Dujardin et al.⁶ allowed the estimation of a surface tension threshold in order to select materials that are good candidates to wet and fill CNTs.

Studies of the adsorption of gases on various adsorbents including CNTs have been intensively conducted both experimentally^{6–10} and theoretically^{11–15} due to the interesting physical phenomena in adsorption processes and the potential for practical applications. Some theoretical studies also predict the increased adsorption capacity and adsorption binding energy of the open-ended nanotubes.^{7,12–14} In our early report,¹⁶ we have studied the comparison of the binding energies of nitrogen on the close-ended and open-ended single-walled carbon nanotubes (SWNTs) at lower coverage and have shown a nitrogen binding energy greater in the case of open-ended nanotubes than in close-ended ones. These energetic studies about adsorptions on nanotubes indicate the usefulness of the carbon nanotubes.

In this paper, we report an experimental study of the adsorption of argon on the open-ended carbon SWNTs. We estimated the isosteric heat of adsorption and the binding energy from isothermal adsorption experiments on open-ended carbon SWNTs below the first coverage.

II. Experimental Section

The apparatus for isotherm adsorption experiments consist of a gas handling system and a refrigerator. The gas handling system consists of 1/4-in. VCR-type valves (Nupro) and a capacitance pressure gauge (MKS Baratron 127). A He closed-cycle refrigerator (CTI model 22 refrigerator) was used for a temperature control.

The nanotube used in this experiment as substrate was produced at Rice University by the pulsed-laser vaporization method.¹⁷ To remove the half-fullerene caps at the ends of the nanotube, the nanotube was annealed at 1073 K for 12 h in a vacuum after an acid treatment.¹⁸ The mean diameter of the SWNT was 1.2 nm.¹⁷ For the 1 g nanotubes the degree of openness needed can be simply evaluated by considering the net diameter of the nanotube (0.95 nm) and the size of the N₂ molecules (0.434 nm) using the result of our earlier report for comparing the nitrogen adsorptions on open-ended and close-ended nanotubes.¹⁶ This indicates that more than 85% of the tubes are open. The nanotube samples were placed in a copper cell and evacuated at 350 K for 24 h before measurements were taken. The mass of nanotubes used in the experiments was 30 mg. Temperature was controlled using a temperature controller (Lakeshore DRC-93CA) with 0.01 K precision. Measurements to obtain the heat of adsorption were performed at five different temperatures: 120.53, 123.50, 126.66, 129.72, and 133.00 K.

III. Results and Discussion

Theoretically possible adsorption sites for the molecules on close-ended SWNTs are the interstitial channel, the ridge, and the outer surface.¹⁹ Talapatra et al.,¹⁹ however, found experimentally that an adsorption occurs only on the ridge and the outer surface for CH₄, Ne, and Xe despite the size of the molecules. We expect that the possible adsorption sites for argon

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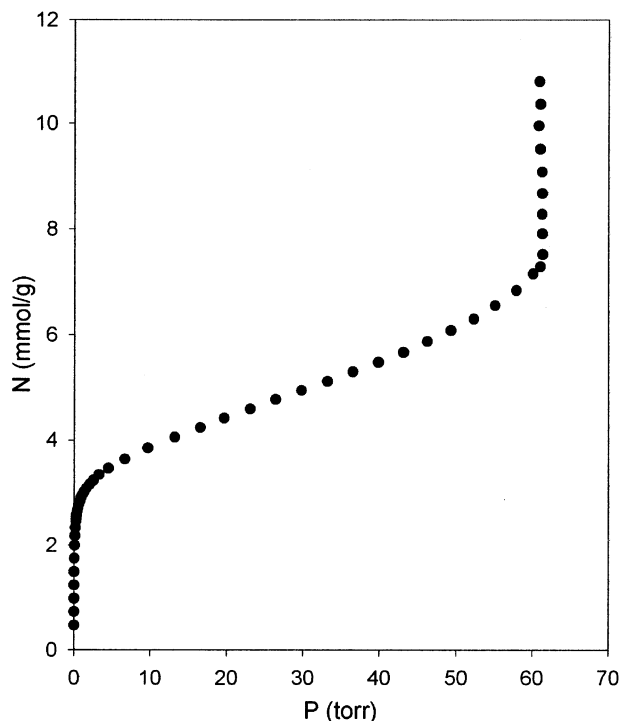


Figure 1. Isotherm adsorption data of argon on the open-ended nanotube bundles at 71 K. The step at around 1.2 Torr corresponds to the first coverage of the adsorbed layer. The saturation pressure is about 60 Torr.

will be the same as the case of the above gases. Because the ridge, which is the region between two adjacent nanotubes, has greater binding energy than that of the outer surface, the gas has a tendency to adsorb on the ridge first. In the case of the open-ended nanotubes, however, inner sites of the nanotubes have a higher binding energy than those of the outer sites. Therefore, the gas is adsorbed on inner sites first.

