Benzene adsorption on carbonaceous materials: The influence of pore structure on the state of the adsorbate

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Received 23 January 2006; received in revised form 29 March 2006; accepted 10 May 2006
Available online 14 June 2006

Abstract

Experimental nitrogen (T = 77 K) and benzene (T = 298 K) adsorption isotherms measured on eight carbons possessing various porous structure are used to evaluate the parameters characterizing the geometric heterogeneity. Additionally, the experimental energetic measurements, i.e. the enthalpy and adsorption related entropy of adsorbed benzene, are taken into considerations. The analysis of experimental data leads to the conclusion that the entropy of C6H6 adsorbed in strictly microporous materials approaches the value characteristic of quasi-solid (a partially ordered structure). On the other hand, for adsorbents possessing wider pores (i.e. the contribution of mesopores to the total porosity is significant) the differential entropy approaches to the value characteristic of liquid. We test a key assumption of the theoretical models describing the mechanism of adsorption, that the adsorbed phase is considered as liquid. This verification leads to the conclusion that the various orientation of the adsorbate in the pore space should be taken into consideration in the theoretical assumptions of a model and in its thermodynamic verification. The significant improvement in the description of benzene experimental data for microporous adsorbents is observed if the “correction term” in the enthalpy of adsorption is considered. This term is correlated with the average pore diameter of studied solids. Our results of the critical pore diameter where the system undergoes an order-disorder transition are very close to obtained by Chakrabarti and Kerkhof via the computer simulation experiments.

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Keywords: Benzene adsorption; Thermodynamics; Porosity; Solidlike and liquidlike structure

1. Introduction

Benzene adsorption experiments are carried out in many laboratories and C6H6 is one of the most frequently used adsorbates [1–6]. Benzene adsorption measurements were recommended by Dubinin and coworkers many years ago [7–9] as the standard test for the calculation of the porosity parameters. On the other hand, it is well-known that adsorption as well as the enthalpy of adsorption can provide valuable information concerning the mechanism of the process, the energetic and structural heterogeneity of adsorbents, the adsorbate–adsorbent interactions, as well as the structure of adsorbate confined in pores [3,8,10–13]. However, the importance of this research is underestimated due to, among other things, mainly by the time consuming experiment. Consequently, the thermodynamic verification of the most popular methods of porosity determination (density functional theory (DFT)) [14], the Horvath–Kawazoe approach [15–18], the Nguyen–Do model (ND) [18–27], Dubinin’s theory of the volume filling of micropores (TVFM) [8,10,12,17,18], and others [28–32] on the basis of the enthalpy data is rarely met in the literature.

The simplest carbon structure is graphite. Therefore, physisorbed layers of benzene on the surface of this adsorbent have been studied extensively. Isirikyan and Kiselev [33] show,
Nomenclature

ASA adsorption stochastic algorithm
A_{\text{pot}} the free energy of adsorption (\( \equiv -\Delta G^{\text{ads}} \))
BET the Brunauer, Emmet and Teller theory
DC the determination coefficient
DFT the density functional theory
\( \Delta G^{\text{ads}} \) the free energy of adsorption equal to RT \( \ln (p/p_s) \)
\( H_{\text{eff}} \) the effective pore width (diameter)
\( H_{\text{eff,av,ND,micro}} \) the micropore average effective width (up to \( H_{\text{eff}} = 2.0 \text{ nm} \))
\( H_{\text{eff,av,ND,tot}} \) the average effective width of all pores taken into consideration in the ND method (up to \( H_{\text{eff}} = 233.9 \text{ nm} \))
\( H_{\text{eff,\epsilon}} \) the critical value of the effective pore width evaluated for \( \Delta H^{\text{corr}} = 0 \)
\( \Delta H^{\text{corr}} \) the correction term related to the partially ordered structure of adsorbed phase
\( \Delta H^{\text{cryst}} \) the enthalpy of crystallization
\( \Delta H^{\text{vap}} \) the enthalpy of vaporization
\( \lambda(H_{\text{eff}}) \) the differential pore size distribution
\( n_a \) the number of adsorbed moles
ND the Nguyen and Do method
PSD the pore size distribution
\( q_{\text{diff}} \) the differential enthalpy of adsorption
\( Q_{\text{int}} \) the integral enthalpy of adsorption equal to \( (1/n_a) \int_0^n q_{\text{diff}} \, dn_a \)
\( Q_{\text{int,max}} \) the maximum value of the integral enthalpy of adsorption corresponding to \( S_{\text{int,max}} \) (the same range of adsorption is analyzed)
\( Q_{\text{int,plat}} \) the average value of the plateau region of the integral enthalpy of adsorption corresponding to \( S_{\text{int,plat}} \)
\( R \) universal gas constant
\( S_{\text{BET}} \) the apparent surface area (calculated in the range of relative pressure ca. 0.05–0.3)
\( S_{\text{diff}} \) the differential molar entropy of adsorbed molecules equal to \( S_g = (q_{\text{diff}}/T) - R \ln (p/p_s) + R \)
\( S_{\text{DFT}} \) the surface area of all pores calculated on the basis of DFT
\( S_{\text{micro, DFT}} \) the surface area of micropores calculated for all the pores with diameters smaller and/or equal to 2 nm
\( S_{\text{meso, DFT}} \) the surface area of micropores calculated for all the pores with diameters larger and/or equal to 2 nm and smaller and/or equal to 50 nm
\( S_g \) the molar entropy of gas
\( S_{\text{int}} \) the integral molar entropy of adsorbed molecules equal to \( (1/n_a) \int_0^n S_{\text{diff}} \, dn_a \)
\( S_{\text{int,max}} \) the maximum value of the integral entropy of adsorbed molecules (the whole range of adsorption is analyzed)

\( S_{\text{int,plat}} \) the average value of the plateau region of the integral entropy of adsorbed molecules
\( S_{\text{liq}} \) the molar entropy of liquid
\( S_{\text{sol}} \) the molar entropy of solid
\( T \) the temperature
TVFM theory of the volume filling of micropores
\( V_{\text{meso, DFT}} \) the volume of the mesopores with diameters (\( H_{\text{eff}} \) larger and/or equal to 2 nm and smaller and/or equal to 50 nm determined from the ND method
\( V_{\text{ND}} \) the total volume of the pores determined from the ND method (up to \( H_{\text{eff}} \) equal to 234 nm)
\( V_{\text{micro, ND}} \) the total volume of the micropores with diameters (\( H_{\text{eff}} \) smaller and/or equal to 2 nm determined from the ND method

