

Thermodynamic properties of benzene adsorbed in activated carbons and multi-walled carbon nanotubes

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Received 21 December 2005; in final form 1 February 2006

Available online 24 February 2006

Abstract

The efficiency of multi-walled carbon nanotubes (MWNTs) and traditional activated carbons for benzene adsorption is studied. Benzene adsorption isotherms and the related values of the calorimetric adsorption enthalpy at 298 K are used to calculate the entropy and the state of the adsorbed molecules. The analysis of the experimental data leads to the conclusion that both thermodynamic functions are related to the kind of porosity present in the studied materials. Our results also show that in the case of MWNTs the adsorption between the tubes is a very important effect which determines the mechanism of this process.

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1. Introduction

Lately, a great attention has been devoted to carbon nanotubes (CNTs) as potential adsorbents for various molecules. They can be applied in the separation of organic molecules with different sizes and shapes [1]. These properties depend not only on the canal diameter but also on the dispersion of diameters and on the functional groups at the edges. In order to understand the molecular sieving effects, the state of the adsorbate confined in the nanopores of various kinds of carbonaceous materials should be known.

Benzene adsorption measurements have been recommended by Dubinin et al. many years ago [2] as the standard test for determining the porosity parameters of activated carbons (ACs). Moreover, since the benzene ring is the major component of aromatic molecules, the latter are known to interact with graphite and with the graphitic

walls of CNTs [1,3–12]. The weak intermolecular forces in a system composed of a closed-shell organic molecule immobilized on a CNT surface are π -stacking interactions. This kind of physisorption and non-covalent functionalization does not significantly perturb the atomic structure of CNTs, their electronic and transport properties, by contrast to their covalent counterpart [3]. The results presented by Tournus et al. [3] imply that the most favorable adsorption geometry must result from bridge to stack when increasing the nanotube diameter, with a cross-over at a given size which is found to depend on the CNTs chirality. Moreover, DFT calculations indicate that changing the substituents on benzene rings has a negligible effect on their interaction with a graphitic slit shape pore or a CNT, unless the group is bulky and can interact with a larger fraction of the interior of the nanopore [6]. Although the latter results show that there is a measurable adhesion between benzene-like molecules and graphite slit shape pores or CNTs, there is very little evidence of selectivity between different types of aromatic molecules.

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The problem of adsorption of organic compounds inside CNT type materials has been also discussed on the basis of theoretical [1,9] and experimental studies [6,10,13–19]. Bhide and Yashonath [9] investigated the structure and dynamic of C_6H_6 in the one-dimensional channels of narrow carbon nanotubes. They observed that the motion in this material occurs predominantly with the benzene plane perpendicular to the motion direction, and that the benzene plane orientation is strongly influenced by the channel diameter and the diameter modulation along the channel. In the case of single-wall carbon nanohorns (SWNHs), the adsorbed benzene molecules are stabilized mainly by weak self-interactions at the central regions of SWNHs, and they are quickly desorbed [5,18]. The tube tips, the walls, and the central regions of the hollow space were found to be the adsorption sites.

It is well-known that enthalpy measurements can provide valuable information on the adsorption mechanism, together with the energetic and structural heterogeneity of adsorbents, the adsorbate–adsorbent interactions, as

well as the structure of the adsorbate confined in pores [20–22]. However, because of the time consuming experiments, the importance of this research is underestimated. Moreover, significant differences have been found between the isosteric (the bunches of isotherms are taken into account) and the differential (i.e., directly measured experimentally) enthalpy of adsorption [20,22]. We have widely discussed the necessity of using the data from calorimetric measurements (in comparison with those calculated from the Clausius–Clapeyron equation) for the description of adsorption processes [20,22].

In this Letter, we study the efficiency of multi-walled carbon nanotubes and traditional activated carbons for the removal of benzene. To our knowledge, it is the first time that the enthalpy of benzene adsorption is studied in CNTs.