Figure 1 shows the isothermal adsorption of argon on open-ended nanotube bundles measured at 71 K. The saturated vapor pressure at 71 K is about 60 Torr. The amount adsorbed, y-axis, is represented in mmol/g. The amount of argon molecules related to the first coverage, which is believed to correspond to the monolayer of the plane graphite, on the SWNTs is about 3 mmol/g.

The opening process using the acid treatment could cause the formation of an oxidized group such as C—O or O=C—O on the nanotube surface. Kuznetsova et al.²⁰ have shown that the thermal treatment of nanotubes decomposes these oxidation groups and that this removing process makes the enhanced adsorption in the nanotubes possible. In our earlier report for adsorption of nitrogen on open-ended nanotubes, we showed that nanotubes annealed at 1073 K after the acid treatment have about 50% larger adsorption capacity than those annealed at 873 K.¹⁶ Therefore, we expect that the adsorption of Ar by the same annealing treatment will be enhanced to a similar degree as for the adsorption of N₂.

A highly uniform surface will be completely wet by an adsorption of gas; that is, the coverage diverges at a saturated vapor pressure.²¹ The data in Figure 1, however, show the finite coverage (about 7 mmol/g) at the saturated vapor pressure. This means that the adsorbate is incompletely wet on open-ended nanotubes and that the uniformity of the surface of nanotubes is different from that of planar graphite. Mackie et al.²¹ have shown that the degree of graphitization of nanotubes became higher with a heat treatment up to 2400 °C, because the amount

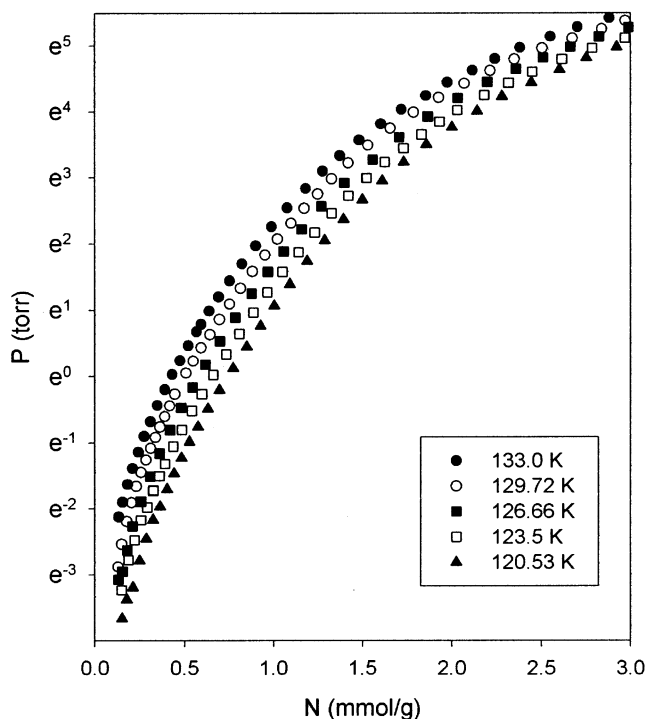


Figure 2. Adsorption data for all temperatures used in this study. Different temperatures are represented by different symbols. The pressure (y-axis) was represented in a natural logarithmic scale. From these data, the isosteric heat of adsorption was estimated using $q_{st} = kT^2(\partial \ln P/\partial T)_N$.

of gas adsorbed on heat-treated nanotubes at a saturated vapor pressure is greater than that on nanotubes without heat treatment. The geometric shape of the nanotubes and the properties of the adsorbate, such as surface tension, will also affect the wetting behavior of adsorbate.

Adsorption is an exothermic process. The energetics of the process can be described in terms of the heat of adsorption. It is the amount of heat released when a molecule adsorbs on a substrate. At finite temperatures and coverages, the isosteric heat of adsorption also reflects the interactions between the gas molecules and the substrate. The isosteric heat of adsorption can be measured calorimetrically, or it can be determined from adsorption isotherm data measured at different temperatures. In the latter case, the isosteric heat of adsorption is defined as,²² $q_{st} = kT^2(\partial \ln P/\partial T)_N$. Here, k is Boltzmann's constant, N is the amount of the adsorbed gas on the nanotubes, P is the pressure of the coexisting unadsorbed gas, and T is the average value of the temperature. Data concerning the magnitude of the heat of adsorption and its coverage dependence can provide useful information concerning the nature of the surface and the adsorbed phase.