Basing on the experimental data, that almost constant adsorption energy over a wide range of coverage is a clear indication of a low level of lateral interactions between neighboring adsorbate molecules. Neutron diffraction studies [34] confirm this observation and show that benzene adsorbs on the basal planes of graphite forming a two-dimensional monolayer in which all the molecules lie flat, or very nearly (\( T < 150 \text{ K} \)). At higher coverage and temperature the molecules have greater orientational freedom, i.e. benzene molecules gradually move away from the flat configuration until the perpendicular orientation predominates. The review of other experimental studies is discussed elsewhere [35].

Activated carbons in the comparison with graphite possess more complicated and so far unknown structure. Only several experimental studies describing the state of benzene adsorbed in pores and evaluating the freezing temperature have been reported. Watanabe et al. [36] stated, based on differential scanning calorimetry (DSC) results, that the structures of liquid and solid phases of C₆H₆ in graphitic micropores of ACFs reported similar effect. The carbon studied by them possessed a geometrical restriction for the formation of the well-crystalline solid structure. Babaev et al. [37], who investigated the enthalpy of benzene adsorption on an activated carbon AC, reported similar effect. The carbon studied by them possessed a significant amount of mesopores (however, the porosity of these samples was not sufficiently characterized). They noticed that for the wide distribution of micropores it is impossible to find the fraction of micropores with diameters close to the diameter of C₆H₆ molecule, in which adsorbed molecules would lose all the translational and rotational degrees of freedom. They concluded that the entropy of adsorbed benzene is located between the value characteristic of a liquid, \( S_{\text{liq}} \) and the entropy of a solid, \( S_{\text{sol}} \) respectively. It should be pointed out that similar results concerning the adsorbate properties confined in the slit-like nanopores of carbonaceous adsorbers have been published for other adsorbate–adsorbent systems, for example for pure alkanes and binary alkane mixtures adsorbed onto graphite (the combination of differential scanning
calorimetry and incoherent elastic neutron scattering) [38], CCl₄ molecules confined in graphitic micropores (in situ X-ray diffraction) [39,40] or in activated carbons (adsorption and enthalpy of adsorption data) [10,11,18,41], water confined in a activated carbon fibres (DSC and dielectric relaxation spectroscopy) [42].

On the other hand, interesting results concerning the configurations of benzene onto the carbon surface (and/or between two graphitic surfaces) can be obtained on the basis of the theoretical considerations, i.e. quantum calculations [43–47] and computer simulations [48–56]. It should be pointed out here that the simulations of benzene adsorption can be performed, if one assumes a model of intermolecular potential (i.e. adsorbate–adsorbate–adsorbent). Moreover, it is well known that benzene molecules are hardly for modeling. Many empirical, semi-empirical, and theoretical relations have been taken into account in order to describe adsorbate–adsorbate and adsorbate–adsorbent interactions assuming different phenomena. On the other hand, it is well-known that for the different functions describing these interactions (not necessarily for benzene molecules) different results can be obtained [19–27,58–69]. Concluding, the problem of the choice the appropriate potentials is very important, however, unsolved so far.

In order to determine the structure and energy of the benzene films adsorbed on graphite Vernov and Steele [48,49] performed computer simulation experiments at two temperatures, i.e. 85 and 298 K. The orientation of benzene molecules (T = 85 K) is not entirely parallel to the surface. The fraction of nonparallel molecules on the monolayer is small (~10%) but increases with increasing coverage. The decrease in the benzene graphite interaction (T = 298 K) on this homogeneous surface is a consequence of the changing orientation of the adsorbate molecules relative to the surface. Vernov and Steele estimated that 45% of molecules in the monolayer are perpendicular to the surface at ambient temperature. Assuming a random distribution, this gives 30% co-parallel pairs, 20% that are both perpendicular, and 50% that have one parallel, one perpendicular. Few years later Matties and Hentschke [50] presented the results of a molecular dynamics simulation of a film of benzene adsorbed onto the basal plane of graphite at monolayer coverage over a wide range of temperatures (60–320 K). The results indicated a solid–liquid transition around 140 K which compares well with the published experimental phase behavior. Next, those authors [51] extended their studies to include the effects of the increasing coverage to multiple layers of benzene adsorbed onto graphite. They observed that the degree of order beyond the nearest neighbors degrades rapidly with increasing coverage and is virtually nonexistent for layers not directly adsorbed onto the surface. In general, the static and dynamic properties at higher coverages are quite similar at comparable temperatures, but are much different from those of the monolayer. Similar results were obtained by Palermo et al. [52]. They found a discontinuous change in anchoring from planar to normal on going from the first to the second adsorbed layer. Palermo et al. [52] concluded that the structure of the first two adsorbed layers is not affected by different director orientations induced in the bulk liquid crystal, but is entirely determined by the surface potential. Very interesting results were recently published by Do and Do [69]. Using numerous data of benzene adsorption measured on graphitized thermal carbon black at various temperatures, those authors have found that the intermolecular interactions (dispersive and electrostatic ones) between benzene molecules must be accounted for to describe correctly the adsorption isotherm as well as the isosteric enthalpy.