2. Experimental

The porous carbon samples used in this work were a strictly microporous activated carbon film (Cox [23,24]),

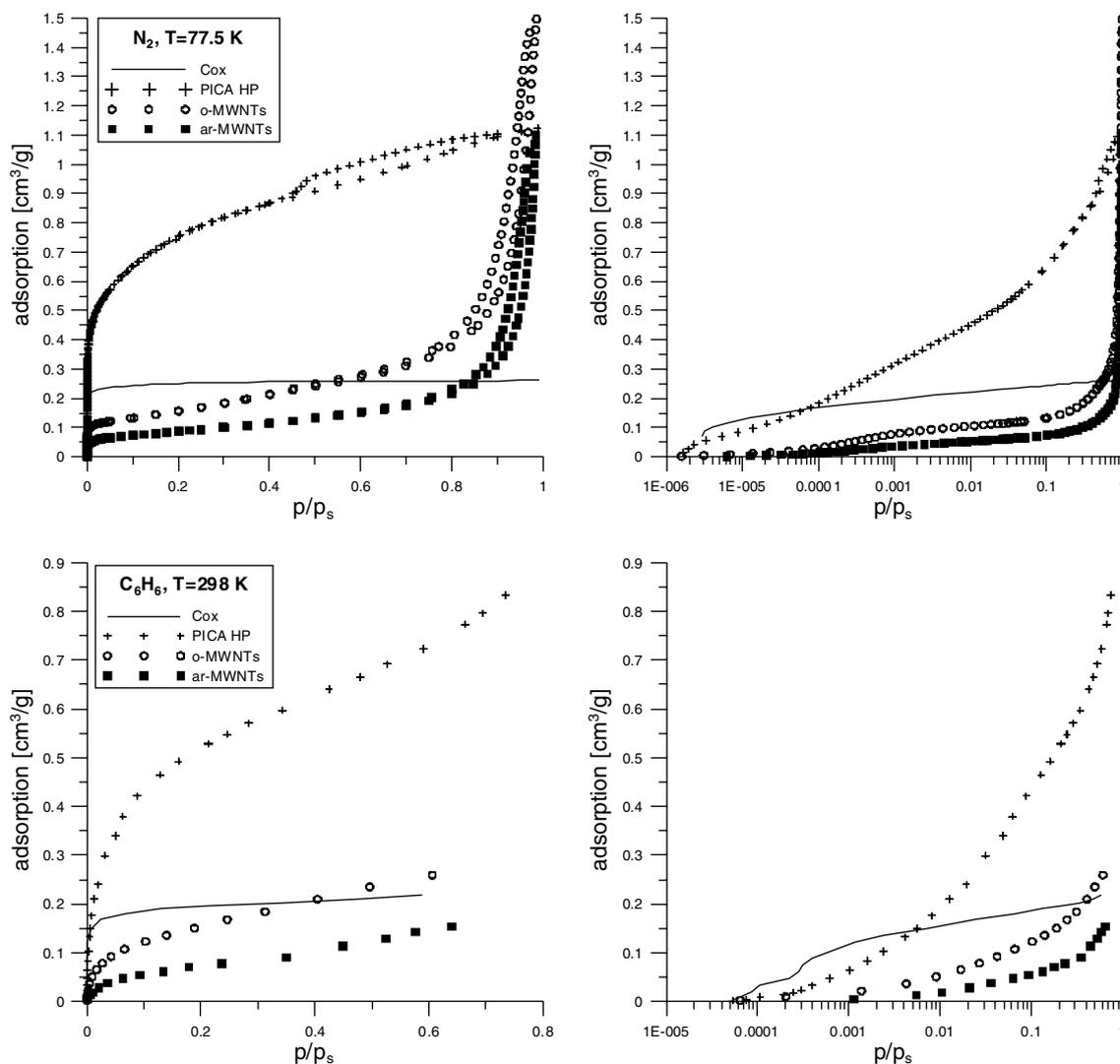


Fig. 1. Nitrogen and benzene adsorption isotherms for the studied carbonaceous adsorbents.

a mesoporous activated carbon (PICA HP, PICA Carbon, Australia [25,26]), as-received MWNTs (ar-MWNTs) and opened MWNTs (o-MWNTs). The preparation of MWNTs, their opening and characterization are described in Refs. [26,27].