Figure 2 is the plot of N vs $\ln P$ at five different temperatures. In Figure 2, we only plot a limited range of data below the first coverage. Using these data and the above equation, we estimated the isosteric heat of adsorption of Ar for different N , and the result is shown in Figure 3. The y-axis was represented in two different units: meV and kJ/mol. Four graphs in Figure 3a represent the coverage-dependent heat of adsorption curves obtained from all possible pairs of temperature intervals for the temperature examined; that is, q_1 is for 120.53 and 123.5 K, q_2 is for 123.5 and 126.66 K, and so on. The average value of the heat of adsorption is also shown in Figure 3b. The small bump in the low coverage region, which may be related to the properties of the adsorbates, was also observed in our previous studies.^{16,23} The maximum value of the heat of adsorption of

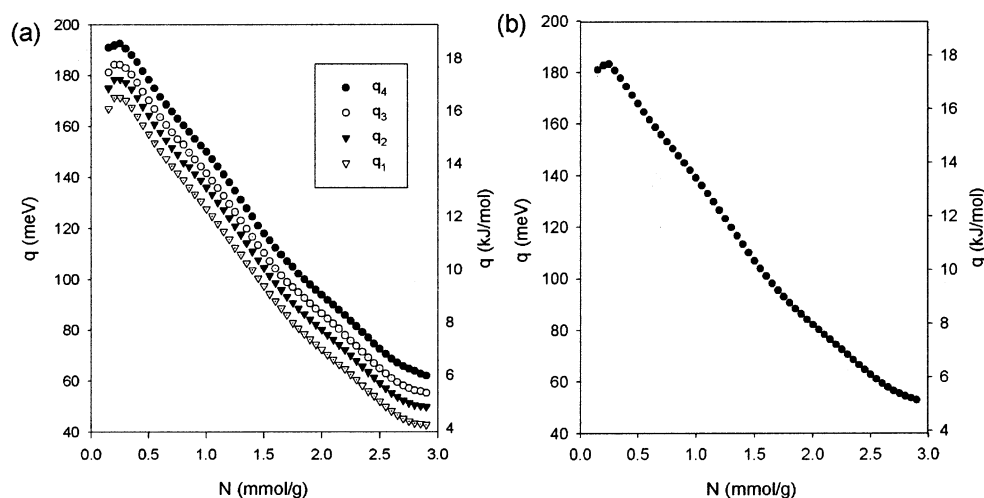


Figure 3. (a) Isothermic heat of adsorption curves for all pairs of temperature intervals examined in this study. q_1 is for 120.53 and 123.5 K, q_2 is for 123.5 and 126.66 K, q_3 for 126.66 and 129.72 K, and q_4 for 129.72 and 133.0 K. (b) Average value of the isothermic heat of adsorption evaluated at each set of temperatures in (a). The y-axis was represented in two different units: meV and kJ/mol. The isothermic heat of adsorption shows a maximum value of 182 meV at N of 0.25 mmol/g.

argon is about 182 meV, and this is comparable to the maximum value of nitrogen (182.6 meV).¹⁶

A main reason for the decrease of the heat of adsorption after the maximum value is the heterogeneity of the nanotube bundles. This implies that the adsorption occurs in different binding energy sites with increasing coverage. In the case of open-ended nanotube bundles, the adsorption sites change from inner sites to the ridges, and outer sites. The abrupt decrease of the heat of adsorption shows that the binding energies among the adsorption sites are much different.

The condition of thermodynamic equilibrium between argon molecules adsorbed on nanotubes and argon in vapor allows us to determinate the binding energy. When the system reaches an equilibrium state, the value of the chemical potential of the adsorbed argon must be equal to that of the vapor that coexists with Ar adsorbed inside the cell. We also expect that at a very low coverage the adsorbate can be considered as a one-dimensional ideal gas and the vapor can be treated as an ideal three-dimensional gas. With these conditions, the binding energy can be estimated in terms of the heat of adsorption, as follows,²² $q_{st} = E_b + 2kT$. Here, “2” in the second term of the right side is related to the difference in the number of degrees of freedom between the vapor and the adsorbed phases. This relation was applied to the coverage below the bump in Figure 3. The estimated average value of the binding energy, E_b , was 180.13 meV. In our previous study,¹⁶ we reported that the binding energy at the first adsorbed sites on open-ended nanotubes is about twice as great as that at the first adsorbed sites on close-ended nanotubes. This implies that the adsorption sites added by an opening process, that is, the inner sites of the nanotubes, have higher interaction energies than those of other sites. The argon, most probably the same as the case of nitrogen, has a tendency to adsorb on inner sites of nanotubes prior to the adsorption on other sites, and the evaluated value of the binding energy of Ar seems to correspond to that of the inner sites of nanotubes. The binding energy of Ar is about twice as high as that of Ar on the graphite (92 meV).²⁴ This is related to the curvature of the tube: i.e., CNTs have a larger number of the nearest neighbors than graphites.

IV. Conclusions

The adsorption isotherm of Ar on open-ended nanotube bundles was measured at different temperatures. The amount

of argon, which corresponds to the first coverage adsorbed on open-ended carbon nanotube bundles, was about 3 mmol/g. We found that the maximum value of the isothermic heat of adsorption is comparable to that of nitrogen on open-ended nanotube bundles and that the value of the binding energy at low coverage is 180.13 meV. This value corresponds to the binding energy at inner sites on nanotubes and is twice as high as that of Ar on graphites. This indicates that the nanotubes have binding energy sites higher than those of graphite and makes the nanotube a more useful material.

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