The behavior of benzene molecules confined in pores of the carbonaceous adsorbents is more difficult to simulate in comparison with graphite surfaces. For dense physisorbed layers composed of larger molecules, the straightforward simulation, starting from an arbitrary molecular arrangement (which during the simulation develops into the thermodynamically stable structure, including surface induced segregation, adsorption, and, possibly translational and/or orientational ordering within the interface) is much more difficult. Therefore, there are only several papers describing results obtained by advanced computer calculations and simulations of benzene adsorbed between graphite surfaces at various densities, temperatures and pore widths. Sliwinska-Bartkowiak et al. [53] reported both experimental measurements (DSC and DS) and molecular simulations (Monte Carlo simulations and Landau free energy formalism) of the melting and freezing behavior of benzene adsorbed in activated carbon fibers, having a mean pore width around 1.7 nm. The evaluated value of the comparison of freezing temperatures (expressed as T_{f,pore}/T_{f,bulk} from simulations is equal to 1.25. Similar results (i.e. T_{f,pore}/T_{f,bulk} equal to 1.23 for a mean pore width of 1.1 nm) were observed by Kaneko and coworkers [36,54] using the DSC technique. Clifton and Cosgrove [55] studied the structure of liquid benzene confined between two graphite surfaces (for the selected widths, i.e. 0.5, 2.0, and 3.2 nm) at ambient temperature using molecular dynamics simulations. They reported that distribution of equilibrated benzene would appear to be homogeneous around the centre of the slit, with at least one structured surface layer apparent in the vicinity of each wall. Both the number and angle distribution results show majority of adsorbed benzene molecules lying close to horizontal configuration with respect to the surface. However, a significant proportion (~40%) is close to a perpendicular configuration (pore width equal to 3.2 nm). Finally, they stated that for the benzene–graphite system current experimental design is inadequate for providing a detailed molecular picture, as compared with computer simulations.

Bouyermaouen et al. [56,57] studied the properties of benzene molecules confined between graphite surfaces at various temperatures (207, 228, 259, 282, 300, 322, and 365 K), for the pore widths (1.836, 2.336, 2.836, and 3.950 nm), and only for several chosen densities, using molecular dynamics simulations. It should be pointed out that adsorption isotherms were not calculated by them. At low densities, the chemical potential for confined benzene has much smaller values than the values for the bulk benzene. One of the main conclusions of their work is the existence of the orientational ordering of the benzene molecules in the adsorbed layers. They adsorb parallel
to the surface in monolayer. In the second and third layers very few of adsorbed C<sub>6</sub>H<sub>6</sub> are disturbed (some of them are perpendicular to the wall surface). Moreover, Bouyermouen et al. [56,57] observed that the local ordering is only very slightly affected in the above mentioned range of temperatures. The orientation of benzene molecules next to a graphite wall becomes however, increasingly flat and the adsorbed layers become narrower as the temperature decreases. At the highest densities studied, they find a bulk-like behavior of benzene in the middle of the pore surrounded by more or less structured layers. On the other hand, in the narrow pore the adsorbate molecules are tilted perpendicular to the graphite surfaces in the middle of the pore.

Presented above results lead to the statement that for the porous carbons the extensive investigation of the behavior of the benzene molecules confined in the pores should be still continued. This paper presents the result of systematic studies covering the materials selected according to different contributions from meso and microporosity to porous structure. The paper is organized as follows. In Section 2 we describe the experimental measurements, studied carbonaceous materials, and the methodology for calculating the thermodynamic functions. Our results are presented in Sections 3 and 4. The quantitative description of the derivation of benzene from liquid state in nanopores is presented in Section 5. Finally, Section 6 gives a summary of obtained results and conclusions concerning the general mechanism of benzene adsorption in carbonaceous adsorbents possessing various porosity.

2. Experimental

Eight samples of activated carbons, differing in porosity are used in the current study: strictly microporous film Cf, obtained from cellophane by Zawadzki and coworkers [17,70–75]; synthetic microporous carbon A obtained from polyfurfuryl alcohol [10–12,18,75]; commercial strictly microporous

Fig. 1. Nitrogen and benzene adsorption isotherms for the studied carbons.
carbon D55/2 (Carbo-Tech, Essen, Germany) [75]; commercial micro-mesoporous carbons: AHD (Hajnówka, Poland) [75–81], WD (Hajnówka, Poland) [75–81], D43/1 (Carbo-Tech, Essen, Germany) [75–81], and PICA PCO (PICA Carbon, Australia) [82]; and micro-mesoporous commercial carbon possessing wider pores than all the mentioned above materials, PICA HP (PICA Carbon, Australia) [82–86]. Since some of the adsorbents are not accessible commercially, the detailed description of their preparation procedure can be easily found in respective references.

Nitrogen adsorption isotherms at T = 77 K were measured using an ASAP 2010 volumetric adsorption analyzer from Micromeritics (Norcross, GA, USA) in the relative pressure (p/p₀) range from about 1 × 10⁻⁶ up to 0.999. Benzene adsorption isotherms were measured at 298 K (1 × 10⁻⁶ to 0.6 p/p₀) applying the volumetric apparatus with Baratron pressure transducers (MKS Instruments, Germany). The related enthalpy of adsorption were obtained applying the isothermal Tian–Calvet microcalorimeter described previously [76–81,87,88]. The errors of the measurements are as follows: for the adsorption isotherms ±1% and for the enthalpy ±1.5% [76–81,87,88]. Before adsorption measurements the samples were outgassed at 473 K.

The thermodynamic functions, i.e. differential and integral molar entropy of adsorbed molecules (Sdiff and Sint, respectively) and the differential enthalpy of adsorption, the integral molar enthalpy of adsorption (Qm) were calculated following the well-known procedure described detailed previously [6,12,17,18,87,88] on the basis of the values of adsorption (n_a) and the differential molar enthalpy of adsorption (qdiff) (both are measured experimentally).

3. Textural characterization of activated carbons

Experimental nitrogen adsorption isotherms measured at 77 K for all studied samples are compared in Fig. 1. Adsorption isotherms for D55/2 and Cf are of type I in the Brunauer, Emmet and Teller (BET) classification, the remaining are of type II. In the other words, it is seen from Fig. 1 that the shape of isotherms progressively changes with the decrease in microporosity (for example, the comparison of Cf with PICA HP). Moreover, when taking look at these plots, the shape of isotherms for some materials become upward at higher relative pressure region (for PICA HP, especially). This behavior confirms that meso- and macropores are present in some samples. However, this upward deviation is rather insignificant for most materials. For some nitrogen–adsorbent systems the hysteresis loops are also insignificant (A, WD, and AHD). The visible difference between the adsorption and desorption branches is clearly observed only for PICA HP. Hence, the pore structure in all carbons consist mainly of micropores; however, the number of mesopores cannot be neglected for some samples. From the analysis of the data in Table 1 it is seen that all investigated samples have apparent BET surface areas (S_BET) close to those calculated for the typical commercial carbons. However, for the studied materials significant differences between S_BET values are observed. The lowest values are evaluated for Cf and largest for PICA HP (equal to 520.1 and 1661.3 m²/g, respectively). Also significant differences between pore volumes are visible (equal to ca. 0.3 and 1.1 cm³/g, respectively).