The nitrogen adsorption isotherms at 77 K were obtained with an ASAP 2010 (Micromeritics, USA), in the relative pressure range from about 1×10^{-6} up to 0.999 p/p_s . The benzene adsorption isotherms were recorded at 298 K (1×10^{-5} –0.6 p/p_s) applying a volumetric apparatus with Baratron pressure transducers (MKS Instruments, Germany). The related enthalpy of benzene adsorption was measured with an isothermal Tian–Calvet microcalorimeter as described previously [20,22,28]. The experimental errors are equal to $\pm 1\%$ for the adsorption isotherms and $\pm 1.5\%$ for enthalpy. Before all adsorption measurements, the adsorbents were outgassed for 2 h at 473 K.

3. Results and discussion

The nitrogen adsorption isotherms of the four samples are compared in Fig. 1. Cox gives a type I isotherm in the Brunauer, Emmet and Teller classification, whereas that of PICA HP is of type II. By contrast, CNTs demonstrate type IV isotherms characterizing mesoporous materials. For the mesoporous adsorbents (PICA HP and both types of MWNTs), hysteresis loops are visible between the adsorption and desorption isotherms. The shape of the isotherms progressively changes with the contribution of mesopores to the total porosity. After opening of the nanotubes tips, the adsorption at low relative pressure remains identical, confirming that the tubes opening did not create additional micropores [27]. The central canal contributes to enhance the adsorbed amount at higher values of relative pressure [27]. Since the hysteresis loop is

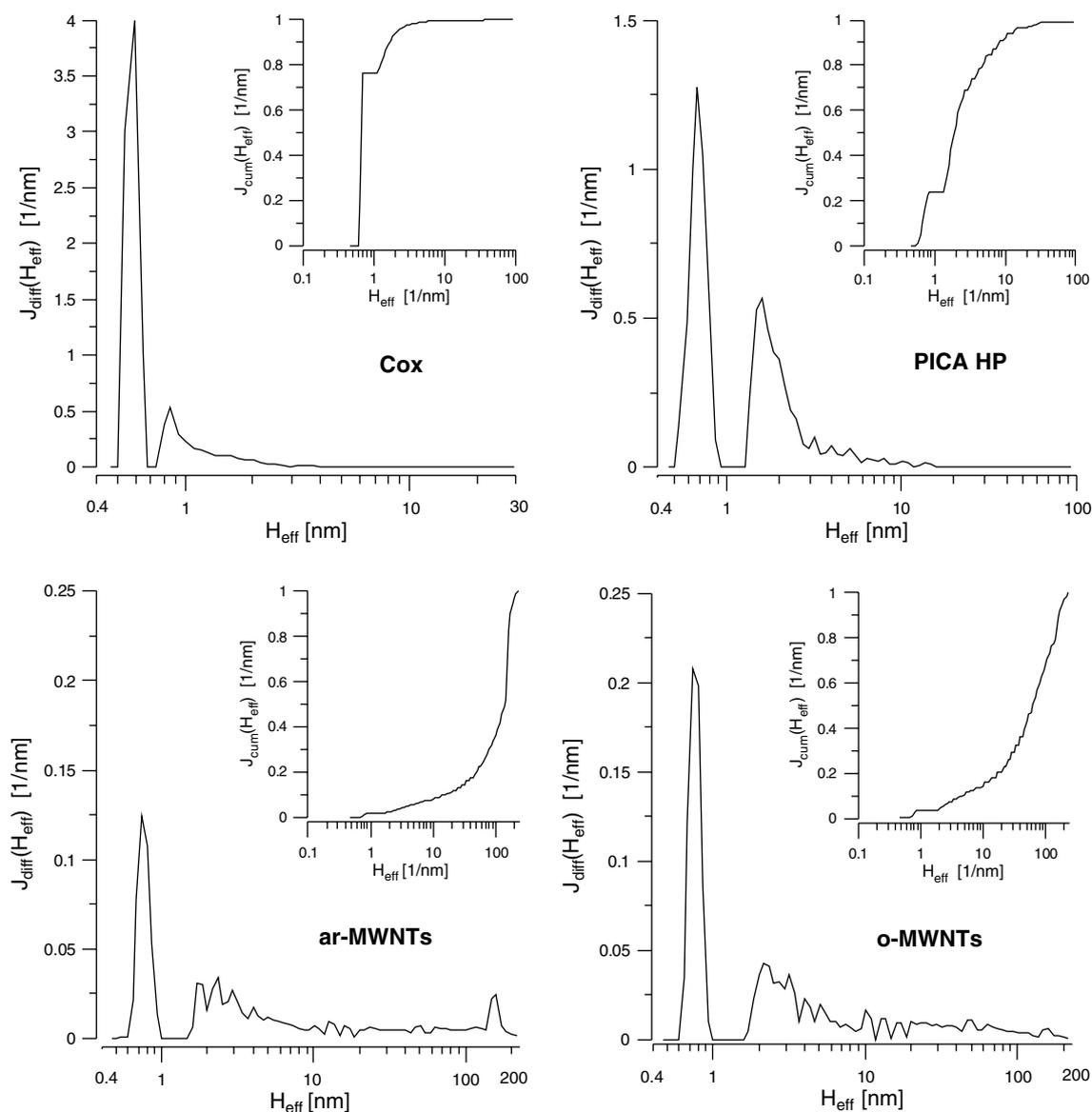


Fig. 2. Differential and cumulative (inset) pore size distributions generated on the basis of the Nguyen–Do method [24,29,30].

only slightly broadened after opening, we conclude that the two kinds of mesopores, due to entanglement and central canal, are of comparable size. The analysis of the nitrogen adsorption–desorption isotherms shows three characteristic regions. In the first one (i.e., up to $0.6 p/p_s$), the adsorption decreases in the following sequence: PICA HP > Cox > o-MWNTs > ar-MWNTs. In the second one ($0.6–0.8 p/p_s$), since the adsorption on Cox reaches a plateau, adsorption in opened MWNTs is larger. Finally in the high pressure range (above $0.8 p/p_s$), we observe a further abrupt increase in the adsorption on ar-MWNTs and o-MWNTs due to capillary condensation. It is very interesting that in the case of benzene adsorption, despite differences in the shapes and molecular diameters, similar behavior with nitrogen is observed in the first considered range (Fig. 1).

The differential and cumulative pore size distribution (PSD) curves were evaluated from the low-temperature ($T = 77$ K) nitrogen adsorption data. We applied the methods leading to exactly the same PSDs as those obtained via the GCMC and/or DFT methods. Therefore, for ACs the original Nguyen and Do method [24,29] was applied. For CNTs we applied the same method, but assuming a cylindrical pore geometry [30]. The PSD curves presented in Fig. 2 suggest that the carbon materials differ in porosity. The carbonaceous film (Cox) is strictly microporous, having a very narrow pore size distribution (i.e., typical for molecular sieves). By contrast, PICA HP and MWNTs contain mesopores. It should be pointed out that the amount of wide pores is greater in CNTs than in PICA HP. On the other hand, there are large similarities in the pore texture of both types of nanotubes. After the opening of tips, a slight increase in