It should be pointed out that in the current study we are interested in the evaluation of the contribution of micropores and/or mesopores to the total porosity. Therefore, important information about the pore structure of adsorbents is obtained from the comparison of the contribution of the micropore volume (V_{micro}ND) with the contribution of mesopore volume (V_{meso}ND). In other words, the mesopore volume (calculated for H_{eff} ≈ 50 nm from the cumulative pore size distribution) is divided by the volume of micropores with diameters smaller than and/or equal to 2 nm (i.e. V_{meso}ND × 100%/V_{micro}ND). Similar calculations are carried out for V_{meso}DFT and V_{micro}DFT, respectively (i.e. V_{meso}DFT × 100%/V_{micro}DFT). The respective evaluated values are given in parentheses in Table 1. The analysis of them shows that the carbonaceous film Cf and activated carbons D55/2 and A, contrary to PICA HP, have pores where the micropore filling process predominates. Recapitulating, studied adsorbents can

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Cf</th>
<th>D55/2</th>
<th>A</th>
<th>WD</th>
<th>AHD</th>
<th>D43/1</th>
<th>PICA PCO</th>
<th>PICA HP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface areas (m²/g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S_BET</td>
<td>520.1</td>
<td>616.0</td>
<td>823.9</td>
<td>1099.7</td>
<td>1387.3</td>
<td>990.5</td>
<td>835.6</td>
<td>1661.3</td>
</tr>
<tr>
<td>S_BET DFT</td>
<td>641.3</td>
<td>643.8</td>
<td>697.9</td>
<td>739.2</td>
<td>775.9</td>
<td>570.7</td>
<td>724.6</td>
<td>903.2</td>
</tr>
<tr>
<td>S_DFT</td>
<td>0.4 (0.06%)a</td>
<td>0.3 (0.04%)a</td>
<td>4.5 (0.6%)a</td>
<td>47.8 (6.5%)a</td>
<td>67.1 (8.6%)a</td>
<td>40.8 (5.5%)a</td>
<td>40.1 (5.5%)a</td>
<td>268.6 (22.9%)a</td>
</tr>
<tr>
<td>V_{meso}ND</td>
<td>0.252</td>
<td>0.308</td>
<td>0.369</td>
<td>0.513</td>
<td>0.527</td>
<td>0.423</td>
<td>0.393</td>
<td>0.738</td>
</tr>
<tr>
<td>V_{micro}ND</td>
<td>0.009 (3.5%)b</td>
<td>0.009 (3.0%)b</td>
<td>0.016 (4.3%)b</td>
<td>0.039 (7.6%)b</td>
<td>0.109 (20.7%)b</td>
<td>0.033 (7.9%)b</td>
<td>0.046 (11.6%)b</td>
<td>0.371 (50.3%)b</td>
</tr>
<tr>
<td>V_{ND}</td>
<td>0.261</td>
<td>0.323</td>
<td>0.512</td>
<td>0.573</td>
<td>0.826</td>
<td>0.474</td>
<td>0.451</td>
<td>1.122</td>
</tr>
<tr>
<td>Average pore widths (nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_{eff,ND,micro}</td>
<td>0.714</td>
<td>0.779</td>
<td>0.890</td>
<td>0.931</td>
<td>0.952</td>
<td>0.933</td>
<td>0.853</td>
<td>1.038</td>
</tr>
<tr>
<td>H_{eff,ND,tot}</td>
<td>0.742</td>
<td>0.820</td>
<td>0.983</td>
<td>1.054</td>
<td>1.490</td>
<td>1.055</td>
<td>0.980</td>
<td>1.539</td>
</tr>
</tbody>
</table>

The meaning of other parameters is presented in the text.

a V_{meso}DFT × 100%/V_{micro}DFT.
b V_{meso}ND × 100%/V_{micro}ND.
be divided into three groups, those being essentially micro-
porous (Cf, D55/2, and A); those microporous, but having
insignificantly small contribution of mesopores to the total
porosity (WD, D43/1, AHD, and PICA PCO), and those having
additionally meso- and macroporosity (PICA HP).

Further information about the pore structure of the
investigated carbons can be obtained from the analysis of the
differential pore size distributions (Fig. 2). The appropriate
calculations are made for all materials, but only four
representative PSDs are chosen and presented in this figure,
i.e. for Cf, A, PICA PCO, and PICA HP. We have limited our
considerations only to most sophisticated, simplest and the
fastest method of porosity calculation, namely the Nguyen and
Do theory [19–27] with the developed by us previously ASA
algorithm [18,65,75]. We used in this method 82 local isotherms
generating for the effective widths changing from 0.465 to
233.9 nm. Nevertheless, it is easy to show that similar results can
be calculated on the basis of the DFT and ND methods
[18,65,75,89–92]. On the other hand, the analysis of the
differential pore size distributions calculated for all materials
indicates that micropores are grouped around two main
diameters. The most microporous is the carbonaceous film,
Cf. Moreover, the majority of micropores possess the same
diameter (0.5 < H_{eff} < 0.7 nm), V_{meso}^{ND} \times 100\% / V_{micro}^{ND} = 3.5\%.
The samples A and D55/2 (V_{meso}^{ND} \times 100\% / V_{micro}^{ND} is equal to 4.3
and 3.0, respectively) are adsorbents having more heterogeneous
porous structure than the former one. However, PDSs show only
the contribution of micropores. The analysis provided by the ND
method confirms a more gradual development of dispersion of
microporosity in the whole range with an important extension
into the mesopores range for the remaining adsorbents (WD,
AHD, D43/1, and PICA PCO), 7.6 < (V_{meso}^{ND} \times 100\% / V_{micro}^{ND})
< 20.7\%. From Fig. 2 it is seen that PICA HP is activated carbon
with significant amount of mesopores, i.e. the dispersion of
porosity increased with a small engage of mesopores,
V_{meso}^{ND} \times 100\% / V_{micro}^{ND} = 50.3\%.

From the analyzed nitrogen adsorption data, the average
pore diameters were calculated on the basis of the numerical
integration of PSDs for two ranges, i.e. only for micropores
(H_{eff,av,ND,micro}) and for all pores taken into consideration in the
ND method (H_{eff,av,ND,tot}). Analyzing data are also collected in
Table 1 it is seen that significant differences between values of
the average pore diameters, calculated for the above mentioned
ranges, are observed. Moreover, the confirmation of the
changes in the structural parameters (i.e. surface areas and pore
volumes, Table 1) related to the mesopores and/or micropores is
the regular trend reported for the change in the average pore
widths.

![Fig. 2. Differential pore size distributions generated on the basis of the Nguyen–Do method.](image-url)
4. Thermodynamic properties of adsorbed benzene

Benzene adsorption isotherms (the molar volume of liquid benzene equal to 89.40 cm\(^3\)/mol is taken for the calculation of adsorption expressed by the pore volumes per gram of solids), related enthalpy and entropy of adsorption, and the pore size distribution functions are compared in Figs. 1–3. We again applied for benzene adsorption data the method proposed by Do and coworkers with recently tabulated \([17,18,26,27]\) parameters of the intermolecular interactions and the ND method. The PSDs are calculated applying constructed by us ASA algorithm. We used in this method 56 local isotherms (generated for the effective widths changing from 0.48 to 19.62 nm). The comparison of the plots of the pore size distributions calculated from benzene adsorption data are presented in Fig. 2 for selected adsorbents (the same as for nitrogen data). The analysis of Fig. 2 leads to the conclusion that the latter ones are shifted towards slightly larger widths in comparison with curves related to nitrogen adsorption. This is due to larger kinetic diameter of benzene molecule and the various shape of the both adsorbate molecules (i.e. we observe here the pore sieve effect). It should be mentioned that similar behavior was observed previously for different carbons \([17,18]\). The most significant differences are observed for the microporous adsorbent. However, what is the most important, the comparison of the sequence of PSD curves \((\text{C}_6\text{H}_6)\) confirms that there is remarkable effect of carbon porosity on benzene adsorption mechanism and therefore, on its behavior in pores. Thus, it can be stated that these adsorbates predict the same total (acceptable to adsorbate molecules) micropore volumes in spite of the differences in the position of the maximum of PSD curves presented in Fig. 2.

Fig. 3. The comparison of the differential molar enthalpy of adsorption \((\Delta q_{\text{diff}})\), the integral molar enthalpy \((Q_{\text{int}})\), and the differential and integral molar entropies of adsorbed \(\text{C}_6\text{H}_6\) \((S_{\text{diff}}\) and \(S_{\text{int}}\), respectively). Horizontal dashed lines – the values of the entropy of liquid \((S_{\text{liq}} = 173.2 \text{ J/(mol K)}\) and solid \((S_{\text{sol}} = 136.50 \text{ J/(mol K)})\), and the enthalpy of condensation \((L = 33.54 \text{ kJ/mol})\).
Knowing that, for a perfect gas and for the standard state of $p_0 = 101,325$ Pa, the molar entropy of the gas, $S_g$ is equal to 269.2 J/(mol K) at $T = 298$ K [64], the respective thermodynamic functions (i.e. $Q_{int}$, $S_{diff}$ and/or $S_{int}$) were calculated. The final results are presented in Fig. 3. This figure shows that the differences in the enthalpy ($q_{diff}$ or $Q_{int}$) of benzene adsorption between various carbons are large. At low and medium coverages the integral enthalpy is the largest for carbons possessing more microporous structure. Lower integral enthalpy is observed for the adsorbent possessing wider micropores and mesopores. These sequence of curves confirms the correlation between porosity and the enhancement of potential energy. Concluding, the structure of the adsorbed $C_6H_6$ is affected by the widths of pores.

Fig. 3 shows that the differences between plots of $S_{diff}$ and/or $S_{int}$ are also significant. The entropy of molecules adsorbed at small pore loadings on all samples is lower than the entropy of solid benzene. At larger fillings the integral entropy curves locate between the entropy observed for solid and for cooled liquid benzene ($S_{liq} = 173.2$ J/(mol K) [93] and $S_{sol} = 136.5$ J/(mol K) [37], respectively). The lowest integral entropy is achieved (in the medium range of adsorbed amount) for Cf and the largest for PICA HP. In other words, it can be seen that the values of the entropy of adsorbed benzene fall close to the value characteristic of a solid, especially for the strictly microporous carbonaceous adsorbents. On the other hand, the entropy of benzene observed for materials possessing significant amount of wider micropores and mesopores is comparable to the entropy of liquid. As can be seen, for larger adsorption an abrupt increase in differential entropy and enthalpy of adsorption occurs. On the other hand, for PICA HP this effect is not observed due to the domination of the mechanism of

![Fig. 4](image-url)

Fig. 4. The dependence between the average values of the plateau region of $S_{int}$ ($S_{int,\text{plat}}$, squares) or the maximum values of $S_{int}$ ($S_{int,\text{max}}$, triangles, the whole range of adsorption is analyzed) and structural parameters: $H_{eff,av,ND,\text{micro}}$, $H_{eff,av,ND,\text{tot}}$, and $V_{\text{meso}}^{\text{ND}} \times 100%/V_{\text{micro}}^{\text{ND}}$. 
secondary micropore filling. This is caused by the commence-
ment of adsorption in the secondary structure of pores where
differential entropy approaches the value characteristic of a
liquid. It should be pointed out that larger contribution of
micropores to the total porosity causes an abrupt increase in
$S_{\text{diff}}$ and $q_{\text{diff}}$ for lower adsorption.