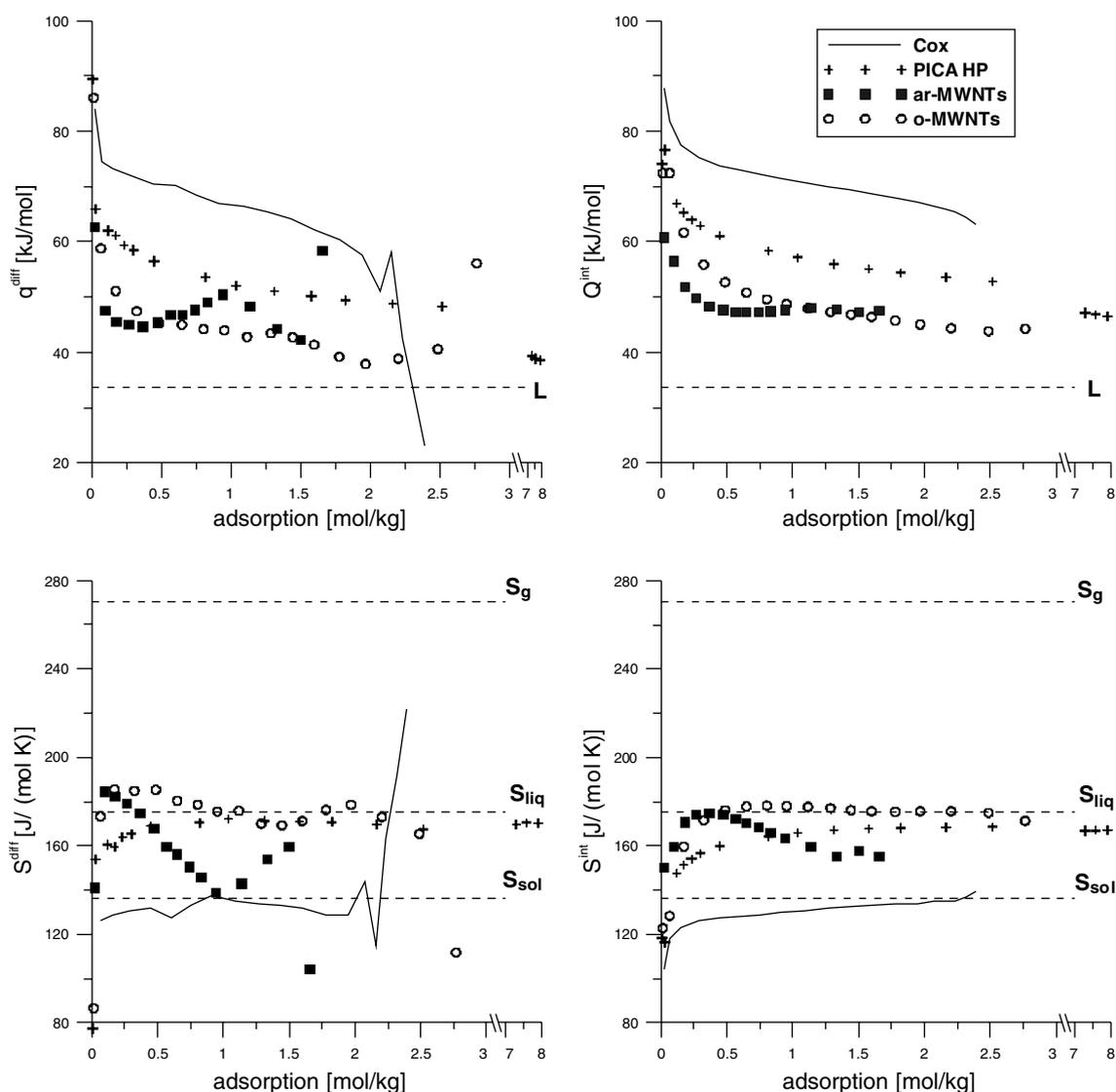


Fig. 3. Comparison of the data for adsorbed benzene in the four substrates: differential molar enthalpy of adsorption (q^{diff}), integral molar enthalpy (Q^{int}), differential and integral molar entropies (S^{diff} and S^{int} , respectively). The horizontal dashed lines represent the values of the entropy of gas ($S_g = 269.2$ J/(mol K)), liquid ($S_{\text{liq}} = 173.2$ J/(mol K)), solid ($S_{\text{sol}} = 136.50$ J/(mol K)), and the enthalpy of benzene condensation $L = 33.54$ kJ/mol.