Thus, from the studies so far undertaken, it is clear that the
differences in entropy values are caused by the orientation of
benzene molecules to the graphite-like walls of the pores. To
confirm this quantitatively we calculated the parameters related
to the order of adsorbed molecules in pores on the basis of the
integral entropy (applying data presented in Fig. 3): the average
value of the plateau region of the integral entropy of adsorption,$S_{\text{int,plat}}$ and the maximum value of this quantity, $S_{\text{int,max}}$ (the
whole range of adsorption is analyzed). Furthermore, we
estimated the corresponding values of integral enthalpy of
adsorption ($Q_{\text{int,plat}}$ and $Q_{\text{int,max}}$, respectively). Fig. 4 shows
selected and representative examples of the correlations found
between $S_{\text{int,plat}}$ or $S_{\text{int,max}}$ and the structural parameters:
$H_{\text{eff,av,ND,micro}}$, $H_{\text{eff,av,ND,tot}}$, $V_{\text{ND}}^{-}\times V_{\text{ND}}^{-}\times V_{\text{meso}}^{-}\times 100%/V_{\text{micro}}^{-}$. Thus,
$S_{\text{int,plat}}$ and $S_{\text{int,max}}$ are correlated with $H_{\text{eff,av,ND,micro}}$ and
$H_{\text{eff,av,ND,tot}}$ this confirms that the orientation of benzene
molecules confined in pores is the function of the average pore
width. The entropy of adsorbed benzene falls close to the value
characteristic of a liquid for adsorbents possessing significant
amount of wider micropores and mesopores (AHD, PICA PCO,
and PICA HP). The confirmation of this statement has been
found in the next plot, i.e. $S_{\text{int,plat}}$ or $S_{\text{int,max}}$ versus
$V_{\text{meso}}^{-}\times 100%/V_{\text{ND}}^{-}$. Summing up, the increase in the
contribution of mesopores in the total pore structures leads

![Graph](image)

Fig. 5. The dependence between the average values of the plateau region of $Q_{\text{int}}$ ($Q_{\text{int,plat}}$, squares) or the maximum values of $Q_{\text{int}}$ ($Q_{\text{int,max}}$, triangles, the whole range of adsorption is analyzed) and structural parameters: $H_{\text{eff,av,ND,micro}}$, $H_{\text{eff,av,ND,tot}}$, and $V_{\text{meso}}^{-}\times 100%/V_{\text{ND}}^{-}$. 

to the increase in $S_{\text{int.plat}}$ or $S_{\text{int.max}}$ tending to $S_{\text{liq}}$. This clearly confirms the influence of the porosity on the orientational ordering of adsorbed benzene molecules and the accessibility of benzene molecules to some pores. On the other hand, similar correlations are observed between $Q_{\text{int.plat}}$ or $Q_{\text{int.max}}$ and the mentioned above structural parameters (Fig. 5). These results confirm the existence of the relationship between the enhancement of the adsorption potential in micropores and the enthalpy of adsorption measured for the adsorbents possessing various pore structure.

5. Quantitative description of the derivation of benzene from liquid state in nanopores

It should be pointed out that one of the methods of a theoretical model verification is to check the applicability of the both adsorption isotherm and related enthalpy equations for the description of experimental adsorption and enthalpy of adsorption data (sometimes other thermodynamic functions are also analyzed). As mentioned in Section 1 the thermodynamic verification of the most popular methods of porosity determination of the carbonaceous adsorbents (density functional theory, Monte Carlo simulations, Horvath and Kawazoe method, and others) is rarely met in the literature. Mainly the Polanyi–Dubinin theory of adsorption has been successfully verified for many adsorbate–adsorbent systems [8–10,12,17,18]. On the other hand, as it was shown recently [12,17,18] for the cases where adsorbate molecules approach to the state of quasi-solid, the fundamental equations of Dubinin’s theory of the volume filling of micropores do not satisfactorily describe the calorimetric data. Theoretical enthalpy and entropy values are usually too low comparing to the experimental ones. These differences are probably caused by the incorrect postulation of the liquid state of an adsorbate (treated as the reference) – the fundamental assumption of the potential theory. Moreover, it is well-known that the results of computer simulations and of adsorption in pores carried out so frequently show that the state of the adsorbate in pores may be distinctly different from that in a bulk liquid.

As was mentioned above, it can be noticed that the liquid state of adsorbate is usually assumed in models and theories describing the mechanism of adsorption on the carbonaceous adsorbents. Therefore, the above mentioned condition leads to the general inequality [15,16,94]:

$$|T \Delta S_{\text{diff}}| \ll |q_{\text{diff}}|$$

(1)

Thus $q_{\text{diff}}$ can be easily calculated based on the following simplified relation [15,16,94]:

$$q_{\text{diff}} = \Delta G_{\text{ads}} - \Delta H_{\text{vap}}$$

(2)

where $\Delta G_{\text{ads}} = A_{\text{pot}}$ and $\Delta H_{\text{vap}}$ is the enthalpy of vaporization (equal with minus sign to the enthalpy of condensation, $L$).

Horvath and Kawazoe [15,16] noticed the similarity of the data calculated based on Eq. (2) with the ‘experimental’ isosteric heat of adsorption obtained from low temperature nitrogen isotherms measured at different temperatures. Using the same procedure, the differential enthalpy of $\text{C}_6\text{H}_6$ and $\text{CCl}_4$ adsorption was calculated by Gauden et al. [18] applying the formalism presented above (i.e. Eq. (2)). Final results showed that for the studied microporous A and B carbon samples Eq. (2) describes the experimental $q_{\text{diff}}$ data ($\text{C}_6\text{H}_6$, $T = 313 \text{ K}$) inadequately, i.e. this relation leads to lower, by about 20 kJ/mol, enthalpy than measured experimentally. Significantly different situation was observed for $\text{CCl}_4$ data ($T = 308 \text{ K}$), where the similarity is larger, especially, for lower values of adsorption. These results suggest that one of the most important and above mentioned postulation of some theoretical models is not always correct for strictly microporous adsorbents. It is obvious that the same conclusion is valid for carbonaceous films possessing only micropores and homogeneous PSD [17,18].