the micropore volume to the total porosity (from 2.2% up to 4.1%) and a more significant one in the contribution of mesopores is observed (from 18.3% up to 38.7%). Therefore, it can be stated here that the procedure of the opening of nanotubes, applied in this Letter, develops mainly mesoporosity. The differential and integral molar entropy (S^{diff} and S^{int} , respectively) of adsorbed benzene molecules (Fig. 3) were calculated following the well-known procedure described previously [20,31]. The standard-state pressure, $p_0 = 101325$ Pa was taken as reference. Additionally, we used the following values for the enthalpy of condensation ($L = 33.54$ kJ/mol), the entropy of gas ($S_g = 269.2$ J/(mol K)), liquid ($S_{\text{liq}} = 173.2$ J/(mol K)) and solid ($S_{\text{sol}} = 136.5$ J/(mol K)) [31]. The enthalpy of adsorption (q^{diff} and Q^{int} , respectively) is the largest for Cox, due to the strong enhancement of the adsorption potential in micropores, and the smallest for as-received MWNTs. From the analysis of the integral and differential molar entropy of benzene adsorbed in the pores, it is seen that benzene is in a quasi-solid state in the narrow slit shape pores of Cox. For PICA HP, and o-MWNTs the adsorbed state is close to liquid-like. Very interesting is the entropy plot for ar-MWNTs, where at low loadings a similarity with opened carbon MWNTs is observed; however, at larger adsorption rates the entropy decreases and tends to the value between liquid and solid benzene. This can be explained as follows. It is well known that, in the case of the theoretical description of adsorption in carbon nanotubes, not only the distribution of different nanotube diameters should be considered, but also the effect of imperfect lateral ordering and adsorption in the heterogeneous interstitial channels, as shown by Shi and Johnson [32] and Bienfait et al. [33]. Therefore, two types of benzene molecules are present in the case of nanotubes: those within CNTs (intra-benzene) and those located outside the nanotube cylinders. The amount of intra-benzene is significantly higher in opened MWNTs than in as received MWNTs. These results fit well with computer simulation showing that the entropy of intra-benzene in mesopores is larger than the entropy of molecules adsorbed between tubes (and/or in narrow cylinders) [9]. Thus, the opening of the tubes leading to the development of mesoporosity, causes the increase in the number of intra-benzene molecules in opened MWNTs. Those molecules having larger entropy than the molecules located outside cylinders rise up the average integral molar entropy of adsorbed phase, in comparison with this observed for closed MWNTs.

4. Conclusions

To our knowledge, this Letter is the first presenting the calorimetric enthalpy of benzene adsorption in MWNTs. It is shown that the values of adsorption enthalpy and entropy of adsorbed molecules are related to the porosity of the materials (i.e., pore shape, diameter and contribution of mesopores to the total porosity). After opening of the tube tips, the pore size distribution remains almost the same, while the pore volume changes. Our results also

show that in the case of ar-MWNTs the adsorption between the tubes is a very important effect and determines the mechanism of this process. Therefore, these results can be useful for the verification of theoretical models and theories describing the adsorption of organic compounds (especially benzene) on carbonaceous adsorbents. To summarize, it should be underlined that measuring only the adsorption isotherms does not give any information on the structure of the adsorbed phase. Hence, the determination of the adsorption enthalpy is necessary for the structural elucidation of the adsorbate behavior.

Acknowledgments

The authors thank Dr. S. Yashonath (Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore) for the useful discussion and critical comments, and also for his valuable suggestions concerning the mechanism of benzene adsorption in CNTs. They also thank Dr. Gayle Newcombe (Australian Water Quality Centre, Salisbury, Australia) for sending the PICA HP sample. It should be pointed out that this adsorbent was extensively investigated at *Carbon Round Robin International Inter-Laboratory Trial for the Determination of Activated Carbon Pore Volume Distributions* (http://www.waterquality.crc.org.au/carbon_rr/round_robin_index.htm).

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