Figs. 6 and 7 show the comparison of the respective thermodynamic functions (the differential (opened symbols) and/or integral (closed symbols) enthalpy and entropy of adsorption ($S$ (i.e. $S_{\text{diff}}$ or $S_{\text{int}}$) and $q_{\text{diff}}$, respectively)), calculated for four representative carbons, i.e. Cf, A, PICA PCO, and PICA HP (the same as in Fig. 2). Additionally, in these figures final results of the computation of $q_{\text{diff}}$ applying Eq. (2) are shown (crosess). It should be highlighted that for the microporous Cf sample this equation describes inadequately the experimental $\text{C}_6\text{H}_6$ enthalpy data ($T = 298 \text{ K}$) (the differences are close to 20 kJ/mol). Similar discrepancy is observed for carbon A. Significantly different results are obtained for PICA HP, where the similarity is larger. It should be mentioned that for this adsorbent the liquid state of an adsorbate is observed (Fig. 7). Moreover, PICA HP still possesses the micropores (Table 1 and Fig. 2). Presented results confirm that for the cases where the adsorbed molecules approach to the state of quasi-solid, the equations of the theories assuming creation of liquid in pores do not describe the calorimetric data. In the other words, for the above mentioned samples usually too low enthalpy and too high entropy values are observed comparing to the experimental ones. Summing up, the large differences between theoretical end experimental entropies and/or enthalpies of adsorption observed for strictly microporous carbons are caused by the incorrect assumption of adsorbed phase state.

Significant improvement in the description of the benzene experimental data for microporous adsorbents is observed, when Eq. (2) is rewritten as:

$$q_{\text{diff}} = \Delta G_{\text{ads}} - \Delta H_{\text{vap}} + \Delta H_{\text{corr}}$$

(3)

where $\Delta H_{\text{corr}}$ is the correction term related to the partially ordered structure of adsorbed phase.

Firstly, $\Delta H_{\text{corr}}$ is assumed as being constant value for all adsorbents and equal to the enthalpy of crystallization, $\Delta H_{\text{frost}} = -9.84 \text{ kJ/mol for } \text{C}_6\text{H}_6$ [95]. This behavior is justified due to the approach that the adsorbed molecules can be treated as the state of quasi-solid in the micropores and narrow mesopores as was described above in details. The comparison of calculated $q_{\text{diff}}$ (Eq. (3), solid lines) and experimental data
(open symbols) is presented again in Figs. 6 and 7. Analyzing both kinds of the curves it is seen that the theory underestimates the experimental data for Cf. Opposite results are observed for PICA HP. Thus, it can be concluded that the constant “correction term”, assumed as $D_{H}^{corr}$ in Eq. (3) is not absolutely correct. Better description of the experimental data is achieved presuming that $D_{H}^{corr}$ is generally the function of the pore structure (e.g. PSD, average pore widths, etc.), and it is slightly depending on adsorption (and, of course, $p/p_{o}$). Therefore, we decided to treated this parameter as the best-fitting one. It should be pointed out that the experimental and theoretical $q_{diff}$ values are compared in the limited range of the adsorbed amount, i.e. up to the abrupt increase and shown for the respective curves in Figs. 6 and 7. The plots generated on the basis of Eq. (3) and calculated $\Delta H^{corr}$ values are shown in Figs. 6 and 7 (short dashed lines). The analysis of plots leads to the conclusion that better similarity for microporous adsorbents is observed for fitted $D_{H}^{corr}$ in comparison with the assumption of $D_{H}^{corr} = D_{H}^{cryst}$. The values of the correction term change from 16.04 kJ/mol (Cf, DC = 0.82) up to 4.20 kJ/mol (PICA HP, DC = 0.94). For A and PICA PCO carbons the following values are calculated: $D_{H}^{corr} = 11.90$ and $7.72$ kJ/mol, and
DC = 0.85 and 0.91, respectively. A general tendency occurs, i.e., that the values of the determination coefficients increase and/or the correction term decrease with the increase in $V_{ND}^{mexo} \times 100\% / V_{ND}^{micro}$.

In Fig. 8 the values of $\Delta H_{corr}$ in the function of $H_{eff,av,ND,\text{tot}}$ are presented (the closed points). Additionally, a trend line plotted through this data is marked as the solid one. All eight adsorbents are taken into account. It can be noticed that the increase in the average pore width leads to the decrease in the value of the correction term. Moreover, in this figure the curve of the enthalpy of crystallization equal to $-9.84$ kJ/mol is plotted (horizontal dashed line). The detailed analysis of the behavior for shown data suggests that only for D43/1, AHD, PICA PCO, and PICA HP the values of $\Delta H_{corr}$ are equal or lower than the enthalpy of crystallization. Thus, $\Delta H_{corr}$ is larger than the enthalpy of solid crystallization only for the systems containing micropores in the structure. This is due to the differences between the crystal structure of benzene created in pores and “normal” solid, since the former process proceeds in restricted geometry. Many adsorbates creates different polymorphic forms (especially some organic molecules) in pores (see for example [96]). Summing up, the border value of the effective pore diameter corresponding to $\Delta H_{corr} = \Delta H_{cryst} = -9.84$ kJ/mol is equal to 1.14 nm (Fig. 8, the intersection of solid and dashed lines, open square). On the other hand, taking into consideration the linear correlation between $H_{eff,av,ND,\text{tot}}$ and $\Delta H_{corr}$ one can calculate the critical value of the
effective pore width for $\Delta f^{\text{corr}} = 0$, i.e. $H_{\text{eff},c} = 2.2$ nm. Thus, the main conclusion drawn from the results of this part of the study is that Eq. (2) is proper for mesoporous adsorbents (i.e. the ‘liquid’ state of confined benzene is reliable only for them).

The value of $H_{\text{eff},c}$ is comparable to those evaluated by Chakrabarti and Kerkhof [97]. Those authors systematically investigated by Monte Carlo simulations the role of the wall structure on a fluid of flat hexagonal molecules confined between two graphite walls at $T = 300$ K. It should be underlined that the theoretical model of the carbon structure is very simple. Their results show that the centers of mass of the molecules in different layers undergo an order–disorder transition as the wall separation increases, irrespective of the details of the wall structure. They investigated adsorbate confined between two graphite walls with widths, $H_{\text{eff}}$ from 0.971 up to 1.943 nm. Chakrabarti and Kerkhof [97] concluded that the system undergoes an order–disorder transition as $H_{\text{eff}}$ increases and the coverage at the substrate layer decreases as the critical value, $H_{\text{eff},c}$ increases. Their calculations suggest that this critical value should lie within the bound $1.619 < H_{\text{eff},c} < 1.943$ nm. Additionally, the order–disorder transition point appears to be insensitive to temperature in the range we consider.

6. Conclusions

A detailed knowledge of the behavior of adsorbed benzene or its derivatives will improve our understanding of the mechanisms of adsorption and the formulation of the proper theories and theoretical models. Presented results show that, generally, the significant influence of the pore structure of adsorbents on the behavior of adsorbed benzene in pores. The entropy of $C_6H_6$ can approach to the values characteristic of quasi-solid (a partially ordered structure) for adsorbent possessing the significant amount of micropores. In the other word, adsorbate molecules formed a partially ordered structure in the micropore even near room temperature. For adsorbents possessing wider micropores the differential and integral molar entropy approach to the value characteristic of a liquid. However, the differences between theoretical and experimental data are still significant. For the materials possessing the significant amount of mesopores the satisfactory correlation is obtained. Moreover, it can be stated that the orientation and ordering of benzene molecules confined in the available pore space is the function of the pore width. In the light of the results discussed in the current paper it is seen that the structure of the adsorbed phases of benzene in graphitic micropores is different from those of the liquid and solid.

For a larger separation between the graphite surfaces of the pore it is observed a larger freedom of the adsorbed molecules to rotate than in the narrower case. Moreover, the behavior of the benzene molecules adsorbed in the wide mesopores is similar to observed on the basal planes of graphite [34,35,48–52,69]. Benzene adsorbs forming a two-dimensional monolayer in which all the molecules lie flat, or very nearly [34,35,48,49,52,69]. The structure of the first adsorbed layer is not affected by different director orientations induced in the bulk liquid crystal, but is entirely determined by the surface potential [52,69]. On the other hand, at higher coverage and temperature (e.g. at ambient one) the molecules have greater orientational freedom, i.e. the benzene gradually moves away from the flat configuration until the perpendicular orientation begin dominating [34,35,48–52,69].

The significantly different behavior of adsorbed benzene molecules in comparison with the flat surface or the wide pores is observed for micropores due to the effect of the enhancement of the adsorption potential. For these fine pores the ‘liquid’ state of confined benzene should be partially ordered, while the ‘solid’ state should be partially disordered due to a serious geometrical restriction for formation of the well-crystalline solid structure (Fig. 9) [17,18,36,37,55–57,96–99]. The current systematic studies confirm the existence of the orientational ordering of the benzene molecules in the adsorbed layers and lost almost all the translation and rotational degrees of freedom. Benzene molecules adsorb near parallel to the surface in monolayer. Therefore, in the case on the narrow micropores only near flat orientation of the adsorbed molecules is observed. Thus, for investigated microporous materials (Cf, D55/2 and A)

![Fig. 9. Schematic representation of three structures of adsorbate–adsorbent systems, i.e. benzene molecules confined in pores of various carbons.](image)
the entropy of adsorbed benzene is located below or close to the value characteristic of a solid (Fig. 9). Taking into considerations the results published by Schroer and Monsena [98,99] it can be stated that from four possible solid structures (Monte Carlo computer simulation, the influence of the pore walls is not studied) two allow the system to reach a high packing density at high pressure through a columnar-like arrangement of the molecules. This closest packing of molecules is the most stable one. It should be pointed out that high pressure observed in micropores parallels the behavior found for the corresponding solid phases of benzene.

On the other hand, for wider micropores and narrow mesopores (WD, D43/1, AHD, PICA PCO, and PICA HP) the influence of the pore walls on the benzene ordering cannot be neglected (Fig. 9). C₆H₆ molecules are disturbed and some of them are perpendicular to the wall. Moreover, the liquid-like benzene molecules in the middle of the pore are surrounded by more or less structured layers. The entropy of adsorbed benzene is located between the value characteristic of a liquid, Sₗiq and the entropy of a solid, S_sol. The comparison of the differential entropy of benzene adsorption on adsorbents possessing various pore structures shows that the increase of S_diff is observed (bringing closer to Sₗiq) for the adsorbent possessing wider pores.

It should be pointed out that the solid and cooled liquid benzene behavior of adsorbate should be taken into theoretical considerations. This hypothesis is verified for the well-known general relationships. The experimental data are determined for the series adsorbents possessing various porosity. The analysis of the experimental and theoretical q_diff leads to the conclusion, that the best similarities are achieved for the adsorbents possessing significant amount of mesopores. For these materials the assumption of liquid state is more reliable. The significant improvement in the description of the benzene experimental enthalpy data measured on the microporous carbons is observed when the correctness term (ΔH_corr) is taken into considerations in the theoretical relation describing q_diff. This behavior is justified due to the approach that the adsorbed molecules can be treated as the state of quasi-solid (a partially ordered structure) for porous materials as was described above in details. Two types of ΔH_corr are taken into account: it is assumed as ΔH_corr = −9.84 kJ/mol or the best-fitting one. The main conclusion drawn from the comparison of theoretical and experimental data is statement that inequality |ΔS_diff| ≪ |q_diff| is proper for adsorbents possessing the average effective pore width larger than ca. 2.2 nm.

Summing up, it should be underlined that only adsorption isotherms measurements give no evidence on the structure of the adsorbed phase. Hence, additional experiments (e.g. the determination of the enthalpy of adsorption) are necessary for the structural elucidation of the behavior of the adsorbate. So, the results of this paper and those presented previously show that calorimetry techniques are helpful for a real thermodynamical description of the adsorption process. It should be underlined that the current and further our studies can be useful for the verification of theoretical models, theories, and computer simulations describing the adsorption of organic compounds (especially benzene) on carbonaceous adsorbents. Consequently, the results of the investigations of the mechanism of C₆H₆ adsorption on the carbonaceous adsorbents possessing different shapes of pores, e.g. cylindrical than the slit-like ones considering in the current studies will be reported in the future.

References
